2018

**Multifunctional nanocomposites in coating technology: synthesis, characterization, formulation, evaluation and application**

Sudeshna Chakraborty

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Application of Nanomaterials using nanotechnology has gained significant attention in the coating industry in recent years. Their application has had a great impact, particularly in the 3C industries (computer, communication, and construction). Incorporation of nanomaterials into polymer carriers through a systematic approach to coating processes can enhance various physical properties, such as mechanical, optical, electrical and thermal properties. The current dissertation focused on the synthesis and characterization of new nanomaterials like mesoporous silica or nanocomposites like copper-doped zinc oxide that can be used in the coating to study thermal cooling performance and enhancement of thermal conductivity. New thermal devices will be built using several ASTM processes to observe molecular fan effect on heat sinks. In addition to those, this dissertation covers new formulation technique using inorganic/organic hybrid nanocomposite coatings for multi-functional purposes, such as heat dissipation, corrosion inhibition and semiconductor applications.

In the first project, we developed a thin inorganic/organic hybrid nanocomposite coating to study corrosion inhibition performance on metal alloys. In this project, we
employed an in-situ phosphatization technique for corrosion protection and a ‘Molecular Fan’ technique to dissipate heat from metal alloys like aluminum/zinc/magnesium. Salt-Fog testing results show we can achieve good protection up to 722 hours. Our goal is to reach 1000 hours. The effect of using ISPR, nanomaterials, pigments etc. is discussed in this project.

In the second project, we made polymer formulations composed of carbon-based nanomaterials exhibiting the Molecular Fan effect. In the first part, we studied its effect on heat sinks using an existing cooling device. In the second part, we designed, developed and built a new thermal device to study the Molecular Fan effect and compared and contrasted it with the existing one. We also tested its application on communication devices such as a cell phone.

In the third project, we synthesized and studied a new type of nanomaterials ‘Copper-doped Zinc Oxide’ in two ways by the ‘solvo-thermal’ method and the ‘precipitation’ method. We discuss each process and its results in detail. We characterized the newly developed materials, studied their properties, and developed emulsion coating formulation and measured thermal performance. In the future, we propose to investigate the mechanical properties, optical properties such as photoluminescence of ZnO, and to find the best way for the possible application (photocatalyst).

In the fourth project, we synthesized and characterized porous nanomaterials ‘Mesoporous Silica’ through an investigation of its physical properties. We formulated nanocoating using silica-based nanocomposite and studied its thermal performance.
MULTIFUNCTIONAL NANOCOMPOSITES IN COATING TECHNOLOGY:
SYNTHESIS, CHARACTERIZATION, FORMULATION, EVALUATION
AND APPLICATION

BY

SUDESHNA CHAKRABORTY
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Doctoral Director:
Chhiu-Tsu Lin
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DEDICATION

To my parents
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Chapter 1. Introduction

1.1 Nanoscience, Nanomaterials and Nanotechnology

Nanoscience represents research and development of materials at nanometer (1 nm = $10^{-9}$ m) scale, finding their structures, properties, application and use of devices suited to studies of nanoscale materials. This is a relatively new field in scientific development. The number of journal articles in nanoscience has been rising exponentially over the past two decades, as demonstrated in Figure 1.1.1.

Figure 1.1. Number of journal publications on nanotechnology over the past 30 years.
Nanomaterials are defined as materials in states in which the single unit is between 1 and 1000 nm in size. However, materials in nanoscale are described usually in 1 to 100 nm, whence almost all atoms in a molecule become surface atoms. Thus, nanomaterials exhibit optical, electronic, physical or mechanical properties that are often strikingly different from corresponding materials in the bulk. Notable characteristics commonly found in nanomaterials include

1. High surface to volume ratio, which makes many nanomaterials good catalysts,
2. Enhanced electrical conductivity due to better ordering and ballistic transport,
3. High surface energy due to large surface area,
4. Distinct magnetic properties, like ferromagnetism due to limited number of atoms,
5. Distinct optical properties due to change in band gap energy,
6. Other optical properties, like the plasmon resonance effect shown in gold nanoparticles,
7. Reduced electrical conductivity due to high surface scattering,
8. Better conductivity of heat,
9. Enhanced mechanical strength (Ex. nanowhisker).

Due to such novel properties, nanomaterials possess great potential for numerous applications in material science, medicine, aerospace, etc. As such, they are drawing much attention and research activity. This dissertation summarizes my research in nanochemistry and nanotechnology over the past five years. The apparatus used are described in Chapter 2. Details of my work are presented in Chapters 3 through 6. Finally, Chapter 7 concludes with some thoughts on future work in the field.
Behavior of a nanomaterial depends on its reduced dimensions, confinement of particles or quasi-particles in a particular crystallographic direction within a structure to which it owes its special physical properties. Classification of nanomaterials is based on the number of dimensions within the nanometer scale:

1. 3-dimensional: Nanoparticles, nanograins, nanoshells, nanocapsules, nanorings, fullerenes, colloidal particles, activated carbon, nanoporous silicon, quasi crystals.²
2. 2-dimensional: Nanorods, nanofilaments, nanotubes, quantum wires, nanowires.²
3. 1-dimensional: Nanodiscs, platelets, ultrathin films, superlattice, quantum wells.²

Nanotechnology plays a major role in the development of new materials. In addition to serving basic scientific disciplines like physics, chemistry and biology, it is strongly integrated with engineering in areas of electronics, material science, and bioengineering. The proper tools are necessary for the fabrication, characterization and utilization of nanomaterials. Growing interest in nanoscience has led to development of a plethora of new devices and tools over the past three decades.

Nanomaterials and nanotechnology offer countless applications in health science – from cancer treatment and detection of tumors to studies of cells, proteins, genetics and bio-engineering.¹ Applications in other fields include catalysis; fabrication of porous materials and oxide-based nanomaterials like zinc oxide and metal doped zinc oxide, graphene oxide (GO) and reduced graphene oxide (rGO); energy storage in lithium ion batteries with perovskites; molecular organic framework (MOF); fabrication of self-assembled monolayers or oligomers, thin film for coating and more. Carbon products like graphene, carbon nanotube, nanodiamond, and others like ZnO, TiO₂, Pt, Au, Ag, Si and polymer nanocomposites have revolutionized
material science with their optical properties, catalytic performance, electrochemical and thermal properties.

1.2 Nanoparticle Properties

Nanoparticles are particles contained in 100 nm or less in at least one dimension. We focused on nanoparticles and nanoclusters – clusters of nanoparticles – to understand their unique optical, magnetic and electronic properties, which are quite distinct from the same material in the bulk.

1.2.1 Optical Properties

Reduced dimensions can have a profound effect on the electronic structure of nanoclusters by influencing their band gap energy ($E_g$, the energy gap between the conduction band and valence band). Conduction band is often known as Lowest Unoccupied Molecular Orbital or LUMO and valence band as the Highest Occupied Molecular Orbital or HOMO. Optical emission and absorption occurs when an electron travels between the valence and the conduction band in HOMO-LUMO transitions.

Some metals (Au, Ag, Cu, In, Sn) and semiconductors (ZnO) exhibit superior optical properties as the particle size changes. For example, colors of gold and silver nanoparticles can change with their size. The color of the colloidal suspension of gold nanoparticles varies from red to pink to purple to green to yellow based on the particle size. Gold nanoparticles or nanocrystals have been used in the glass industry since ancient Roman times as early as the Fourth Century. The spectacular glasswork in the Roman Lycurgus cup, currently on display at the British Museum, astonishes with its remarkable color. Figure 1.3 exhibits the two distinct
colors of gold/silver nanoparticle suspension used in making the cup. The vibrant colors come from the nanocrystals used by the Roman glassblowers. TEM studies have shown that the gold particles were between 50-100 nm in size. X-ray analysis revealed the use of silver/gold alloy in the ratio 7.3 with 10% copper. The colloidal system can cause light scattering. These nanocrystals were not red or green by themselves. They changed in color with the change in size and shape and the oscillation of electrons in the process causes the change in color. The gold component scatters light in the visible range of red, and silver scatters the same in green.

![Roman Lycurgus Cup](image)

Figure 1.2. Roman Lycurgus Cup (4th century): 16.5 cm high, 13.2 cm in diameter in reflected (left), and transmitted light (right).

Nowadays, gold nanocrystals are used as catalysts in chemical reactions and high-density data storage devices.
Figure 1.3 shows gold nanocrystals of different shapes. Mulnaney et al. used the idea of Roman gold nanocrystals and used them as a color-coded catalyst, where the transfer of electrons between molecules acts as an electron reservoir. The kinetics of the reaction is controlled by speeding up the transfer of electrons and is observed by the change in color.²

In 1857, Michael Faraday astonished the audience at the meeting of the Royal society in London with his report on his observation of the ruby red color of gold. He noted that the interaction of light with fine particles of metal, “very minute in their dimensions,” could cause the change in color. His systematic studies marked the birth of modern colloidal chemistry. Faraday used an aqueous solution of a gold compound, yellow colored sodium chloroaurate (NaAuCl₄), and reacted it with a reducing agent like phosphorus in carbon disulfide. Within minutes the yellow color transformed into a deep ruby pink of colloidal gold. He realized the ruby colored solution is due to very finely divided particles of gold, but he could not determine their dimensions, as suitable instruments were not available back then.⁷ Nearly 100 years later, Turkevich et al. measured the dimensions of Faraday’s ruby gold nanoparticles with the help of an electron microscope at 6 ± 2 nm.⁸⁻⁹
The optical and electronic properties of gold nanoparticles can be finely tuned by varying the size, shape, surface chemistry or aggregation state. Figure 1.4 shows the possible colors of monodispersed gold nanoparticles. The change in color is explained as a Surface Plasmon Resonance Effect. Plasmon is a collective oscillation of the free electron density often found at optical frequencies. Plasmon Resonance refers to coherent excitation of all free electrons within the conduction band, which leads to an in-phase oscillation if the particle size is less than the wavelength of the incident light. The electrons can then move at the same frequency as the light’s. When the two are in resonance, the electrons absorb and scatter light.

Figure 1.4. Colors of various sized monodispersed gold nanoparticles.¹¹

Surface Plasmon (SP) is plasmon confined to a surface or interface and interacts with the light. Figure 1.5 shows a schematic sketch of how SP is developed by collective oscillation of valence electrons in a solid surface stimulated by incident light.⁵⁰ The electric field of the incidental light polarizes the free electron at the surface, creating a net charge difference at the surface, which effectively works as a restoring force. Dipolar oscillation of electrons occurs with a certain frequency with respect to a time period.
Surface Plasmon Resonance (SPR) is the collective dipolar excitation of the entire particle between the negatively charged free electrons and its positively charged lattice. The energy of the SPR depends on free electron density and the dielectric medium surrounding the nanoparticle. For larger particles, the resonance sharpens as the scattering wavelength increases. Gold’s SPR frequency happens to be in the visible range, allowing us to observe the change in color with fine-tuning of particle size, shape and surface charge with naked eyes. Figure 1.6 schematically depicts the SPR phenomenon for gold. The thickness of the surface needs to be ~50 nm to develop a near field (the deep blue area under the gold surface). This happens due to the exponential decay of the electromagnetic field, without absorption, as a function of distance from the boundary. The energy, which is confined in a small area, can be found by solving Maxwell’s Equations.
While the exponential decay occurs on both sides of the interface, the wave only propagates along the longitudinal direction and the longitudinal oscillation is found quantized. The range of frequency at which the SPR is observed can be described as follows:

\[ \omega_{sp} < \omega_p (1 + \varepsilon_d)^{-\frac{1}{2}}, \]  

(1.1)

where, \( \omega_{sp} \) and \( \omega_p \) are the SP and Plasmon angular frequencies, respectively, and \( \varepsilon_d \) is the dielectric constant.

When SPR occurs, we can observe the depth of the intensity at a particular angle \( \theta_0 \) where the SP is excited. This angle is shifted from its corresponding critical angle (\( \theta_c \)). This phenomenon is used in biosensors to detect biochemical interactions as they happen on the surface.
Gold spheres with diameters in the 10-20 nm range appear red, while those in the 20-100 nm range appear purple. Spherical silver nanoparticles ~40 nm and ~100 nm appear blue and yellow, respectively. Prism-shaped silver nanoparticles appear red.

For small monodispersed gold nanoparticles of size ~30 nm, the SPR causes an absorption of light in the blue-green region (~450 nm) in the visible spectrum, while the red light (~700 nm) is reflected, yielding a rich red color. As particle size increases, the wavelength of SPR-related absorption shifts to a longer redder wavelength. Red light is then absorbed, and blue light is reflected, yielding a pale blue or purple color. With further increase in particle size, as it continues toward the bulk limit, the SPR wavelength moves into the IR portion of the spectrum and most visible wavelengths are reflected, giving the nanoparticles clear or translucent color. Thus, SPR can be tuned varying the size or shape of the nanoparticles, leading to particles with tailored optical properties for different applications.

A coherent delocalized electron oscillation can exist at the interface between any two materials where the real part of the dielectric constant and permittivity change signs across the interface. The dielectric medium can be air, water or vacuum. Varying the size of the particles can also impact other properties like photocatalysis, photoconductivity, photoemission and electroluminescence. Figure 1.7 shows how Surface Plasmon Absorption changes with the size of the associated nanoparticles.
1.2.2 Electronic Properties

Quantum Transport of nanomaterials and small devices can be extremely sensitive in size and surroundings. Conduction in highly confined structures, such as nanodots, can be affected by

Figure 1.7. Dependence of surface plasmon absorption on size of spherical nanoparticles.\textsuperscript{10}
the presence of charge carriers. Thus, charged state of nanodot like small structure become sensitive. We discuss three types of charge transport mechanisms, namely ballistic conduction, coulomb charging and tunneling conduction. These were studied extensively in the mid-90s. Ballistic conduction occurs when the length of the conductor is smaller than the electron mean free path. No energy is dissipated away, and there is no elastic scattering to reduce the transmission coefficient and electrical conductance. Frank and his coworker first studied and reported the ballistic conduction in carbon nanotubes. Extremely high stable current densities \((J > 10^7 \text{ A/cm}^2)\) can be achieved.

Coulomb Charging or Coulomb Blockade involving a single electron can be observed in reduced-size systems. It can be exploited to minimize operational energy in transistor, switch or memory elements in applications like resonant tunneling transistors and single-electron transistors (SET). Nanoparticles with diameters below 2-3 nm can be used as the basic component of SET. At such dimensions, metal or semiconductor nanocrystals exhibit strong quantum effects like discrete charging of metal particles. Discrete electronic configurations can display charging by one electron at a time. The V-I characteristics of this phenomenon is known as Coulombic Staircase. Coulomb Charging occurs when the contact resistance is larger than the resistance of the nanostructure and the total capacitance of the nanomaterial is so small that adding a single electron requires a significant amount of charging energy since it is not a part of the bulk material.

Tunneling Conduction is another kind of charge transport mechanism where charge transport occurs through an insulating medium separating two very closely spaced extremely thin conductors. Under such conditions, an electron’s wave function in the two conductors overlap
inside the insulating medium, enabling them to tunnel through the dielectric material when an electric field is applied. The electrical conductivity decreases with increasing thickness of insulating layer.\textsuperscript{30} This can be also explained by band theory. Conductivity of a reduced nanosystem increases below a critical length scale, as the band gap energy ($E_g$) continues to reduce, the valance band overlaps with the conduction band and the nanolayer of a material that’s an insulator in the bulk behaves like a conductor between the two closely spaced metal surfaces. Figure 1.8 depicts this behavior.\textsuperscript{30}

![Figure 1.8. Behavior of an ideal insulator, semiconductor and conductor.\textsuperscript{30}](image-url)
1.2.3 Mechanical Properties

Mechanical properties of materials can be enhanced with a decrease in particle size. One-dimensional structures like nanowhiskers show superior mechanical strength when the diameter is less than 10 microns. Herring et al. first showed that the mechanical strength of a perfect crystal could exceed the real one by two or three orders of magnitude.

1.2.4 Physical Properties

Nanoparticles of metals, semiconductors, crystals, and inert gases exhibit lower melting temperatures compared to their bulk when particle size decreases below 100 nm and when the surface energy increases dramatically. The decrease in phase transition temperature may be related to the changes in the ratio of surface energy to volume energy as a function of particle size.

1.2.5 Chemical Properties

Although bulk gold does not show any catalytic property, but gold nanocrystals can be excellent catalysts because of extremely low melting point and can catalyze reactions at low temperatures. The melting point of bulk gold is 1337 K, but gold nanoparticles’ melting point decreases exponentially below 100 nm and even more rapidly when the size falls below 5 nm, as shown in Figure 1.9.45.
1.2.6 Magnetic Properties

Distinct magnetic properties arise due to the sudden drop in size. Large surface-area-to-volume ratio allows a substantial proportion of atoms to acquire different magnetic coupling with their neighbors. Thus gold (Au) and platinum (Pt) nanoparticles exhibit ferromagnetism absent in bulk. Gold nanoparticles become ferromagnetic when they are capped with proper surface modifiers like mercapto or thiol, an organosulfur compound (R-S-H). Thiols are similar to alcohols or phenols, with an oxygen atom replaced by a sulphur atom.

Figure 1.9. Melting point depression of gold nanoparticles.
Combining weaker magnetic elements like chromium (Cr) or copper (Cu), with nanoscale multilayers of strong ferromagnetic elements like iron (Fe), cobalt (Co) and nickel (Ni) can give rise to Giant MagnetoResistance (GMR) effect, which finds application in data storage and sensing.

When particle size drops below a certain size, ferromagnetic particles become unstable. In this situation, polarization direction continuously changes with abruptly increased surface area. As a result, ferromagnetic materials become paramagnetic. This change in magnetic behavior is different from the conventional paramagnetism and thus referred to as supermagnetism.

1.3 Nanocomposites

Composites are in general multiphase material with significant proportions in each phase. To understand nanocomposites, first we need to understand the nature of a reinforcing phase. Nanomaterials with appropriate shape and size incorporated into a matrix can act as reinforcing phase, as it reinforces the newly developed materials with distinct properties significantly different than those of its host material.

The nanoscale reinforcing phase can be grouped into three categories, namely, nanoparticles (0-D), nanotubes (1-D), and nanoplates (2-D). In the case of nanoparticles, their size and distribution are of crucial importance. Depending on the type of nanoparticles added, the mechanical, electrical, optical, and thermal properties of polymer nanocomposites can be altered. In the mechanical domain, changes in modulus and strength depend strongly on the degree of interaction between the particle and the polymer.
A nanocomposite is a multiphase solid material in which one of the phases of reinforcing material has one, two or three dimensions of less than 100 nm. Nanocomposites can be structures having nanoscale repeat distances between the different phases that make up the material. It is a solid combination of nano dimensional phase(s) into a bulk matrix engineered into new materials with different tunable properties, including mechanical, electrical, thermal, optical, electrochemical, and catalytic properties. Nanocomposites can include porous media, colloids, gels and copolymers.

Nanocomposites differ in properties from its conventional composite materials due to the high surface-area-to-volume ratio of the reinforcing phase and its high aspect ratio. The reinforcing materials can be nanoparticles such as nanosilica or minerals, nanosheets such as graphene or exfoliated clay stacks and nanofibers such as carbon nanotubes or electro-spun fibers. The area of the interface between the matrix and reinforcement phase(s) is typically an order of magnitude greater than that found in conventional composite materials. The matrix materials properties are affected by the reinforcement.

Nanoparticles of different size ranges can exhibit different properties. Catalytic activity comes with particles less than 5 nm. With less than 20 nm in size, hard magnetic materials can be soft. With sizes less than 50 nm, changes are seen in refractive index. Supermagnetism and enhanced mechanical strength can be achieved below size 100 nm.

Nanocomposites are found naturally in abalone-shell and bone, ancient Mayan blue paint, and nanoscale organo-clays.
1.3.1 Ceramic Matrix Nanocomposites (CMC)

The first kind of nanocomposites we discuss are ceramic matrix nanocomposites (CMCs). These are nanocomposite materials in the ceramics group, where ceramic fibers are embedded in a ceramic matrix, forming a ceramic fiber reinforced ceramic material.\textsuperscript{51}

The matrix and fibers may consist of any ceramic material. The main part of a CMC is occupied by a ceramic, which is a chemical compound commonly from the group of oxides, nitrides, borides or silicide. Carbon and carbon fibers can also be considered as ceramic materials. In some cases, a metal is employed as the second component in ceramic-matrix nanocomposites. Here both components, the metallic and ceramic need to be thoroughly dispersed in each other to attain enhanced nanoscopic optical, electrical and magnetic characteristics as well as corrosion-resistance and other protective properties.\textsuperscript{51,52}

It is important to select the components wisely to fabricate the CMC, as they can undergo chemical reaction with each other. Some metals can easily react with the ceramic. Thus, immiscible metals are good options. CMC also requires a high process temperature. Therefore, selecting the metals and ceramic matrix with high melting point is advisable. A good example of such a combination is the ceramic-metal composite of titanium dioxide (TiO\textsubscript{2}) and copper (Cu). Nanocomposite layers of this combination featuring high mechanical strength, small coefficient of friction and high corrosion resistance were developed using a vacuum-based deposition technique called the hollow cathode technique.\textsuperscript{51,52}
1.3.2 Metal Matrix Nanocomposites (MMC)

Metal matrix nanocomposites are also known as reinforced metal matrix composites and are classified as continuous and non-continuous reinforced materials. A popular material in this category is carbon nanotube metal matrix composites (CNT-MMC), which exhibits high tensile strength and electrical conductivity. Boron nitride- and carbon nitride-reinforced metal matrix are also gaining popularity.

To achieve a good quality carbon nanotube (CNT), boron nitride (BN), or carbon nitride (CN) reinforced metal matrix nanocomposites, it is necessary to have homogeneous dispersion of nanotubes in the metal matrix. If CNT, BN, or CN is dispersed well in the matrix, then metal matrix nanocomposites can show strong interfacial adhesion to the metal matrix. In some cases, an inorganic agent, such as tungsten disulfide nanotubes (TDN), could help achieve better reinforcement than CN alone. Studies show that when TDN is dispersed in a propylene fumarate (PPF), it can yield higher Young’s modulus and compressive yield strength. Inorganic nanotubes in the polymeric matrix can lead to increased crosslinking density of the polymer, thus enhancing its mechanical properties.39-41 Another kind of MMC is a silica-based hybrid sol-gel. When incorporated with nanoscale metal oxides, new materials like superthermite can be developed.53, 54

1.3.3 Polymer Nanocomposites (PNC)

Polymer-matrix nanocomposites consist of a matrix made from a polymeric material, either polymer or copolymer, having nanoparticles or nanofillers dispersed in the polymer matrix. At least one dimension must be in the range of 1-50 nm. PNC’s can be of multi-phase systems. The second phase, usually a few percent by weight, has nanoscale dimensions and is
dispersed within the matrix. The small size of this phase leads to unique properties. Due to the nanoscale size of the reinforcing phase, the surface-area-to-volume ratio is significantly higher than in conventional composites. As a result, the volume fraction of the phase can be reduced without degradation of the desired properties.

In general, the controlled addition of nanoparticles to a polymer matrix can enhance its performance, but it must be well dispersed with the right loading amount to achieve a stabilized uniform dispersed phase, often called nanofilled polymer composites. Special care must be taken while incorporating nanoparticles into the matrix, as clustering can generate aggregates causing structural defects.

Layer-by-layer (LBL) assembly of nanoparticles and a polymer can yield a structural performance 10-1000 times higher than traditional nanocomposites. Graphene, carbon nanotube or silica can be used as the reinforcing agent to fabricate biodegradable polymeric nanocomposites exhibiting strong mechanical properties. A range of property combinations can be engineered in this approach. Thus, polymeric nanocomposites can be widely used for
biomedical applications such as tissue engineering, drug delivery, and cellular therapies. A few natural and synthetic polymers used are starch, cellulose, chitosan, gelatin, polyvinyl alcohol (PVA) and polyethylene glycol (PEG).55, 56

1.3.4 Organic-Inorganic Hybrid Nanocomposites

A mixed-type composite called organic-inorganic hybrids are materials in which organic and inorganic components interpenetrate each other at nanoscale and form percolated three-dimensional networks. Some hybrids are referred to as ormosils (organically modified silicates) or ormocers (organically modified ceramics). Hybrid nanocomposites are generally classified in two types:

1. Hybrids are made of organic molecules, oligomers or low molecular weight polymers embedded in an inorganic matrix held together by weak hydrogen bonds and van der Waals forces.

2. Hybrids in which organic and inorganic components are linked to each other by covalent bonds. Here the hybrids form a huge molecule that links organic and inorganic components through chemical bonds. Sol-gel route is a typical way to prepare these.57-60

1.4 Nanocomposite Coating

Nanomaterials are in high demand in the coating industry. Nanocomposites such as silica, clay or carbon blacks were used in early days of nanocoating. Toyota Motor Company carried out some research and development in coating with nylon/nanoclay composites. In recent years,
advancement in nanotechnology has helped the coating industry improve techniques and coating properties. Nanocomposites are now being used to make heat dissipative coatings, corrosion protection coatings, UV shielding coatings, super-hard coatings, abrasion- and scratch-resistant coatings, photocatalytic coatings, self-cleaning coatings, antibacterial coatings, etc.

Incorporation of inorganic fillers into organic resin helps to improve coating properties. Nanocomposite coatings formulated from inorganic reinforcing agents with organic polymers attain high interfacial contact. With nanoscale inorganic materials instead of microscale, the interfacial interaction improves significantly due to the availability of higher surface area. Modern nanotechnology allows efficient incorporation of nanomaterials into the polymer matrix leading to better coatings.

Many types of nanomaterials with different size and morphology are used to improve coating performances. Most common are silica\textsuperscript{34} (SiO\textsubscript{2}) alumina\textsuperscript{35} (Al\textsubscript{2}O\textsubscript{3}) and zirconia\textsuperscript{36} (ZrO\textsubscript{2}), which are used to improve abrasion and scratch resistance, hardness and UV-shielding. Zinc oxide\textsuperscript{37} (ZnO), and Titania\textsuperscript{38} (TiO\textsubscript{2}), or titanium dioxide are used to improve UV-shielding and bacterial resistance. Calcium carbonate\textsuperscript{39} (CaCO\textsubscript{3}) is used to improve whitening and mechanical properties. A broad view of common nanomaterials used for enhancement in coating properties are listed in Table 1.2.\textsuperscript{40}

One of the main challenges in nanocomposite coating is effective dispersion of nanoparticles or nanomaterials in the host matrix or organic resin. Improper dispersion can lead to various defects in morphology and compromise coating properties such as transparency, impact resistance, increase in viscosity, reduction in coating impact and physical appearance. Nanomaterials with high surface area such as CNT are difficult to disperse in organic coatings, as they tend to form aggregates. Aggregated particles in the coating will show poor performance
in exhibiting mechanical properties.\textsuperscript{41} Therefore, special care must be taken to avoid aggregation and flocculation of nanoparticles.

Table 1.1
Inorganic Nanomaterial Candidates for Enhancement of Coating Properties

<table>
<thead>
<tr>
<th>Nanomaterials</th>
<th>Coating Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO, TiO\textsubscript{2}, CuO</td>
<td>Anti-bacterial, Anti-microbial</td>
</tr>
<tr>
<td>Nanoclays</td>
<td>Gas barrier</td>
</tr>
<tr>
<td>Nanoclays, boehmite</td>
<td>Corrosion</td>
</tr>
<tr>
<td>Nanoclays</td>
<td>Fire retardant</td>
</tr>
<tr>
<td>Fe\textsubscript{2}O\textsubscript{3}</td>
<td>Magnetic</td>
</tr>
<tr>
<td>TiO\textsubscript{2}, In\textsubscript{2}O\textsubscript{3}</td>
<td>IR-Absorbent</td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2}, ZrO\textsubscript{2}</td>
<td>Scratch resistant</td>
</tr>
<tr>
<td>TiO\textsubscript{2}, ZnO</td>
<td>Photo catalysis, Self-leaning</td>
</tr>
<tr>
<td>TiO\textsubscript{2}, ZnO, BaSO\textsubscript{4}, CeO\textsubscript{2}</td>
<td>UV shielding</td>
</tr>
<tr>
<td>SnO\textsubscript{2}</td>
<td>Electrical conductivity, Static charge dissipation</td>
</tr>
</tbody>
</table>

To prevent aggregation, inter-particle attractive forces between individual particles must be reduced. Some common strategies to reduce attractive forces between particles and obtain uniform dispersion are surface modification, grinding (Stirring) and ultrasonication.

Surface modification can be done either physically by adsorption of surfactant on the surface of nanoparticle or chemically by surface reaction with coupling agents, macromolecule
or alcohol. Another common way is grinding or stirring with proper propeller size, shape, and speed to disperse nanoparticles in a liquid. Lastly, the ultrasonication process with high frequency sound waves is the most effective way to disperse viscous materials in small volume by generating high impact energy. We normally use two types of sonication: 1) mild sonication in ultrasonic bath and 2) high power sonication using ultrasonic probe (>20 kHz). All three approaches were utilized in our research.

Nanocomposites can be directly incorporated into the resin polymer by dispersion or it can be incorporated into monomers by in-situ polymerization approach to synthesize nanocomposite-incorporated resin. Formulation steps can be different based on the required coating property, host matrix, and nanomaterial properties. For example, corrosion protection, heat dissipation and UV shielding coatings are all different, yet there are similarities in the general route. In the first step, nanoparticles in the powder form are dispersed into little volume of solvent in presence of surfactant by sonication or grinding method. The surface modification requirement of the nanoparticles depends on the properties of the nanoparticles and the characteristics of the host matrix, such as hydrophobic, hydrophilic, water-based or solvent-based. In the second step, dispersed nanoparticles obtained from the first step are incorporated to the monomer or resin matrix using grinding or stirring. In the third step, solvents and other additives are added, while the grinding continues. Finally, the end product is homogenized to have a uniform formulation for coating application.

Sol-gel is another route for preparing nanocomposite coatings. Here inorganic nanoparticle dispersion in organic resins is achieved in the presence of a coupling agent. The sol-gel process is well known and commonly used. This is usually a low cost, low temperature
process and offers molecular level homogeneity. This process is useful in preparing inorganic-organic hybrid materials and metastable materials.

### 1.5 Applications of Nanocomposite Coating

Coatings are used in everyday life for many purposes like protections from weather, insects, heat, light, abrasion, or simply for visual appeal. Thus, coating has a wide range of applications. Paint is used on interior and exterior of buildings, vehicles (automobiles, airplanes, ships), infrastructure units (roads, bridges), ammunition, utilities (electricity, water, gas supplies), telecommunication, art, etc.

In this study, we focused the research on nanocomposite coatings for different purposes such as heat dissipation and corrosion protection. In future work, we will focus on UV shielding and hot water spring protection. All our coatings are based on green chemistry to make them environment-friendly and therefore did not use toxic chemicals. We also tried to reduce solvent-based coating; thus, most of our coating formulations are water-based and made of water compatible epoxy polymer.

#### 1.5.1 Heat Dissipation Coating (Radiative Cooling)

In this type of coating, we formulated an epoxy emulsion coating with carbon-based nanofillers, such as graphene and carbon nanotube. The main purpose of formulating the coating here is to dissipate excess heat from miniature condensed objects like compact electronics.

Conventional cooling techniques like heat sink or phase transfer require other additional inexpensive components like a cooling fan or power supply; whereas other cooling systems like ionic winds are expensive. Conventional cooling techniques like heat sink or phase transfer require other additional inexpensive components like a cooling fan or power supply; whereas other cooling systems like ionic winds are expensive. Conventional cooling techniques like heat sink or phase transfer require other additional inexpensive components like a cooling fan or power supply; whereas other cooling systems like ionic winds are expensive. Conventional cooling techniques like heat sink or phase transfer require other additional inexpensive components like a cooling fan or power supply; whereas other cooling systems like ionic winds are expensive.
and smaller with modern technologies. Generated heat must be channeled out of the hot objects in an efficient way, regardless its size, to protect it from overheating and malfunctioning. To solve this challenge, our group has previously designed a novel cooling technique called the Molecular Fan. Molecular Fan is an inorganic-organic hybrid nanocomposite coating, containing thermally conductive nanomaterials, which demonstrates high surface emissivity. This is a spaceless, powerless radiative cooling process and dissipates heat by emitting electromagnetic radiation in IR region. It requires high lattice quantization to release heat by vibrational motion of molecules.

We have chosen carbon-based nanomaterials for their chemical versatility, physical, thermal and mechanical properties, unique morphology and structural stabilities. Spatial conformation and hybridization state of carbon materials lead to special electronic and chemical properties. Thus, overall carbon material could be a better candidate to be a reinforcing agent in the organic emulsions for the Molecular Fan coating. Our group previously explored graphene, single and multiwall carbon nanotube, nanodiamond and fullerene in this respect. Among them, graphene was the best, exhibiting highest emissivity and cooling efficiency.

Different carbon allotropes hybridized to sp\(^3\), sp\(^2\) or sp configuration. We found carbon in graphene or graphite as a planer with a planer sp\(^2\) hybridized state; whereas carbon adopts tetrahedral sp\(^3\) configuration in diamond; carbon black and carbon nanotube attains an intermediate stage between sp\(^2\) and sp\(^3\) hybrid. They also build spatial structures like zero-dimensional (0D) fullerene (C\(_{60}\)) or Buckyball, one-dimensional (CNT) nanotubes, two-dimensional graphene (2D) and three-dimensional (3D) graphite and diamond.

Graphene showed excellent thermal performance in microelectronics and was used in epoxy composites exhibiting high efficiency thermal interface. Another carbon allotrope CNT
shows excellent thermal properties. They were used to derive thermally conductive polymer composites for many applications such as power electronics, heat exchangers, electric motors and generators.\textsuperscript{41} Additionally, their prominent thermal and mechanical properties make them right candidate for heat management applications.\textsuperscript{48} Thus, we adopted the similar technique with CNT and graphene to be implemented into polymer organic emulsions to formulate the desired molecular fan coating. Chapter-4 will discuss this topic in detail for heat dissipation studies.

1.5.2 Corrosion Inhibition/Heat Dissipation Coating

We designed and formulated another type of coating to prevent corrosion of the metal and its alloys. We prepared transparent and non-transparent coatings. Transparent coatings are only primers and non-transparent coatings are generally topcoats with pigments or abrasion and corrosion resistant reinforced agents. In this project we also used carbon nanotubes as nanofillers and in-situ phosphatizing reagents (ISPR) to enhance heat dissipation and corrosion inhibition, respectively. Previously our group carried out corrosion inhibition and heat dissipation both on different metal alloys such as hot dip galvanized steel (HDG), electro galvanized steel (EGS), cold rolled steel (CRS), etc. Chapter 3 has a detailed discussion of this project, with a focus on magnesium alloys such AZ91 (Al: 9%, Zinc: 1%, Mg: 90%).
1.6 References

1. Kostoff, R. N., Koytcheff, R., Lau, C. G.; Structure of the global nanoscience and nanotechnology research literature. “Science Citation Index/ Social Science Citation Index (SCI/SSCI)”. (Retrieved May 7, 2018).


10. Cao, Guozhong; Wang, Ying; “Nanostructures and Nanomaterials”. pp 473.


14. Xuan Yang; Miaoxin Yan g; Bo Pang; Madeline Vara; Younan Xia. "Gold Nanomaterials at Work in Biomedicine". Chem. Rev. 2015, 115: 10410–10488. Doi:10.1021/acs.chemrev.5b00193.


45. Cao. Guozhong; Wang, Ying; Nanostructures and Nanomaterials, pp 462-464.


Chapter 2. Instrumentations and Facilities

Research in material science requires many kinds of instruments to serve different needs. This chapter contains a brief description of instruments used in our research: heating devices of various types from low to high temperatures and special ceramic tube furnace, monitored cooling device, spectral analysis such as Fourier Transform Infra-Red (FTIR) spectroscopy to identify functional groups or to study Raman frequencies, UV-VIS analysis to see photo-catalytic effect, Transmission Electron Microscope (TEM) to find structures, Scanning Electron Microscope (SEM) to detect morphology, X-ray Diffraction (XRD) for powder diffraction, Salt Spray Chamber to observe corrosion on metals, Sonication Bath and Ultra Sonication device to disperse nanomaterials uniformly, Power Stirrer to prepare formulations, coating devices such as Spin Coaters and Spray Gun, Centrifugal Machine to separate solid from suspension, Homogenizer to defoam and homogenize formulations, Argon gas tube to anneal freshly synthesized new materials, UV/IR cut device to observe the transparency and UV cut of the incident light on our UV cut formulations etc.

2.1 Transmission Electron Microscopy (TEM)

Upon synthesizing a new material, our first objective is to determine the morphology of its constituent particles. A technique known as (Conventional) Transmission Electron Microscopy (TEM or CTEM) allows a beam of electrons transmit through an ultrathin specimen to image its constituents. The specimen is usually a suspension on a TEM grid or a section less than 100 nm thick.
Before 1927, electrons were only understood as matter particles. De Broglie hypothesis was published in 1927, where the wave-particle dual nature of electron was introduced. A beam of electrons can be diffracted like a beam of light or water wave. De Broglie wavelength of electrons was found to be many orders of magnitude smaller than the wavelength of visible light. Application of this concept allowed microscopy at atomic scales.

The resolution of a light microscope (LM) is limited by the wavelength of the light used to probe the sample. The smallest length that an LM can probe is given by
\[ d = \lambda \left(2n \sin \alpha \right)^{-\frac{1}{2}} \quad (2.1) \]

where, \( \lambda \) is the wavelength of the photon (400-700 nm for visible light), \( n \) is the index of refraction of the medium in which the lens is working, \( \alpha \) is the half-angle of the cone of light that enters the lens. The term \( n \sin \alpha \) represents Numerical Aperture.\(^5\)\(^6\)

According to de Broglie’s theory (1927),\(^3\) an electron also behaves as a wave, whose wavelength \( \lambda \) is related to its kinetic energy \( E \) as

\[ \lambda = h\left(2mE\right)^{-\frac{1}{2}} = h\left(2mqV\right)^{-\frac{1}{2}} \quad (2.2) \]

where \( V \) is the potential difference through which the electron has been accelerated, while \( m \) and \( q \) are the mass and the electric charge of the electron, respectively.

In TEM, since the electron beam is accelerated to pass through a sample specimen, an additional correction must be made to account for the relativistic effects caused by the electron velocity approaching the speed of light. Hence equation 2.2 can be further modified as

\[ \lambda = h \left(2mE \left(1 + \frac{E}{2mc^2}\right)\right)^{-\frac{1}{2}} \quad (2.3) \]

where \( h \) is the Plank’s constant and \( c \) is the speed of light.\(^7\)

It is easy to use electrons with de Broglie wavelengths much smaller than that of visible light are easy. With the ability to create images with much higher resolution than visible LM, TEMs became an important tool in nanoscale research in material science, semiconductors, as well as in fields of biotechnology and bioengineering, cancer research and virology.
In optics, contrast is a measure of the difference in luminance or color that allows an object to be distinguished against a background. In TEM with lower magnifications, contrast arises from differential absorption of electrons by materials of different composition and thickness. On the other hand, with higher magnifications, complex wave interactions modulate the intensity of the image. Alternate modes allow specific modulations in chemical identity, electronic and crystal structure, as well as electron phase shift induced by the sample. 

A schematic view of three types of electron microscopes: LM, TEM, and Scanning electron microscope (SEM) is shown in Figure 2.2. The basic principles of all three are similar until the third stage, where they differ in the way the image is received. In SEM, electrical and magnetic fields are applied to scan the object in a series of tiny steps to achieve higher resolution.

Figure 2.2. A schematic view of the operational principles of LM, TEM, and SEM.
In TEM, a monochromatic beam of electrons is accelerated first through a potential field of 40 to 100 kilovolts (kV) and then passed through a strong magnetic field that acts as a lens as well. Modern TEMs have resolution of about 0.2 nm, a thousand times greater than that a typical LM and half-a-million times greater than that of the average human eye.

Figure 2.3. TEM.
Note: Left: The basic principle of TEM. Right: Modes of operation available in a modern TEM.

The left half of Figure 2.3 shows a diagram of a conventional transmission electron microscope on the top path and a scanning transmission electron microscope on the bottom path. The selected area electron diffraction (SAED) aperture (Ap), the sample or the specimen (Spec) are indicated in the diagram and so are the different lenses like the objective (Obj), the projector
(Proj) or condenser (Cond) lenses. The right half of Figure 2.3 depicts the position of different signal detectors in the TEM column used different modes of operation.

In recent advancements of technology, high resolution transmission electron microscopes (HRTEM) offering resolutions finer than 0.05 nm has become an indispensable tool in the field of nanotechnology. Improved techniques also reduce spherical aberrations and allow imaging of lighter atoms, which scatter electrons less efficiently. This tool can even distinguish between the ions with different oxidation states such as Iron (I) and Iron (II) or Fe$^{1+}$ and Fe$^{2+}$. An HRTEM would be useful for our studies, but it was not available.

To run a TEM, first we have to prepare the sample. We dissolve our nanomaterials or nanocomposites in ethanol and add one or two drops on a TEM grid like the one shown in Figure 2.4.

![TEM Grid](image)

Figure 2.4. A TEM Grid sample support mesh “grid” with ultramicrotomy sections.

Regions of higher atomic numbers or denser packing will appear darker while those with little or no material in the beam path appear lighter.$^{10}$ A high frequency sound wave generated by
a Sonicator is used to achieve uniformity in a colloidal mixture for best viewing of silhouettes of nanoparticles to study their shapes and sizes. Depending on the instrument, we can also use TEM to study to some extent the Morphology, that is arrangement of particles at the scale of atomic diameters. We can also find compositional information like redox specification, such as Fe$^{1+}$ and Fe$^{2+}$. With HRTEM, it is possible to obtain some crystallographic information from the diffracted electrons, study the arrangement and order of atoms, and detect atomic-scale defects.

As shown in Figure 2.5, at the top of a TEM is an electron gun – a tungsten filament thermionic emission source of electrons discharging through an electrical potential difference of ~100-300 kV. The electrons are passed through a Wehnelt Cylinder to form a properly focused beam. The upper lenses focus the electron beam again to get the desire size and location. Electrons move according to the left-hand rule under the presence of magnetic field, which then allows the formation of a magnetic lens with variable focusing power. Furthermore, an electrostatic field causes the electrons to be deflected at a constant angle. Two deflections then become coupled in opposite directions with a small parting between them, resulting a shift in the beam path in TEM. Beams are passed through other levels of lens to achieve the final image.
Figure 2.5. The overall layout of the optical components in a TEM.\textsuperscript{11}
Figure 2.6. An Abbe diagram of how diffraction pattern and corresponding real space image in a TEM are formed simultaneously.
Figure 2.8 shows how the real image is formed over the image plane of Objective lens (OL), and how using thin lens can focus the two parallel inclined rays. These steps occur after the electrons pass through the condenser lens followed by the specimen. The rays then split up and pass through the objective lens as parallel rays to be focused on the image plane of the objective lens. The outgoing rays from the objective lens once again cross each other to go through the projector lens. Finally, the refined rays are received as the image to be recorded.
The TEM in our facility is a Hitachi H-600, with an accelerating voltage of 100 KeV.

![Image of TEM image](image)

**Figure 2.8. TEM image.**
Note: Left: Real image formation in TEM upon diffraction\(^2\), Right: Focusing of inclined parallel rays by thin lens\(^2\)

## 2.2 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy conceptually is akin to TEM in the sense that an electron beam is applied instead of light to create an image. The beam is accelerated under high electric potential and focused by magnetic lenses on the object of study. The object sample emits secondary electrons, which are then detected by surrounding sensors. The number and distribution of detected electrons depends on the variations of the sample surface. Scanning the surface with the beam and analyzing the variation of number of electrons detected allow reconstruction of the surface topography.\(^{13}\)

A SEM performs progressive line-by-line Raster Scanning of the object, much like a reader’s gaze travels along the lines of text.\(^{13}\) The resultant micrograph can capture a large depth of field and three-dimensional appearance of the surface structure of the sample with a wide range of magnification. This feature is immensely useful in analyses specimen morphology (size, shape and order of orientation of the particles) in micro or nanoscale,
making SEM a highly valued equipment in material science, biological science and nanotechnology laboratories.

Figure 2.9 (left) shows schematically how scanning of the surface of a sample – the white 3-D object – is done by the electron beam (orange cones) passing through a magnetic lens (the dark grey ring) and detected by an electron detector (the dark grey square with a light grey sensor at its center). The reconstructed image appears on the black screen at the left upper corner. Figure 2.9 (right) an actual SEM image of a mixture of pollen collected from different plants.

An SEM incorporates a high-vacuum system to achieve good optics with the electron beam and to prevent oxidation and burning of the electron source (a tungsten filament). We used a Tescan Vega 3 SBH, with variable electron gun potential from (200 V to 30 kV) and scanning speed from 20 ns to 10 ms per pixel, adjustable between continuous and step-
scanning modes. The vacuum in the working chamber could go as low as $9 \times 10^{-3}$ Pascal with pumping time less than three minutes between specimen changes. The machine was also equipped with liquid-nitrogen-free INCAX-act analytical standard Electron Dispersive X-Ray (EDX) detector for elemental analysis, (the electron beam can cause the sample under study to emit X-rays, which carry information about its chemical composition and molecular orientation). Both SEM and EDX are controlled by computer software. The first SEM in operation and the SEM in our lab are shown next to each other in Figure 2.10.

![Figure 2.10. Left: The first SEM. Right: The SEM in our laboratory.](image)

### 2.3 X-Ray Diffraction (XRD)

An X-ray Diffractometer employs an X-ray beam to study crystal structure – size and orientation – at the atomic scale. Figure 2.11 shows various types of crystals studied with XRD.
X-rays striking a crystal lattice undergo elastic scattering by atomic electrons. The constructive and destructive interference between scattered spherical waves revealing the arrangement of the atoms close to the surface. The phenomenon is explained by Bragg’s Law, shown in Figure 2.12, where $n$ is an integer, $d$ is the spacing between two parallel diffracting planes, $\lambda$ is the wavelength of the incident ray, and $\theta$ is the incident angle.

\[
2d \sin \theta = n \lambda
\]

- $d$: Interplanar spacing
- $\theta$: Bragg’s angle / angle of incidence
- $n$: order of reflection (integer)
- $\lambda$: wavelength of X-ray source

Figure 2.12. Bragg’s law governing X-ray diffraction.
Figure 2.13 shows a schematic and an actual XRD machine with its three main components highlighted. The set-up consists of a source generating a collimated X-ray beam, a sample mount and a detector. Two of the three components can rotate during operation to perform a 3-D surface scan.

Different devices are used for powder diffraction and for single crystal diffraction, with the choice depending on the quality and texture of the crystals. Both types of devices were available for the work presented here. The powder XRD machine was a Rigaku Miniflex, shown in Figure 2.14, which uses a copper (Cu K\(_\alpha\)) source to produce 1.54178 Å X-rays, and is equipped with six sample-holders, each with its own setting of time, speed and scan angle as needed, independent of others.
Operational parameters of an XRD include slit width, scan range, scan speed, step width, time per step, and source power. These must be chosen carefully to achieve best results for the task in hand. Best identification of an unknown sample is possible when the sample is homogeneous and single-phase. For example, a mixture of carbon allotropes (graphene, carbon nanotube, carbon nanodiamond) would give a messy diffraction pattern. For composite and mixed materials, the limit of detection is about ~2%. That is, in the composite if any component is present accounts for 2% or less of the whole, then XRD may not be able to detect it. One also needs access to a standard reference pattern of a known material to match the experimental peaks with. Peak overlay may occasionally worsen high angle reflections, causing inaccurate peak profiles. Materials to be tested need to be uniformly packed on the sample holder. They are usually ground into a uniform powder using a mortar and pestle. Silicon paste or double-sided scotch tape is used to pack the material over the center of the sample holder.

With the above conditions satisfied, we can expect to see sharp distinct peaks of a good crystalline material. Our result displays the peak positions at angle measurement $2\theta$ in degrees.
along the $x$-axis and intensity in arbitrary units along the $y$-axis. From this angle measurement we can identify the Miller indices ($hkl$) of the crystal’s unit cell from each peak position. We used Jade, a software packaged with Miniflex, to record our XRD data and Origin (Version 8 or above) to analyze further.

XRD also allows us to determine the size of the particles in our sample. For which we use Scherrer’s equation

$$D = \frac{K\lambda}{B \cos \theta_B}$$

(2.4)

Where $B$ is the full width half max (FWHM) of a peak, $\theta_B$ is the diffraction angle and $K$ is the Scherrer’s constant. Equation 2.4 is an estimate, not an accurate measure, of the size of the particle.

Overall, XRD is a widely used powerful equipment to characterize sample material. The technique helps us determine its composition (like metal – Cu, Zn, Au, Au), structure (Simple cubic - SC, Body centered cube - BCC, Face centered cube - FCC, or hexagonal close pack etc.), particle size, and Miller indices of the unit cell, unit cell dimension, arrangement and orientation of atoms in the lattice.

### 2.4 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform infrared (FTIR) is a type of absorption spectroscopy. When an infrared radiation passes through a substance (solid, liquid or gas), the electromagnetic wave interacts with the medium, which causes some of the energy to be absorbed. FTIR measures the intensity (in arbitrary unit) of the transmitted radiation as function of frequency (in cm$^{-1}$). The resultant spectrum shows the absorption or transmittance frequencies, from which the substance
can be identified. This method is primarily used to identify functional groups (ex. carbonyl groups in ketone or aldehydes, alcohol, carboxylic acid etc.) in organic or oxides (ex. Zinc Oxide or Si-O-Si) in inorganic compounds.

Figure 2.15 depicts the basic schematic of FTIR technique in the form of a Michelson Interferometer. When IR passes through a compound, the part that is not absorbed by the sample is transmitted according to Beer’s Law and picked up by a detector. The resulting signal is processed by a PC attached. Fourier Transformation produces a spectrum of intensity as a
function of frequency. The result is unique to the compound since no two types of molecules produce the same spectrum.

The sample preparation instrument and the FTIR instrument used in the present work are shown in Figure 2.16. To prepare a sample, first we grind a little amount of solid sample into warm KBr pellets by mortar and pestle. A small circular hole-cut is made at the center of a small piece of manila folder paper (1x1 square inch) in prior, which is placed securely onto a circular metal holder. The powdered mixture is then spread into the hole evenly and pressed by another circular metal sample holder placed atop. Now the sample stays secured between a pair of metal circular sample holder. This assembly (the dry sample powder mixture sandwiched between two metal sample holders) is then placed on the Raman Module (RAM) under hydraulic
pressure at 60 psi for about 30 seconds, controlled by a hand lever. Figure 2.16 left shows the assembly inside RAM. Upon releasing the pressure, we receive an opaque thin sheet of sample inside the hole-cut square paper. We then place this prepared sample inside the sample holder of the FTIR machine shown in Figure 2.16 right. We run FTIR under optimized conditions and parameters to see absorption peaks. Figure 2.17 shows a typical spectrum obtained by this method. The x-axis represents wavenumbers, i.e., the inverse of the wavelength of the light that was absorbed by the functional group(s) in the sample. The y-axis represents either Absorbance or Transmittance (being complementary to each other, they convey the same information, with one dipping where the other peaks).

Figure 2.17. FTIR spectrum of vanillin.

2.5 Curing Devices
2.5 Curing Devices

A material science laboratory must be equipped with ovens to drive moisture and volatile impurities out of samples prior to analysis. In our facility we have three furnaces. A “blue” metallic furnace with double racks and a vent pipe is used for low temperature curing up to 150°C. This oven is used primarily to evaporate excess solvent from the coating sprayed over a metal substrate.

The higher-temperature curing instrument is a “brown” oven, with a ceramic chamber in which freshly prepared samples are placed either in a glass beaker or a porcelain dish that can withstand temperatures of 150-1000°C with no physical or chemical damage. Prior to heating, the chamber is filled with Argon, an inert gas, and sealed, to prevent the sample from reacting chemically with air molecules. Special attention must be paid to what is being placed in this oven since it has no vent to diffuse away any undesired byproduct given off by the heating process.

Finally, a LINDBERG/BLUE STF55433C, an ultra lightweight and economical “3-Zone tube furnace” provides a low thermal mass insulation/heating unit (Moldatherm) for fast, energy-efficient duty cycles of temperatures up to 1500°C. This high range curing facilitates synthesis of ZnO-based samples or porous materials like mesoporous silica. It accepts different sizes of tube adaptors to accommodate various processes. A user-friendly control panel allows flexible programmed operation. The furnace model and the control panel are shown in Figure 2.18. The ceramic tube running across through the furnace holds the sample to cure.

Operation of the tube furnace requires caution.

- Heating of sulfates, chlorides, fluorides, alkalis and other highly reactive materials such as V_2O_5 is discouraged as they can corrode the ceramic tube.
- Although rapid heating or cooling does not damage the unit, prolonged use can cause hairline cracks in the insulation material. Therefore, the unit should be powered off when not in use.
- The pressure gauge needs to be checked frequently to avoid risk of explosion.
- The area housing the unit must be free of vibration have proper ventilation.
- Materials that are combustible or release toxic vapor or hazardous fumes upon heating must not be heated in the unit.

Operators must wear proper personal protection equipment (PPE) like long sleeve lab coat, heat resistant long gloves, and goggles to avoid skin contact with high heat.

### 2.6 Cooling Device: Instrument for Heat Dissipation

This instrument was designed and assembled in our lab by our research group back in 2012. This assembly was developed to study the heat dissipation process from a warm object and cool off to reach at the equilibrium temperature. Our group developed Molecular Fan technology during 2010. For this research, we needed some tools to observe how excess heat is dissipated away from our coated metal panels, heated by an electrical heater. Here we will discuss how the instrument was developed and introduce with each necessary components. Details can be found from the publication by Suryawanshi et al. This instrument was developed with a purpose to evaluate the performance of heat dissipative coatings as well as to determine the relative
Figure 2.18. Left: The Lindbergh Blue STF 55433C Tube Furnace. Right: Its control panel.
emissivity of the same. In my research, I never had to calculate emissivity, but I used all other features entirely for my Heat Dissipation Studies discussed in chapter 4. A simple mathematical model was employed based on different heat transfer mechanisms (Conduction, Convection and Radiation) to determine cooling performance of the coated aluminum, iron or magnesium panels with or without molecular fan (MF). Although we heavily use this instrument to study MF cooling efficiency, but in wide range we use coatings of all kinds. Our group studies showed that convection plays an important role as about 90% heat is transferred by convection. But with the MF incorporated coating, heat can be transferred up to 30% by radiation process. All these cooling tests were performed using this instrument.

![Schematic diagram of thermal cooling assembly](image)

**Figure 2.19.** Schematic diagram of thermal cooling assembly [3]
The instrument hardware consists of a thermal assembly tower (shown in Figure 2.20), a copper disk heater, heater cartridge, resistance temperature detector (RTD) sensor, J-type thermocouple sensor, an Infrared thermometer (Omega OS530LECF), a control unit for power supply with voltage regulator and control panel to monitor the temperature. By controlling the voltage, we can control current input to pass through the copper block and heat it up. An additional thermocouple sensor is used to measure the temperature of a sample specimen surface, like heat sink shown in the Figure 2.20.

Figure 2.19 shows a schematic diagram to design a cooling device using general physics heat laws.

Figure 2.20 left shows the entire cooling device with the coated heat sink on top of the copper block, which is surrounded by a thermal insulator. Figure 2.20 right shows the entire cooling assembly consists of a heat source (heater), cooling device and the computer attached with the device. This is our pre-existing cooling device built by our research group. Data were
collected using ‘Cosmol Physics’ software. This process was also described in the chapter 4, section 4.

Figure 2.21. Left: Schematic diagram of the assembly. Right: Thermal cooling device.

Figure 2.21 left shows a schematic diagram of how the substrate to be tested rests on the copper block. Two input and output sensors are shown under the substrate. Figure 2.21 right shows built cooling device; at the center there is a copper block, which was protected by a thermal insulator (thermal sponge around it); on the right side there are sensors, which flows heat in to the block. The block then gets heated and the object that sits over it gets heated too. The hot object then tries to cool off by conduction and convection method. The thermal sponge, which works as an insulator, minimizes the heat loss by conduction method. When our substrate is coated with molecular fan coating, this can be cooled off by radiation process. Our goal is to minimize the heat transfer process by conduction and/or convection method, and to maximize the radiation process. Because radiation is the most effective way of heat transfer as it is space less, powerless and radiates heat in the infrared range (1350-2700 cm\(^{-1}\) for MF nanocoating). The resultant temperature is carried out of the block by a sensor and is recorded by the Cosmol Multiphysics simulation software. These data then gets stored in an excel spreadsheet.
An electrical heater (a heat source) heats the copper block. We set a certain voltage on the heater and a temperature monitor guides us to monitor temperature.

2.7 Chemical Resistance Test (ASTM D308)

This is a simple test to check how well a coating is able to provide resistance against the application of any reagent. In this testing, we observe for any physical changes happen over the surface either over any film or just a pure substrate, during the contact of various reagents. This test primarily focus only on one point of a coated or uncoated metal surface to observe any effect due to chemical reaction occurred between the metal and the reagent, during a specific period of time (1-2 minutes). All observation should be clearly recorded before, during and after the test as per ASTM D308.26

2.8 Cross Cut Adhesion Test (ASTM D3359)

Sticky tape testing has been in use in the research laboratories as early as 1930’s. This is the easiest yet most effective and common type of testing to check Adhesive properties of any coating. This type is particularly designed for metal substrates and not for film on plastic substrates. Cross Cut Adhesion test is a standardized testing process followed by American Standard Testing Method D3359 or abbreviated as ASTM D3359. According to the standard, a piece of adhesive tape is pressed against a coating or film applied on a metal substrate, followed by peeling it off the surface area from the substrate at once with force. After this testing process, the result is evaluated by observing how much the film is peeled off by the adhesive tape. To determine the grade of coating stability by the Adhesion test, we follow certain guidelines
following the ASTM D3359 expectation. Figure xxx explains different extent of Adhesion result.\textsuperscript{25}

Here we obtain \textit{method A} by scribing a 1.5-inch X-cut or \textit{method B} by scribing 1 mm x 1 mm squares over the film after it has been cured. A cross-hatched pattern of approximately 100 squares are scribed on the film. During the carving process, keen \textit{observation}, like smooth surface or trapped bubbles, flaking or brittle and \textit{feeling} of cutting, like soft or hard, smooth or grainy, are to be recorded. In case of scaling off, also make sure of amount is peeled off the surface. All these could be graded in the scale of 0B (the worst) to 5B (the best) as per the coating description in words described in Table 2.1 and the picture depicted to classify the grades as per method B given in the Figure 2.22.\textsuperscript{26}

<table>
<thead>
<tr>
<th>Grade</th>
<th>Coating Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>5B</td>
<td>The edges of the cuts are completely smooth; none of the squares of the lattice are detached.</td>
</tr>
<tr>
<td>4B</td>
<td>Small flakes of the coating are detached at intersections; less than 5% of the area is affected.</td>
</tr>
<tr>
<td>3B</td>
<td>Small flakes of the coating are detached along edges and at intersections of cuts. The area affected is 5 to 15 % of the lattice.</td>
</tr>
<tr>
<td>2B</td>
<td>The coating has flaked along the edges and on parts of the squares. The area affected is 15 to 35 % of the lattice.</td>
</tr>
<tr>
<td>1B</td>
<td>The coating has flaked along the edges of cuts in large ribbons, and whole squares have detached. The area affected is 35 to 65 % of the lattice.</td>
</tr>
<tr>
<td>0B</td>
<td>Flaking and detachment worse than Grade 1.</td>
</tr>
</tbody>
</table>
Figure 2.22. The different classification grade and % area removed due to flaking along with the picture of surface area. 

<table>
<thead>
<tr>
<th>Classification</th>
<th>% of Area Removed</th>
<th>Surface of Cross-cut Area From Which Flaking has Occurred for 6 Parallel Cuts &amp; Adhesion range by %</th>
</tr>
</thead>
<tbody>
<tr>
<td>5B</td>
<td>0% None</td>
<td><img src="image1" alt="Image" /></td>
</tr>
<tr>
<td>4B</td>
<td>Less than 5%</td>
<td><img src="image2" alt="Image" /></td>
</tr>
<tr>
<td>3B</td>
<td>5 - 15%</td>
<td><img src="image3" alt="Image" /></td>
</tr>
<tr>
<td>2B</td>
<td>15 - 35%</td>
<td><img src="image4" alt="Image" /></td>
</tr>
<tr>
<td>1B</td>
<td>35 - 65%</td>
<td><img src="image5" alt="Image" /></td>
</tr>
<tr>
<td>0B</td>
<td>Greater than 65%</td>
<td><img src="image6" alt="Image" /></td>
</tr>
</tbody>
</table>
2.9 Salt-Fog Test (ASTM B117)

Corrosion and weathering of metals are common phenomena in the adverse condition of weather, like wet salty weather of sea beach, salty sand dessert with wind, snow storm etc. Salt – Fog testing allows us to observe how well a metal surface can provide resistance under the heated salt mist condition over the desired period of time, typically in 1 to 30 days cycle. Based on the observation, we can determine how our coating formulations would be to give corrosion protection.

Salt fog or salt spray testing is widely used testing method used in the corrosion industries and research laboratories to observe corrosion effect on metals or alloys. This is an artificial corrosion chamber created as per American Standard Testing Method B117 (ASTM B117). This machine is shown in the Figure 2.23. The entire assembly consists of a spray chamber with a spray nozzle inside, along with a hanging tray to hold samples, and salt solution reservoir, air saturated tower, a heater and monitoring controls outside.

Figure 2.23. Salt spray chamber used in our experiment.
Optimal conditions for Salt-Fog testing are given below:²⁶

Temperature: 94 °F
Pressure: 16 psi
Salt: 5% (sodium chloride mist)
Inclination: 45° (Coated side facing up)

Conversion factor: 100 hours Salt Spray Testing is equivalent to 15 years of natural corrosion in the desert or Florida beach environment.

2.10 Thickness Probe

Every coating panel needs to be examined well to check for the thickness. Coating with larger thickness film, easier the metal surface to be oxidized. However, we try to keep coating thickness as thin as 25 to 30 micron for corrosion testing samples and about 40-50 micron for heat dissipative samples. Too thick coating is not desired because it would consume more chemicals and thus become more expensive process. Getting the best outcome like corrosion resistance or heat dissipation with uniform minimum thickness is ideal.

In our lab thickness measurements are performed by Electromatic DCN-900 coating thickness gauge. The gauge comes with a probe and a control monitor. The thickness of coating is read digitally by the gauge. The measuring range is between 1-999 microns. We use different probes for different metal substrate like aluminum or aluminum alloy and steel or ferrous substrate. Figure 2.24 shows an aluminum thickness probe finds the coating thickness of 60 micron, which is bit higher range.
Before we make any thickness measurement, first we must calibrate on a bare metal substrate. Thickness gauge is very simple to operate. We keep our substrate flat on an even surface. We apply the probe vertically and gently over the substrate. The number on the control panel may change rapidly. Wait a little till the signal is stronger. Measurement must be taken at all four corners and directly in the middle. The average thickness from all these five points becomes the resulting thickness.²⁶
2.11 References


9. "The objective lens of a TEM, the heart of the electron microscope". rodenburg.org.


15. Von Ardenne M; “Improvements in electron microscopes”, GB 511204, (Germany) 18 February 1937.


25. Kane, H.; PhD Dissertation, NIU, **2012** (with advisor’s permission).


CHAPTER 3
IN-SITU PHOSPHATIZING REAGENT CATALYZED POLYSILSESQUIOXANE OLIGOMER: APPLICATIONS IN CORROSION PROTECTION FOR MAGNESIUM ALLOYS

Abstract: In-situ phosphatized coating (ISPC) offers corrosion protection for the metals like aluminum, iron, magnesium, which can be easily oxidized when exposed to air or humid weather, by creating a thin and stable organic-inorganic hybrid phosphate layer (Corrosion Inhibitor) on the surface of the metal. In this process, in-situ phosphatizing reagent (ISPR) forms a dense and uniform interfacial phosphate layer over the metal substrate and links to the polymer top layer via covalent bond. We synthesized ISPR catalyzed polysilsesquioxane (PSSQ) oligomer, where we incorporated phosphatizing reagent (ISPR) along with resin, solvent, anticorrosive agent, adhesion promoter and surface modifier to make a robust protective layer for metals like magnesium and its alloys with aluminum and zinc such as ‘AZ91’ (Al: 9%, Zn: 1%, Mg: 90%). This coating acts as an interfacial passivation layer of PSSQ, which resides directly on the metal surface and underneath the polymer layer and is often incorporated with nanomaterials and/or pigments for corrosion inhibition of magnesium alloys.

We investigated its robustness first by an adhesion test followed by a salt-fog test. The polymer coatings with nanomaterials and pigments of various types with ~25 μm thickness were applied on magnesium alloys of different shapes and sizes, by drawbar, spray or dip coating techniques. The corrosion performance from the adhesion test (ASTM D 3359) and salt–fog test (ASTM B117) were investigated closely and are discussed within. We also like to determine any molecular fan effect by measuring the cooling efficiency on the aluminum substrate.
3.1 Introduction

3.1.1 Magnesium Alloys

Magnesium is the lightest metal in the earth. Due to its low density ($d=1.48\text{g/cm}^3$) and high specific stiffness, it is high in demand as a structural material for automobile, aerospace, building, construction, communication tower etc. Magnesium and its alloys like AZ31, AZ61, AZ91 are used every day in 3C industries, such as computer technology, communication devices, and consumer electronics.\(^1\) However, poor corrosion resistance and high chemical reactivity make magnesium vulnerable. In our lab we developed nanocoatings to protect the metal surface from the corrosion. This project focused on studying magnesium alloys like AZ91 (Al: 9%, Zn: 1%, Mg: 90%)

3.1.2 Corrosion

Corrosion is a chemical process. This process is performed in nature by redox reaction, which occurs due to the presence of moisture, oxygen and metal. As a result, this process forms metal oxide (e.g., rust is a form of iron oxide). Initially, metal oxide acts as a protection barrier against the external and internal environments. However, over the long period, this metal oxide layer will corrode through the metal and flake off. Thus, it is important to offer corrosion protection to save structural, automotive and appliance industries.
Reactions through anodic and cathodic process:

*Anodic* (Half Reaction): \( \text{Mg} \rightarrow \text{Mg}^{2+} + 2e^- \) **Oxidation**

Oxidation is denoted by increase in oxidation number on metal: \( \text{Mg}^0 \rightarrow \text{Mg}^{2+} \)

*Cathodic* (Half Reaction): \( 2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \) **Reduction**

Reduction is denoted by decrease in oxidation number: \( \text{H}^{+1} \rightarrow \text{H}^0 \)

Or \( \text{O}_2 + 4e^- \rightarrow 2\text{O}^{2-} \) **Reduction** (\( \text{O}^0 \rightarrow \text{O}^{2-} \)) Overall Combined Reactions:

\[
\text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + \text{H}_2
\]

Or \( 2\text{Mg} + \text{O}_2 \rightarrow 2\text{MgO} \)

### 3.1.3 In-Situ Phosphatizing Coating (ISPC)/In-Situ Phosphatizing Reagent (ISPR)

Metals need to be protected from corrosion caused by their surroundings. Phosphate conversion coating such as in-situ phosphatized coating (ISPC) offers corrosion protection by forming a very thin layer of phosphate (~3-5 micron) over the surface of the metal. Phosphate is widely known as corrosion inhibitor. \(^{[4]}\)
Here we introduced an in-situ phosphatizing reagent incorporated with nanocomposites, resins, solvents and anti-corrosive agents etc. to develop various formulations. These formulations were then applied on the metal surfaces. We observed how the metal surfaces reacted with our phosphatizing coatings when they were put into an artificial corrosion chamber for several days.

Our group previously published its initial work and took a patent in 1994 on the In-Situ Phosphatizing Coating (ISPC) technique. [2,3] This project is a continuation of previous work in which AZ91 was tested with anticorrosion up to 120 hours in the Salt-Spray chamber.

3.1.4 Formation of Interstitial Layer

3.1.4.1 Principle (Sol-gel Chemistry)

The sol-gel process involves the formation of sol, which is a stable suspension of colloidal particles, and gel, which is a three-dimensional interconnected solid network. This gel expands in a stable fashion in a liquid medium. During the sol-gel process, the molecular weight of the oxide product continuously increases, eventually forming a high viscosity gel.[18] In this project, when we formulated our emulsions, we needed to be very careful, not to let the gel formation happen. We controlled the reaction in a way so the condensation process can go slowly and steadily. Typically, acid catalyzed hydrolysis (first step) goes fast, followed by a slow condensation (second step-a rate determining step) process that inhibits high viscous gel from forming. On the other hand, a base catalyzed hydrolysis can go slow (first step) but is followed by a fast condensation (second step) process in which gel forms rapidly. We discouraged a base catalyzed reaction here.
Figure 3.2. Acid and base catalyzed reaction in sol-gel chemistry\cite{18}

Figure 3.2 describes how sol-gel chemistry is controlled by the acid or base catalyzed hydrolysis of a soluble chemical precursor that then condenses with itself to form an extended network.\cite{18}

Figure 3.3. Left: SEM image showing coagulating polymer. Right: Gel formation dispersion due to condensation

Figure 3.3 left is an SEM image describing how coagulation of polymer dispersion happens due to fast condensation. Figure 3.3 right is a schematic diagram of the different stages of gel formation. We strictly allowed only sol not gel in our experiment.
Following the above-mentioned sol-gel technique, we created polysilsesquioxane (PSSQ). In this compound we had an organic functional group (‘R’) and an inorganic siloxane bond (O-Si-O). The inorganic component (siloxane bond) contributed the resistance properties such as heat resistance, electrical resistance, weather resistance and hardness.[19] Whereas, the organic functional group provided compatibility or flexibility, dispersion stability, reactivity (epoxy, acryl, alkyd etc.).[19] Together this PSSQ acquired the potential to strive for corrosion. Figure 2.4 below shows a diagram for a PSSQ unit.

![Figure 3.4. Polysilsesquioxane (PSSQ)](image)

Polysilsesquioxane, commonly represented as PSSQ or PSQ, is a silicone resin. It is synthesized by a trifunctional organosilane compound and an organic-inorganic hybrid material that combines the inorganic characteristics presented by the siloxane bond (O-Si-O), which constitutes the main chain. Organic characteristics are presented by the organic functional group that constitutes the side chain. Typically raw materials are prepared in the paint or coating industry, using this technique, by varying organo-trichloro silane and organo-trialkoxy silane.

We followed the same principle. The next section explains how the reactions went.
3.1.4.2 Reactions: Formation of PSSQ

![Diagram of sol-gel reaction to form polysilsesquioxane (PSSQ).][19]

In the sol-gel process, we first hydrolyzed an organosilane (trichloro) or a metal alkoxide such as trialkoxysilane, followed by a condensation process to make a siloxane bond (O-Si-O). Figure 2.5 shows a basic sol-gel reaction we conducted in our experiment.

Where R denotes an alkyl group, typically methyl, ethyl, vinyl or phenyl group and R’ can be a bulky group such as propyl or butyl.

![Different orientation of polysilsesquioxane (PSSQ).][19]
PSSQ could shape differently, either as a random structure in Figure 3.6(a), ladder structure in Figure 3.6(b) or cage structure like shown in in Figure 3.6(c). The shapes can be controlled by fine-tuning of the temperature, selection of the precursor, etc. In our experiment, we made random structured PSSQ, as the nano network keep expanding in all directions.

3.1.5 Corrosion Inhibitors

We have learned from surface chemistry that surface reactions are strongly influenced by the presence of foreign molecules. Corrosion is surface reaction process and is controlled by compounds known as inhibitors, which adsorb on the reacting metal surface. Adsorption refers to the molecules directly attached to the surface. Typically, one atom thick, it does not penetrate into the bulk metal substrate. A corrosion inhibitor blocks active sites on the metal surface many ways, such as restricting the rate of the anodic or cathodic process. Another possible way it may act is by increasing the potential of the metal surface so the metal enters the passivation region where a natural oxide film develops. Another work strategy is forming a thin layer on the surface, contributed to by the inhibiting compounds, which restrains the corrosion process. In this project, we used various corrosion inhibitors such as Nacorr 1352, 1552, etc.

3.2 Experimental Details:

3.2.1 Metal Substrate Preparation:

The foremost step is cleaning the surface of the metal substrate. Otherwise, adhesion testing on top of a surface will not be successful and we cannot progress. There are many ways to clean metal surfaces; out of them solvent degreasing (IPA wash), acid pickling, alkaline cleaning
(an economic and alternative treatment for organic solvent), and sand blasting (expensive process, only for those samples that cannot be chemically cleaned) are quite common. To get rid of any dirt, contaminants, corrosion deposits, oil or grease from the metal surface, in this project we used solvent degreasing (IPA wash) and acid pickling. Both are quite simple and inexpensive as opposed to the sand-blasting procedure.[1]

3.2.2 Surface Pretreatment:

3.2.2.1 Acid-Pickling Bath:

In a large beaker we measured out an amount of Milli-Q Water (98.5%). Into that, we added sodium nitrate salt (0.9%) and mixed well under a magnetic stirrer. Now slowly we added nitric acid (0.6%) into the water and sodium nitrate mixture. We continued mixing with a magnetic stirrer and cooled it at room temperature.

*Note: Exothermic reaction. Take proper care.*

Figure 3.7. Magnesium substrate is in acid-pickling bath

Figure 3.7 captures an acid pickling bath showing the surface chemistry began right there (i.e., metal surface gets into chemical reaction as soon as it gets into contact with acid pickling bath) (HCl:HNO₃)
3.2.2.2 Wastes Product from Surface Pretreatment – Liquid, VOC and HAP

Our cleaning process created liquid and volatile waste, whereas the surface treatment, primer, topcoats all contributed to solid waste too.

Our pretreatment process involved certain solvents such as propylene glycol butyl ether (PnB) and butylcarbitol (BC), which created volatile organic chemicals (VOC) as well as hazardous water pollutants (HAPs). Therefore, we had strict boundaries of solvent usage in our pretreatment/formulations (31-33%).

![Figure 3.8. Left: VOC. Right: HAP.](image)

3.2.2.3 Phosphatizing Surface Pretreatment:

Phosphating is a well-known industrial process for surface pretreatment for metals and their alloys. This allows metals to achieve excellent properties such as corrosion resistance, wear resistance, adhesion and lubrication. Phosphatizing has drawn a lot of attraction for being fast, cost-effective and economic and, thus, is heavily used in automotive and appliance industries. Phosphating allows forming an effectively hard, highly adhesive, electrically non-conducting
surface coating of insoluble phosphate. This process creates a thin film in which the substrate metal integrates itself within.\textsuperscript{[4]}

**3.2.3 Chemistry of Phosphating:**

When a metal (iron, magnesium, copper) is brought into contact with the phosphating solution (commonly diluted phosphoric acid solution of alkali metal ions), a redox reaction is initiated with the microanodes present on the substrate.\textsuperscript{[4]}

Here magnesium undergoes through oxidation (0 to +2 oxidation number) and hydrogen undergoes through reduction (+1 to 0 oxidation number), evolving hydrogen gas.

\[
\text{Mg} + 2\text{H}_3\text{PO}_4 \rightarrow \text{Mg(H}_2\text{PO}_4)_2 + \text{H}_2
\]

Metal reacts with phosphoric acid, creating a metal-phosphate complex. Observing reaction conditions like temperature, precise amount of phosphoric acid, and operating conditions are necessary to obtain a desired amount of phosphate deposition over the metal surface and to avoid hydrolysis. An excess amount of phosphoric acid can cause delays in coating formation and detrimental loss of metal substrate.\textsuperscript{[4]}

The phosphate coating process can be done more efficiently with the help of three kinds of acceleration mode, namely chemical acceleration, mechanical acceleration and electrochemical acceleration, which are widely used in industry. The chemical acceleration process introduces oxidizing material, which controls the rate of the phosphate coating yield, whereas, mechanical acceleration process ensures a constant fresh bath often used by a spraying process. In an electrochemical acceleration process, phosphate deposition is done by electrochemical reaction.
3.2.3.1 Advantage:

A phosphate conversion bath has an advantage over the conventional chromate bath since it avoids toxic waste products.\cite{1}

3.2.3.2 Disadvantages:

There are some downsides of using a phosphate conversion bath. Since this process is high-cost in operation, it needs to be run at an elevated temperature and frequently needs a desludging process. Also a concentrated phosphate bath can cause harm in ground and water ecology.\cite{1}

In this project, we introduce in-situ phosphatizing reagent (ISPR) for the phosphate conversion bath, where we use phytic acid (PTA) Vs widely used phenyl phosphonic acid (PPA).

3.3. Synthesis of Coating: Metal Conversion Coating

Dr. Lin’s group developed a surface treatment method, called in-situ phosphatizing coating (ISPC).\cite{2,3} This process is inexpensive, simple and yet environment friendly as opposed to carcinogenic chromate bath or conventional phosphate bath.

Our group previously used phenyl phosphonic acid (PPA) in metal conversion coating. This project will use phytic acid (PTA) instead of phenyl phosphonic acid (PPA). Our studies show that PTA works even better than PPA. Having four phosphate groups in PTA, it works better with epoxy groups present in epoxy silane (Gamma-g (3glycidoxypropyl-trimethoxy silane) in the emulsion we prepare.
3.3.1 Materials Needed:

A. ISPR - ISPR related reagents such as phenyl phosphonic acid (PPA) and phytic acid (50 wt% solution in water) were purchased from Sigma Aldrich. Solvent 1-methoxy-2propanol (PM 99.5%) and tetraethyl orthosilicate (98%) were also purchased from Sigma Aldrich.

The main solvent we used is Millipore or Milli-Q water with resistivity higher than 18 Megohm, which was obtained from our laboratory machine.

B. Emulsion – The first and foremost chemical to make emulsions are resin binders, which were received from Alberdingk Boley and Duramac water reducible alkyd were obtained from Hexion Specialty Chemicals. The cross linkers like Cymel 303, Cymel 385 were sent from Cytec Industries Inc. All organofunctional silanes (e.g. 3-glycidoxypropyltrimethoxysilane, tetramethoxy silane, methyltriethoxy silane, tetraethyl orthosilicate) were purchased from Gelest, Inc.

The solvents such as propylene glycol butyl ether (PnB) and butylcarbitol were purchased from Aldrich.

Some magnesium alloy panels were bought from M & B MAG, Ltd. (West Ontario, Canada) and Lunt Manufacturing Co., Inc. (Schaumburg, Illinois, USA), whereas most of the thick panels and thin alloy sheet were sent from China (company name?).

C. Nanocomposite coating - For nanocomposite coatings, nanomaterials such as carbon nanotube (CNT-163), graphene-C are obtained from China. Hexagonal Boron Nitride (HBN – 99.5%) and zinc oxide (ZnO – 99.8%) were purchased from Sky Spring Nanomaterials, Inc. Titanium dioxide (TiO2) is brought from DuPont Miracles of Science.
3.3.2 Synthesis of ISPR

We prepare ISPR in our lab. The entire procedure is about 4 hours long. We divide the entire process mainly in three sections.

**Procedure:**

I: In section I, we sonicate PM and gamma G together for ~ 2 minutes by the powerful sonicator. We label this mixture #1.

II: Next we sonicate PM and phytic acid together for ~ 2 minutes by the powerful sonicator. We label this mixture as #2.

III: Next we combine #1 and #2 by the sonicator for complete blend.

IV. Reflux at 80°C for 90 minutes.

V. Cool, let it age overnight.

VI. Store in bottle for later use.

3.3.3 Synthesis and Use of Organic/Inorganic hybrid nanocomposite

Figure 3.9 is a tree structure displaying our overall coating layout used for the applications.
The tree structure, Figure 3.9, can be explained as follows:

A. **Primer (Clear Transparent)**

We prepared three kinds of clear primers. They will be called 8603, 8104 and 8105.

1. 8603 - Transparent
2. 8104 - Light reddish in color
3. 8105 - Light brownish in color

B. **Top Coating**

We prepared several types of top coatings – some with molecular fan nanocomposites, some with abrasion resistant metal such as aluminum flake and some with pigments. We used
two kinds of pigments white and green. For each category, we have two types. White pigments are called PACG2 and PACG3 (industrial name). The green pigments used were solvent based (0521) and water based (0522).

(1) With MF (Grey Emulsion)

(i) 8104 MF – Modified 8104 with Molecular Fan mamocomposites

(ii) 8105 MF - Modified 8105 with Molecular Fan mamocomposites

(2) With Abrasion Resistant Al flake (Alumina)

(i) Silver emulsion with alumina paste

(3) With Pigment

(i) Green

(a) 8104/0521 (Solvent Based) – modified 8104 with pigment 0521

(b) 8104/0522 (Water Based) - modified 8104 with pigment 0522

(ii) White

(a) 8104/PACG2 - modified 8104 with pigment PACG2

(b) 8104/PACG3

Next section will discuss how primers are made, how to work with the primers and testing procedures with primers

3.3.3.1 Synthesis Procedure of Primers

Below we give a description of some formulations.

**Primer 8603 – ‘a’ - Type-I Formulation** – This process has mainly two parts.

In part I, we mixed PM, butylcellosolve and butylcarbitol with a drill presser (Specification?) for 15 minutes. Next, we added our lab synthesized ISPR to the above mix while
the drill press was running. We further mixed both for another 15 minutes. Note that we do 
not need to add metal beads here to further grind.

In part II, we added a few drops each of FSN (fluoro-surfactant), Nacorr1552 (corrosion 
inhibitor), DMEA (pH controller, to cut down little acidic nature), and BYK 333 (surface tension 
controller). We continued mixing with the drill presser for another 15 minutes.

Next, we strained and defoamed it in a homogenizer (Thinky mixer/defoamer) for 20 
minutes. Finally, we strained it again to get rid of any unwanted particles formed during the 
mixing process, collected and stored it in a bottle for coating (dip/spray) later.

Note: We modified this formulation from our original one, where we did not use 
butylcellosolve. PM is hydrophilic, so it is a good solvent for preparing ISPR, since ISPR needs 
little water as a co-solvent. However, butylcarbitol is hydrophobic. So together PM and 
butylcarbitol do not work well. Besides butylcarbitol is immiscible with PM but a better miscible 
with butylcellosolve. On the other hand, hydrophobic butylcarbitol is a better miscible with 
butylcellosolve. Hence is the change. This way we could stop defects like peeling edges on the 
surface.

Note: Clear primer 8603-’a’ does not contain any resin like Duramac. Whereas the other 
two primers, 8104B and 8105B, are both made of resins.

Primer ‘8104 B’ Type-I Formulation

This primer is composed of two types of resin, Duramac 74-7495 and Duramac 73-7331, 
along with cross-linker Cymel-303 and solvent butylcarbitol.
Primer ‘8105 B’ Type-I Formulation

This primer is based on Resin Duramac 207-3738 only rather than cross-linker Cymel303 and solvent butylcarbitol.

3.3.3.2. Primer Dipping Process: In a tall beaker, each piece of aluminum or magnesium panel was dipped with a steady hand for 2 minutes, making sure every surface was completely immersed in the liquid. While the panel was immersed, shaking was also necessary to have an uniform layer of primer over the metal surface.

3.3.3.3 Primer Flush time: We hung each panel to dry for 10 minutes.

3.3.3.4 Primer Curing Process

The panels were cured in a preheated oven at 120 degrees Celsius temperature for 20 minutes and cooled off at room temperature before the adhesion testing.

When an emulsion coating was sprayed on a metal surface or a metal plate was dipped in an emulsion, we shook it off and laid or hung it to dry to reach proper flush time. Then we cured the coated substrate in an oven at a high temperature to have a uniform permanent film over the metal surface. This film layer is what protected the metal from corrosion. The picture below describes how the curing process worked.
Figure 3.10 describes different stages during a curing process. Stage-1 on the upper left shows how the colloidal particles are scattered further apart in an emulsion at room temperature when it is freshly applied on a metal substrate. Stage-2 on the upper right shows colloidal particles are now being accumulated in an ordered fashion, like in arrays upon heating at high temperature (~120°C). In this stage, the particles are very closely located but there still remain interstitial or intermolecular spaces. Stage-3 shows the particles are now grouped together in a single unit to form a uniform film having no intermolecular spaces. This film is formed upon cooling at room temperature (22-25°C).

3.3.3.5 Adhesion Test/Cross cut Tape Test on Primer 8603-’a’

The results show excellent adhesion 5B (5B is the best, as per the ASTM D3359 standard, discussed in the Introduction Chapter).
3.4 Different class of formulation

In this project we formulated a wide range of coatings. Some included nanomaterials, some had metal oxides as fillers, some had pigments and others are clear primers. Below is an outline of the entire process, explaining each individual component’s property.

3.4.1 Metal Incorporation

Some well-known metals as zinc or titanium were used in the paint industry as far back as the 12th century. Zinc was first acknowledged as a metal in India (Zawar), where both zinc and zinc oxide were produced between the 12th and 16th centuries, until manufacturing was moved to China by the 17th century. Since then, among the many usages of zinc, the major use of this metal was to prepare anti-corrosion coatings for other metals like galvanized steel and paints for artists. Because of its anti-corrosive property, a large amount of zinc oxide was consumed in the rubber industry. By the 1970s, zinc oxide was largely used in photocopying as well. Titanium took its place in photocopying soon after.

Looking at the rich history of those metals in the past, we tried to incorporate several metals into our organic-inorganic hybrid emulsions as necessary, like zinc, titanium and aluminum for their excellent properties. Below the properties of each metal and description will be discussed.
(a) Zinc as Zinc Oxide (ZnO)

Figure 3.11. ZnO\[^{13}\]

The zinc oxide (molar mass: 81.38 g/mole) used in this experiment is a white nanopowder (size < 100 nm), insoluble in water, an inorganic ionic compound (with radii for \(\text{Zn}^{2+}\) is 0.074 nm and \(\text{O}^{2-}\) is 0.14 nm).\[^6\] Zinc oxide naturally occurs as a mineral, namely zincite. But most zinc oxide for lab use is synthetically produced.\[^7\] It is high in demand for industrial use. Zinc oxide is commonly used as an additive in many materials, such as plastics, rubbers, glass, cement, paints, ointments, lubricants, adhesives, sealants, pigments, batteries, fire retardants, and first-aid.\[^8\]

Figure 3.12 Zinc Oxide, hexagonal Wurtzite Structure \[^{13}\]

Zinc oxide usually crystallizes in two forms, hexagonal wurtzite and cubic zincblende. The wurtzite structure is the most stable at ambient conditions and hence is widely used. In both cases, zinc and oxide form tetrahedral geometry, as shaded in the above diagram with point group \(\text{C}_{6\text{v}}\). Zinc oxide is a well-known semiconductor. It has a relatively large band gap of
~3.3eV at room temperature. With its high melting point 1,975°C, zinc oxide becomes a safe additive in the paint and coating industry.

(b) Titanium as Titanium dioxide (TiO₂)

![Figure 3.13. Left: TiO₂. Right: The unit cell of Rutile in TiO₂.](image)

Titanium dioxide or titanium (IV) oxide is also known as titania (Molar mass: 79.866 g/mol). When it is used as a pigment, it is known as Titanium White. This oxide occurs in nature as an odorless white solid. It comes mostly in three forms of minerals like rutile, anatase and brookite and two high pressure forms as monoclinic and orthorhombic. Its main ore is Ilmenite. Rutile and anatase forms are metastable. These phases can convert to a rutile phase irreversibly upon heating between 600-800 °C.

Like zinc oxide, titanium dioxide also has a high melting point, 1,843°C, and boiling point, 2,972°C, and is insoluble in water. Its band gap in rutile form is 3.05 eV.

Titanium dioxide is widely used (80% of world’s consumption) in paint and varnishes and also in paper and plastics. Due to its highly refractive index and brightness, titanium dioxide is a good candidate for pigment. Thus, it is also used as pigments in food coloring, sunscreen, printing inks, fibers, rubber and cosmetic products. Titanium dioxide can act as excellent reflective optical coating when deposited as a thin film. It is also an excellent opacifier in powder form. Its opacity can be controlled by finely tuning the optimal sizing of the titanium dioxide particles. Thus, it can be used as pigment to provide whiteness and opacity in paints and coatings industry, papers, inks, food, medicines and toothpaste. In the paint industry, titanium dioxide is
called as “the whitest white” or “the perfect white.” Titanium dioxide has a high refractive index and its strong UV light absorbing capabilities and its high resistance to discoloration under UV light made it an indispensable component in our other project called UV/NIR cut coating for glass substrates. Titanium dioxide is also used as pigment in sunscreen lotions to protect the skin from UV rays. Typically 30-50 nm scale sized nanoparticles of titanium dioxide can scatter visible light as well as provide UV protection.[12]

(c) Aluminum as alumina flake (Al₂O₃)

Figure 3.14 Alumina paste, ZQ40610 (Solvent-based) and ZQ9012 (Water-based)

Abrasion resistant pigment Alumina is incorporated into our coating emulsion to provide toughness and silver color with a shiny texture. It also acts as a filler to thicken the film when cured. Fillers are inexpensive and inert materials. Alumina pigment and filler provide exterior durability and better opacity.[16]

3.4.2. Nanomaterial Incorporation

To bring special qualities such as a Molecular Fan effect, we also incorporated some nanomaterials such as graphene, carbon nanotube and hexagonal boron nitride.
3.4.3 Pigment Incorporation

We introduced two types of pigments, white and green. All are non-toxic.

Among the white category, we tried

1) PACG 2 - 170703 (Supplier did not reveal the detail)
2) PACG 3 - 170704 (Supplier did not reveal the detail)
In the yellowish green category, we used

1) 20170521 (solvent based)
2) 20170522 (water based)

Note: More resins and little less solvent can hold more pigment. So, we tried new modified versions of formulations with a 20% increase in resins. In this case we completely took away ISPR and Nacorr while being formulated, since in our previous trial, formulation with the above pigment did not bind well over the primer 8603-’a’, which contains a large amount of ISPR. However, while rested overnight, we observed this new version turned very thick. Then we had to adjust it with additional solvent (1g butylcarbitol + 1g PM + 1g butyl cellosolve under magnetic stirrer for 15 minutes). Even though our pigment was yellowish green, our final product was gray in color. We followed a similar routine while using white pigment PACG2-170703 and PACG-3-170704.

After performing adhesion tests on all of the formulation trials, we decided to follow the same procedure for the white and green pigments, but we added 12g ISPR and 3g of Nacorr for those with alumina and Molecular Fan fillers. Our testing results guided us to select only a few as finalists from each category. We picked PACG 3 -170704 from the white and 0521 from the green pigments, ZQ40610 from alumina and CNT-163/HBN nanomaterials for the Molecular Fan fillers.

Our final set of primers and top coatings for Adhesion Test (ASTM D3359) and Corrosion Test (ASTM B-117) are as follows:

1) 8603 - ‘a’ - clear transparent primer
2) 8104B – clear, copper-red primer
3) A (8104B-PACG 3 -170704) – 8104B with white pigment
4) B (8104B-20170521) – 8104B with yellowish green pigment
5) C (8104B-Al2O3 - ZQ40610) – 8104B with silver alumina flake
6) D (8104B - MF) – 8104B with nanomaterials (CNT and HBN)

We tried different combinations of primers and topcoats from the above list for testing with many sets.

![Figure 3.18. The final set of primers and four top coatings](image)

3.5 General Lab Coating Procedure:

3.5.1 Substrate Preparation

Substrate preparation was done following the directions listed below:

1. Cut the magnesium and aluminum panels in approximately equal sizes (2”x3”).
2. Clean them first with isopropyl alcohol (IPA). Wipe them with Kimwipes to dry.
3. Run IPA by dropper over the metal surface.
4. Wipe them clean and dry making sure there is no oil, grease or fingerprints over the surface.
3.5.2 Dipping in the Primer (first coating layer)

Dipping was done following the directions listed below. All glassware used here was cleaned with a sponge and soap, washed with tap water several times, and dried.

1. Pour the liquid in a shallow dish.
2. Dip each metal panel in the liquid, keeping for 1 minute, making sure all of the surface is in contact with the liquid.
3. Take the panel out of the liquid and shake off of the liquid for 1 minute.
4. Rest for 1 minute.
5. Air dry for 10 minutes.
7. Cool off at the room temperature (22-25°C).
8. Measure thickness (Desired 3-5 μm).
9. Perform Adhesion test (ASTM D3359). Goal is achieved with grade 4B-5B.

3.5.3 Top coating with other Primer/Nanocomposite coating (second coating layer)

The following instructions were followed strictly to complete each set of top coating.

1. Application of emulsion on the surface either by spraying, draw bar technique or dipping.
2. Spray coat nice and smooth with even layer of top coating.
3. Air dry (flash time) for 10 minutes.
4. Cure in the oven at 119°C for 15 minutes.
5. Cool off to the room temperature (22-25°C).
7. Perform Adhesion test (ASTM D3359). Results must be within grade 4B-5B to pass the industrial standard. If not, reformulate coating and repeat the above steps.

8. Perform Salt Spray Test (ASTM B-117) with desired number of hours, starting from 24 hours and progressively completing 240, 340, 540, 740, 840 and finally up to 1000 hours.

3.6: Adhesion Test (ASTM D3359) Procedure and Result:

3.6.1 Preparation of Set-1 Testing Panels and Adhesion Test Result:

Each aluminum Q-panel under columns I, II and III was dipped for 2 minutes (plus shake/drip for 1 minute) in clear primer 8603 – ‘a’ (Type-I), 8603 – ‘a’ (Type-II) and 8603 – ‘a’ (Type-III), respectively.

Next, they were hang-dried for 10 minutes, followed by a curing process in a 120°C oven for 20 minutes. An adhesion test was performed after cooling off to room temperature.

Rows display the results of the samples sprayed by top coating, namely 8104-MF, alumina (abrasion resistant silver pigment), PACG-3 (white corrosion pigment) and 0521/0522 (greenish yellow pigment), respectively. They were also hang-dried for 10 minutes, cured in 120°C oven for 20 minutes, and cooled off to room temperature before an adhesion test was performed. All testing panels came smooth in texture.

Set – 1: Primer 8603 - ‘a’ with different top coating over Aluminum Q-panels:
Table 3.1 Showing all initial work with base primer 8603 – ‘a’ (Type I, II, III) and their adhesion testing results as per ASTM D 3359, (0B → 5B, 0B was the worst with peeled off coating surface and 5B was the best). ‘0521’ and ‘0522’ were corrosion pigments:

<table>
<thead>
<tr>
<th>Primer 8603-‘a’</th>
<th>I</th>
<th>II</th>
<th>III</th>
</tr>
</thead>
<tbody>
<tr>
<td>‘a’</td>
<td>5B</td>
<td>5B</td>
<td>5B</td>
</tr>
<tr>
<td>‘a’ + 8104 MF</td>
<td>0B</td>
<td>0B</td>
<td>0B</td>
</tr>
<tr>
<td>‘a’ + alumina</td>
<td>5B</td>
<td>0B-3B</td>
<td>3B-4B</td>
</tr>
<tr>
<td>‘a’ + PACG-3</td>
<td>5B</td>
<td>4B-5B</td>
<td>5B</td>
</tr>
<tr>
<td>‘a’ + 0521</td>
<td>0B-2B</td>
<td>0B</td>
<td>0B-2B</td>
</tr>
<tr>
<td>‘a’ + 0522</td>
<td>0B</td>
<td>0B</td>
<td>0B-2B</td>
</tr>
</tbody>
</table>

3.6.2 Preparation of Set-2 Testing Panels and Adhesion Test Result:

Dipping and coating procedures are similar to set-1 as mentioned above. All testing panels after the topcoat, flushed, dried, cured and cooled off, came with a nice and smooth texture.

Set – 2: Testing of a primer over another primer:

Primer 8603 - ‘a’ as base coating and primer 8104B as top coating over Aluminum Q-panels:

Table 3.2. Adhesion testing results as per ASTM D-3359 for base layer ‘8603’ and top coating with ‘8104’; (0B → 5B, 0B-worst, 5B-best) were reported under each section:

<table>
<thead>
<tr>
<th>Primer 8603-‘a’</th>
<th>I</th>
<th>II</th>
<th>III</th>
</tr>
</thead>
<tbody>
<tr>
<td>‘a’</td>
<td>5B</td>
<td>5B</td>
<td>5B</td>
</tr>
<tr>
<td>‘a’ + 8104 (I)</td>
<td>5B</td>
<td>5B</td>
<td>5B</td>
</tr>
<tr>
<td>‘a’ + 8104 (II)</td>
<td>5B</td>
<td>0B</td>
<td>5B</td>
</tr>
<tr>
<td>‘a’ + 8104 (III)</td>
<td>5B</td>
<td>3B</td>
<td>5B</td>
</tr>
</tbody>
</table>
Table 3.2 displays Adhesion testing of all initial work, first with transparent base primer 8603–‘a’ (Type I, II, III). Over which we coat with copper-red primer 8104 ((Type I, II and III) as top coating.

### 3.6.3 Preparation of Set-3 Testing Panels and Adhesion Test Result:

The dipping and coating procedure was similar to set-1 as mentioned earlier. After the topcoat, all testing panels were flushed, dried, cured and cooled off before adhesion testing.

**Set – 3:** Primer 8104B with different top coatings over Aluminum Q-panels:

<table>
<thead>
<tr>
<th>Primer 8104B</th>
<th>I</th>
<th>II</th>
<th>III</th>
</tr>
</thead>
<tbody>
<tr>
<td>8104B</td>
<td>5B</td>
<td>5B</td>
<td>5B</td>
</tr>
<tr>
<td>8104B + 8104 MF</td>
<td>5B</td>
<td>0B-2B</td>
<td>0B-3B</td>
</tr>
<tr>
<td></td>
<td>Spotted, grainy Surface Tension - poor</td>
<td>Grainy surface Surface Tension - bad</td>
<td>Grainy surface Surface Tension - bad</td>
</tr>
<tr>
<td>8104B + alumina</td>
<td>0B</td>
<td>0B Thin Topcoat</td>
<td>0B Thin Topcoat</td>
</tr>
<tr>
<td>8104B + PACG-3</td>
<td>2B-3B Thin, smooth</td>
<td>5B Thin, smooth</td>
<td>5B Thin, smooth</td>
</tr>
<tr>
<td>8104B + 0521</td>
<td>0B Thin, smooth</td>
<td>0B Thin, smooth</td>
<td>0B Thin, smooth</td>
</tr>
<tr>
<td>8104B + 0522</td>
<td>0B-2B Smooth and shiny S.T. - good</td>
<td>0B Smooth and shiny S.T. - good</td>
<td>0B Smooth and shiny S.T. - good</td>
</tr>
</tbody>
</table>

Rows display the results of samples sprayed by top coating, namely 8104-MF, alumina (abrasion resistant silver pigment), PACG-3 (white corrosion pigment) and 0521/0522 (greenish yellow corrosion pigment), respectively.

*Note:* We found the following observations are noteworthy from our experience:
1. If the coating is too thick, the adhesion test can be 4B-5B or worse.

2. Smooth and shiny surfaces do not necessarily give a good adhesion test.

3. When the topcoat texture is nice and smooth, the surface tension may not be even.

### 3.6.4 Preparation of Set-4 Testing Panels and Adhesion Test Result:

The dipping and coating procedure is similar to set-2 as mentioned earlier. After the topcoat, all testing panels were flushed, dried, cured and cooled off before adhesion testing.

**Set – 4**: Testing of a primer over another primer:

Primer **8104B (I, II, III)** as base coating and the same as top coating over Aluminum Q-panels:

Table 3.4 Showing all initial work with copper red colored primer 8104 B (Type I, II, III):

<table>
<thead>
<tr>
<th>Primer 8104B</th>
<th>I</th>
<th>II</th>
<th>III</th>
</tr>
</thead>
<tbody>
<tr>
<td>8104B</td>
<td>5B</td>
<td>5B</td>
<td>5B</td>
</tr>
<tr>
<td>8104B + 8104B (I)</td>
<td>5B</td>
<td>5B</td>
<td>5B</td>
</tr>
<tr>
<td></td>
<td>Smooth, uniform, shiny</td>
<td>Smooth, uniform, shiny</td>
<td>Smooth, uniform, shiny</td>
</tr>
<tr>
<td>8104B + 8104B (II)</td>
<td>5B</td>
<td>5B</td>
<td>5B</td>
</tr>
<tr>
<td>8104B + 8104B (III)</td>
<td>4B</td>
<td>5B</td>
<td>4B-5B</td>
</tr>
</tbody>
</table>

In Table 3.4, rows display top coating with samples namely 8104 B (I), 8104 B (II), and 8104 B (III) respectively. Adhesion testing results per ASTM D 3359, (0B → 5B, 0B-worst, 5B-best) and surface texture was reported under each section.

Investigating all of the above results from Tables 2.1 through 2.4, we decided to upgrade or modify our formulations for 8104B – PACG-3, 8104B-0521, 8104B – Al₂O₃ and 8104BMF, which we like to call A, B, C and D, respectively, in short.

Afterwards, some (12) AZ91 magnesium panels were ready to be tested.
3.6.5 Testing of Set-5:

Notation: A: 8104B – PACG-3, B: 8104B-0521, C: 8104B – Al₂O₃ and D: 8104B-MF.

All panels (1-6) shown above were first dipped in a clear transparent primer 8603- ‘a’ type-I. Panel 7 was dipped in a clear transparent primer 8603-‘a’ type-III. Panels (8-12) were not dipped in anything or were left bare on purpose for further testing. Next, the front side of panels 2 and 8 were sprayed with 8104B(I); likewise the front side of panels 3, 4 and 10, 5 and 11, 6 and 12 were sprayed with aforementioned A, B, C and D, respectively.

Figure 3.19 Testing Preparation of metal Panels
3.6.5.1 Adhesions and Thickness Testing Result of the above Set-5:

Table 3.5 Adhesions and Thickness Testing Result of testing Set-5:

<table>
<thead>
<tr>
<th>Panel Numbers</th>
<th>Adhesion Result</th>
<th>Thickness (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5B</td>
<td>59</td>
</tr>
<tr>
<td>2</td>
<td>5B</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>5B</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td>5B</td>
<td>81</td>
</tr>
<tr>
<td>5</td>
<td>3B</td>
<td>87</td>
</tr>
<tr>
<td>6</td>
<td>1B</td>
<td>96</td>
</tr>
<tr>
<td>7</td>
<td>5B</td>
<td>61</td>
</tr>
<tr>
<td>8</td>
<td>5B</td>
<td>72</td>
</tr>
<tr>
<td>9</td>
<td>5B</td>
<td>75</td>
</tr>
<tr>
<td>10</td>
<td>5B</td>
<td>76</td>
</tr>
<tr>
<td>11</td>
<td>5B</td>
<td>78</td>
</tr>
<tr>
<td>12</td>
<td>4B-5B</td>
<td>92</td>
</tr>
</tbody>
</table>

From Table 3.5 we see only panel 6 gives extremely poor adhesion and panel 5 gives moderately low adhesion. One possible reason could be the panel 6 coating thickness is extra
thick (96 μm). Typically, it is hard to find good adhesion on a surface with too thick coating. Scotch tape sticks to a thick surface coating when being peeled off, whereas with a uniform thin coating it comes off clean. Otherwise rests are all in satisfactory range.

Since our adhesion testing is quite satisfactory, we can now proceed for the corrosion testing in the salt spray chamber (ASTM B-117).

3.7 Corrosion Test (ASTM B-117) or Salt Spray Testing (SST): Result

This section will display the results of the corrosion tests at different time intervals. Our goal is to reach 1,000 hours, and little or no corrosion is desired. Therefore, at every stage it is necessary for keen observation and discussion.

Figure 3.20. SST Result of coatings for 240 hours

Figure 3.20 displays magnesium panels with primers 8603, 8104 and 8105 after SST for 240 hours. Results show no corrosion till 240 hours. The panel surface looks nice, clean, smooth and shiny.
Figure 3.21 displays magnesium panels with 8104-MF and 8105-MF only (top two panels). The bottom two magnesium panels show base primer 8603-’a’ as the first layer and over that 8104 and 8104-MF as a topcoat. All four panels survived well under SST for 240 hours. No corrosion is observed.
Figure 3.22 shows four Mg panels. The bottom left is showing a topcoat prepared with 5g of green pigment (0551) without corrosion inhibitor Nacorr 1552. Here we observed a trace of spots (not sure if it should be called corrosion). The bottom right is showing a similar topcoat with less (3g) 0551 green pigment with corrosion inhibitor Nacorr 1552; where we cannot identify any corrosion until 366 hours. This observation suggests that it is wise to add little less pigment along with a corrosion inhibitor. Both survived pretty well for 366 hours under SST.
Figure 3.23. SST Result of coatings for 744 hours

Figure 3.23 shows the SST results after 744 hours. The purpose of this testing was to investigate a comparison between a pair of coatings comprised of a nanocomposite coating vs the same over a primer. This testing would indicate our coating efficiency. The left top two panels are with only primer 8603-’a’ (two kinds), and both look affected by corrosion effect. This observation tells us that metal surfaces coated only with primer will not sustain from corrosion long enough, so they need top coating to protect them from possible corrosion in long run. The middle two panels on the top row are with primer 8603-’a’/primer 8104 and just primer 8104 only. Both look ok, nice, smooth, shiny surface and free of corrosion. This observation tells us, a second coating with primer can also act as good as other nanocomposite top coating. The right
pair of panels on the top row are with primer 8603-’a’/PACG3 and PACG3 only. Both look free of corrosion.

The left two panels in the bottom row are with primer 8603-’a’/0521 and only 0521. We noticed some rough edges. They are due to some procedural errors. No corrosion is noticed on them. The middle two panels on the bottom row are with primer 8603’a’/alumina and alumina only. The surface shows a thick coating layer, but no corrosion effect is seen. Lastly, the right pair of panels on the bottom row is with primer 8603-’a’/MF and MF only. Both were free of corrosion.

Figure 3.24. SST Result of coatings for 1008 hours

Figure 3.24 shows two panels were coated with just clear primer 8603-’a’. The result of left panel was observed from the experiment facing down and the same with the right one facing up. Facing up shows more reaction happened over the surface, as the salt water vapor progress up the chamber and react over the faced-up surfaces more than those faced down. This observation suggests that to have effective corrosion protection, we need a top coat over a primer. Black stain should be overlooked, as some samples were smeared with the MF paint inside the corrosion chamber. This was repeated and seen in the following result as well.
Figure 3.25 shows three panels of our results with primers. The leftmost one is with clear primer 8603-'a’, the middle one is with a reddish primer 8104B, and the rightmost one is with 8104B over the base primer 8603. The observation could not differentiate much from the extent of corrosion. All of them were somewhat affected by corrosion. Again, this observation mainly suggests that metals just with primer are still vulnerable and need further protection by appropriate top coatings. The researcher kindly asks the viewers to overlook the black stain on the testing panels, as they were smeared with the MF paint during the reactions in the corrosion chamber.
Figure 3.26 shows an overall result of our best coating’s clear primer 8603-’a’, reddish primer 8104B, top coatings (A) 8104B/PACG-3 (White), (B) 8104B/0521 (green), (C) 8104B/Alumina (silver) and (D) 8104B/MF. Each kind of coating was done on two panels for better comparison. One to observe the results facing down and the other to observe the results facing up. Details are discussed with a closer look with figures below.
Figure 3.27 shows a pair of each kind of testing panels, where the left one stayed facing down and the right one was facing up at a slanted angle of 45°. Salt vapor reactions acted over the faced-up surfaces more aggressively. Salt-water vapor rises faster, and reactions happen with the available faced-up surfaces more than the faced-down surfaces. From the above observation, we see that the upper left panels with top coating ‘8104B’ over the same as primer are affected slightly the (right one in that pair) and the right panel of the lower left paired panels with just 8104B/Alumina was affected the most (faced up surface at an angle of 45°). Whereas the upper right and bottom right paired panels with 8603-’a’/8104B0521 and just 8104B-MF, respectively, both remained unaffected by the corrosion chamber at the end of 1008 hours. From the same
observation, we can infer that top coating with 8104B/Alumina needs a base primer to successfully pass the SST for a 1,000 hours test.

Figure 3.28 SST Result of coatings for 1008 hours

Figure 3.28 shows all four panels, which were facing down, survived well past 1,000 hours in the salt spray chamber. Facing down means, the salt vapor reactions were less. Still this is quite a phenomenal achievement. Our objective was to reach to 1,000 hours in the corrosion chamber with our best coating and to keep them protected from possible corrosion. The left upper panel is reddish primer 8104 over the same, the right upper panel shows coating with 8104B/0521 (green pigment) over clear primer 8603; the bottom left panel is coated with just 8104B/alumina (silver pigment) and the right bottom corner panel is with just 8104B/MF
(black). All passed the 1,000-hour test in the salt spray chamber. From our observations, we can proudly say that we successfully met our goal.

![Image of communication device](image)

Figure 3.29. A large communication device coated with 8603-’a’/8104B-0521 over primer 8603-’a’; Shipped to China for testing

Investigating some of our best results, we have prepared some big scale samples for a communication device made of magnesium alloys for industrial use. Figure 2.27 shows one of them. We prepared about 15 liters of clear primer 8603-’a’. We poured that in a large storage bin to dip the entire device into the primer. We had built a special mechanical hanging device, so our sample board could be hung to dry without having any fingerprints. We went through all the procedures mentioned before to flush, air dry, cure, etc. It was cured in a special large clay oven. When ready, we coated the front or topside with coating 8104B-0521. Again, following a similar curing process, we prepared our final sample to be tested in China. We prepared four more similar large communication devices coated with 8603-’a’/8104B, 8603-’a’/8104B-PACG3, 8603-’a’/8104B-alumina, and 8603-’a’/8104B-MF, respectively. One of them, we left with just primer 8603-’a’. That added up to six communication devices in total that we shipped to China for further testing.
3.8 Discussion

We wanted to analyze our experimental results to establish a strategic design of the pathway. Below is a possible schematic diagram of our nanocoatings that was developed by an in-situ method.

![Schematic diagram of nanocoating by in-situ method](image)

**Figure 3.30 Schematic diagram of nanocoating by in-situ method\textsuperscript{[18]}**

- Dispersion Nanocontainers
- Dispersion Nanoparticles

In Figure 3.30, the top layer in green indicates organic resin film, and the bottom layer in light gray indicates the metal substrate. The polysilsesquioxane layer resides compactly between the top and bottom layers. Together they take a sandwich like shape.
The formation of the Si-O-Si siloxane bond, M-O-P metal phosphate bond, Si-O-P bond, P-O-P bond, Si-\(\text{O}\)-bond are all combined in the middle layer. Nanoparticles are dispersed in a scattered way in the structure.

The diagram above explains how the nano network was built and stays as an interstitial passive layer between the polymer on top and the metal substrate at the bottom. As a part of our research, in the next step, we wanted to analyze our experimental work under a transmission electron microscope (TEM) and a scanning electron microscope (SEM). The former takes the image of the nanocoating, and the latter provides elemental analysis by EDS mapping. These two instruments are extremely helpful as we could visualize our in-situ phosphate coating structure in nanoscale.

![Figure 3.31. Left: Nanocoating on AZ91 by TEM.[1] Right: EDS mapping of Nanocoating.[1]](image)

The TEM image in Figure 3.31 left shows the nanocoating on the AZ91 metal substrate. On closer look, we noticed three different layers. The EDS mapping in Figure 3.31 right captures the three individual layers by identifying three types of elements shown in three colors. They are
carbon in green, phosphorus in blue, and magnesium in red. The top layer in green is detected as carbon, the polymer layer that comes from the resin. Next is the phosphate layer (phosphorus) in blue, in the middle as our polysilsesquioxane interstitial passive layer. Finally, the bottom layer, magnesium in red, is the AZ91 metal substrate. The EDS mapping also gives us the approximate thickness of the passive layer in blue, which is under 500 nm by scale. Both the TEM image and the EDS mapping helped us to understand how the nano network structure is built in the PSSQ-ISPC technique.

3.9 Conclusion

In this project we wanted to present an in-situ phosphatizing coating (ISPC) technique for metal alloys, like AZ91, by the formation of metal-phosphate bonds through an in-situ phosphatizing reagent (ISPR) and nanocomposite coating. We showed our experimental set up, procedures and results in a progressive manner to achieve enhanced surface-adhesion as well as high resistive corrosion-inhibition.

We synthesized proper nanocoatings by dispersion of ISPR-catalyzed polysilsesquioxane (PSSQ), which made a passive structural network at the substrate-coating interface. Our nanocomposite coating was generated by encapsulation and dispersion of colloidal silica, alumina, CNT, graphene, HBN in polymer matrix (resin). The dispersion was impregnated with active corrosion inhibitors to produce an effective anti-corrosion and heat dissipative coating for magnesium alloys, bicycle tubes, heat sinks, computer device, automotive parts and communication device, where metals need to be free of excess heat and corrosion to avoid malfunctioning. Experimental results show our ISPR/PSSQ coating with abrasion resistant and active nanomaterials topcoat can inhibit corrosion of metal alloys AZ91 (Al, Zn, Mg) starting
from 240 hours to 360 hours to 720 and finally up to 1,000 hours in the salt spray chamber.

We were able to develop a technique that allowed us to create a colloidal nanocoating to provide chemical resistance (corrosion), heat resistance, abrasion resistance and anti-fingerprint resistance. Aerospace, military and 3C (computer, communication and consumer electronics) industries will certainly benefit from our research.
3.10 References


12. Dan, Yongbo; Measurement of Titanium Dioxide Nanoparticles in Sunscreen using Single Particle ICP-MS.


CHAPTER 4
HEAT DISSIPATION STUDY

Thermal cooling using Molecular Fan Technology: Applications in miniature electronics and Heat Sinks

Abstract: Molecular fan, a radiative cooling mechanism, was followed to prepare coatings with active nanomaterials such as graphene, carbon nanotube and hexagonal boron nitride. A new formulation was developed for hot objects like compact electronics and heat sinks. We investigated thermal cooling efficiency on various types of heat sinks using Cosmol Multiphysics simulation software. Here in, we also developed a new cooling device following American Standard Testing Methods (ASTM D5470-06). We ran experiments on cell phones and objects of different sizes and shapes to understand the cooling process.

4.1 Introduction

This research project is geared toward cooling hot objects in an efficient way, so they can function properly over a long period of time. For objects of any size from car engines to small machines to phones to watches, regardless of sizes, cooling is necessary to maintain proper functionality and longevity.

As current electronic industries offer more tools and technologies in smaller scales, reducing the size forces development of compact and dense electronic devices. These miniature size electronic devices often suffer from overheating, while functioning. Trapped excess heat can destroy their functionalities, making them unstable and often cause malfunctions. Thus,
generated condensed heat must be dissipated away concurrently to have it perform with the desired efficiency.

During the last ten years of research studies, Dr. Lin’s group at NIU designed, developed, investigated and patented an innovative and efficient technique named molecular fan technology,[1] which dissipates heat into its surrounding environment through a radiation process.

Heat management becomes challenging as objects become smaller and smaller. Effective thermal management can face various challenges like product miniaturization, harsh environments, reduced form factors, reliability and performance. Cooling devices like physical fans or running cool water are effective remedies for large hot objects. However, when we talk about compact electronics, our molecular fan technique plays an important role. Molecular fan coating itself can work as a miniature-cooling device and yet can maintain high performance by avoiding structural damage of the small components.

4.2 Heat Transfer

Every hot object likes to cool off by releasing heat into its surroundings. Heat transfer mainly occurs by three different mechanisms: conduction, convection and radiation.

Figure 4.1. Heat Transfer Methods[2]
Conduction is the transfer of heat through molecular activity. The energy of molecules is transferred by collisions from one molecule to another. Heat flows from the higher temperature matter to the lower temperature matter.

Convection transfers heat by mass movement or circulation within a substance (fluids like water and air). It causes thermal expansion of the matter.

Radiation transfers heat from a hot object as electromagnetic waves without a medium. Radiative cooling is a unique mechanism for thermal dissipation, since radiation is a spaceless and powerless process. Thus, it becomes the highest potential mechanism among those three.

Figure 4.2 describes how the three mechanisms work to transfer heat while boiling a liquid.

Project Outline: In this project, our goal was to maximize radiative cooling. We built a system to study heat dissipation, investigate thermal radiation, measure cooling efficiency, and find applications of molecular fan cooling technology. We wanted to use certain nanocomposites to formulate a proper molecular fan coating. Our molecular fan coating is formulated as an organic-
inorganic hybrid emulsion containing well-dispersed nanomaterials with high surface emissivity, well aligned thermal conductivity, and high dielectric.

### 4.3 Principle

With optimized conditions, we can develop proper molecular fan nanocoatings that are environmentally friendly, easily processed and cost-effective.

Molecular fan nanocoating works as a miniature radiative cooling machine. Herein, the nanomaterials (well dispersed) needed to possess active quantized lattice motion assembly to absorb heat from the heat source. This absorbed energy helps them to promote to a higher quanta vibrational state and emits excess energy by radiation to cool off. This is a spaceless and powerless method. Molecular Fan (MF) gains the power directly from the heated device; thus, it acts as a powerless heat sink assembly.

The molecular fan nanocoating has to have well-dispersed nanomaterials to have an enhanced surface area, quantized surface molecular motions, which creates an assembly of active molecular vibration groups to release energy by radiation. All of these properties can be achieved by controlling how well we can process the nanomaterial. Figure 4.3 depicts how the MF technique works.
Figure 4.3. Schematic diagram of Molecular Fan working principle

Figure 4.3 (a) is the best outcome with well dispersed nanomaterials, (b) is mediocre with less dispersion forming platelets, and (c) being the worst possible scenario with poor dispersion forming stacked layers.

Due to the kinetic energy of the molecules, they acquire quantized lattice motion that absorbs energy from the heat source and becomes excited, resulting in faster vibrations. Figure 4.3 (a) shows how well dispersed the nanomaterials in the molecular fan nanocoating can exhibit maximum possible energy absorbed by the assembly of surface molecular motion, which are quantized and become excited resulting in faster vibration. They then go to the higher quanta vibrational state with more energy, which needs to be released to achieve a stable state by radiative means. The faster the vibrations (higher the energies) are in the excited states, the more quantized molecules with lattice motions release their excess energy by infra-red (IR) radiation, which acts as one molecular fan. Scenario (a) is the most desired for maximum efficiency with molecular fan nanocoating. We can achieve this state by using a high frequency sonication device.
Figure 4.3 (c) shows the case of overlapping vibration energy levels caused by molecular aggregation. This happens when the nanoparticles are poorly dispersed or not all dispersed. In this case molecular motion cannot be quantized. Thus, instead of releasing excess energy out of the molecular assembly, by releasing IR radiation, they channel through the molecules by a non-radiative process, which leads to self-heating the device, causing malfunction or damage to the system. Thus, scenario (c) should be highly avoided.

Scenario (b) is somewhere between (a) and (c), with platelets formation. Thus, the absorbed energy is released by means of both partially radiative and nonradiative processes.

Our group has previously reported the work principle\textsuperscript{1} and their results using a variety of nanomaterials like graphene, MWCNT, NDP, and carbon black through which we found how they achieved higher cooling efficiency and emissivity.\textsuperscript{6} Among them, graphene showed the best performance. The current project used some of previous research knowledge.\textsuperscript{[1,3,6]} Knowing that graphene-MF gives the best performance with cooling efficiency up to 23% and emissivity up to 0.99,\textsuperscript{[6]} and the same for MWCNT up to 22% and 0.98.\textsuperscript{[6]} We used these nanomaterials to prepare our nanocoatings for the current heat dissipation study. Gaining high emissivity close to 1 is desired, since graphene can mimic the black body radiation where maximum possible energy is absorbed. The above-mentioned result for both MWCNT and graphene is close to 1. Therefore, we could expect to have maximum possible radiation when using MF nanocoatings.

\textbf{4.4 Materials and Experimental}

All chemicals needed to formulate nanocoating are listed in Table 4.1, and they were bought from Sigma Aldrich or another vendor.
### 4.4.1 Materials needed to prepare Nanocomposite Coating

Table 4.1 Various components needed to prepare Molecular Fan formulation:

<table>
<thead>
<tr>
<th>Chemicals/Material</th>
<th>Amount (Wt.%)</th>
<th>Properties/Functionality</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin/Acrylate</td>
<td>60%</td>
<td>Acrylic copolymer resin</td>
</tr>
<tr>
<td>Solvent</td>
<td>20%</td>
<td>Diluent for viscosity/pH adjustment</td>
</tr>
<tr>
<td>Well–dispersed nanomaterials</td>
<td>0.93%</td>
<td>Radiative emission/ High Thermal Conductivity/Dielectric/High Surface Emissivity</td>
</tr>
<tr>
<td>Self cross-linkers</td>
<td>(0.5-2 wt%)</td>
<td>Crosslink polymer for resistance properties</td>
</tr>
<tr>
<td>Co-solvents (Water, PnB, DMEA)</td>
<td>(4.5+6+0.5)%</td>
<td>Matting agent for gloss reduction</td>
</tr>
<tr>
<td>Additives</td>
<td>1-2% (Total)</td>
<td>Surfactants/Wetting/agent/Defoaming/Coalescing agent for film formation/Thickener/Hardening Agent</td>
</tr>
<tr>
<td>Wet Link 78 Silane</td>
<td>1%</td>
<td>Cross-Linker</td>
</tr>
<tr>
<td>Mercapto</td>
<td>2%</td>
<td>Adhesion Promoter</td>
</tr>
<tr>
<td>WI-300</td>
<td>1%</td>
<td>Corrosion Protection</td>
</tr>
<tr>
<td>Aerosil R816</td>
<td>0.3%</td>
<td>Hardening Agent</td>
</tr>
<tr>
<td>BYK-348</td>
<td>0.3%</td>
<td>Improves Surface Tension</td>
</tr>
<tr>
<td>BYK-024</td>
<td>0.3%</td>
<td>Water based De-foaming agent</td>
</tr>
<tr>
<td>DSX 1550</td>
<td>0.2% or 2 drops</td>
<td>Thickener; caution - only if needed!</td>
</tr>
<tr>
<td>ISPR (Optional)</td>
<td>2%</td>
<td>In combination with co-solvent water (2.5%)</td>
</tr>
</tbody>
</table>

Table 4.1 tabulates the general distribution of the components needed to formulate proper emulsion molecular fan coating, such as “P-48[6] MFC-1”. This coating was used later for testing.
In Table 4.1, PnB and DMEA stand for propylene glycol butyl ether (linear formula: \(\text{CH}_3(\text{CH}_2)_3\text{OC}_3\text{H}_6\text{OH}\) and MW: 132.20g) and N,N-dimethylethylamine (linear formula: \(\text{CH}_3(\text{CH}_2)_3\text{OC}_3\text{H}_6\text{OH}\) and MW:132.20g) respectively.

### 4.4.2 Procedure

**P-48\(^6\) MFC Coating Formulation**

We formulated this Molecular Fan Coating (MFC) by following P-48\(^6\) direction. We divided the procedure mainly into four sections:

**Part-I: Prepare Nanomaterials**

In Part-I, we prepared the solvent with surfactants before we added any nanomaterials. Here typically we took our desired solvent, in this case water (20%), which then underwent sonication with surfactants at 50% strength for three minutes. Next, we slowly added the nanomaterials (~1%) like carbon nanotube and/or graphene etc. one at a time over an electric stirrer with a magnetic stir bar for about ten minutes. Next, we set the mixture for sonication under a cold-water bath (solvent/surfactants/nanomaterials) with periodic pulses (30 seconds), making sure there was no lump formation. We continued this sonication process for five minutes at 30% strength and next at 50% for another five minutes, until all nanomaterial was thoroughly incorporated into the solvent and made a uniform dispersion. As a caution, we needed to change the water bath with fresh cold water frequently during the sonication process, as it generated heat, and this excess heat could destroy the structures of the nanomaterials and, thus, their properties. This was the most critical step of making formulation.
Part-II: Prepare Resin:

In Part-II, we prepared a resin/polymer/acrylate mixture along with other additives. We put our desired polymer (60%) into a thick plastic beaker and ground it with metallic beads (50g) under a mechanical beater at 80 psi pressure and medium speed for 10 minutes. Next, we added the additives like cross-linker, wetting agent, matting agent, and coalescing agent as needed (~3%) into the polymer mixture one at a time while the grinding process was on. We ground it for 10 minutes till we found it all uniform.

Then we added Part-I (solvent/nanomaterials mixture) into Part-II (polymer mixture) a little at a time and continued grinding for 30 minutes.

Part-III: Prepare Solvent:

Meanwhile we prepared Part III, where we took water and co-solvent (~10%), which we stirred together with a magnetic bar for 10 minutes. Since the grinding procedure made the formulation gradually thicken, we needed to add further solvent. Now we added the Part-III solvent mixture into the above Part-I/Part-II mixture under the grinder little at a time to thin the mixture and continued grinding for 10 minutes. The entire process made the formulation slightly acidic. Therefore, we added a little DMEA to neutralize. We continued grinding for another 10 minutes. Finally, we added water based a defoamer and surface tension controller reagent (~0.5%) by drops. The entire mixture (Part-I/Part-II/Part-III) was now further ground for another 15 minutes.
Part IV: Homogenize:

The above mixture was then strained to separate it from the metallic beads. Next it went into a homogenizer, called Thinky, to defoam and homogenize the entire formulation for a 20-minute cycle. The final product was run through a strainer another time to make sure to separate any clot or unwanted chunk of particles. It was then collected and stored in a plastic container in room temperature overnight to settle.

4.5 Coating Technique:

Substrate Preparation: First we prepared our sample substrate, either an aluminum or iron Q-panel, by cleaning with isopropyl alcohol (IPA) and chem-wipe. We repeat three times.

There are various ways of performing a coating technique: drawbar, dipping, powder coating or spray coating. We used a dipping technique to test samples like wires cut into small strips. Since our substrates are flat surface Q-panels, we did not use the dipping process for this purpose. We coated them either by a drawbar or spraying technique.

Drawbar: We used a drawbar of the desired groove size. The higher the number of the drawbar, the thicker the grooves are and so it accumulates a higher amount of coating material. Thus, if we needed thicker coating, we used a higher numbered drawbar. Typically, we chose 24 or 26 to maintain a uniform thickness of 20-25 micrometers. We used a drawbar to do preliminary testing to check the physical properties like surface texture (smooth, grainy, bubbly etc.), surface tension, consistency, stickiness, and cross-cut test.

Spraying: We found the spraying technique was the most desired one in this purpose in terms of efficiency and to meet industrial requirements. We set our spray gun with an air pipe under 20 psi, and with a medium slit setting, we sprayed the panels for about two to three
seconds per piece. We made sure our contact angle stayed around 45° and we maintained a constant movement of the spray gun so as not to accumulate coating material at any area over the substrate. It needed to be uniformly distributed all over the area of the substrate to maintain a uniform thickness. Otherwise our adhesion test would not pass.

Flush Time: After spraying the coating over the metal substrates, we air-dried them for 20 minutes to settle the coating over the substrate.

Curing: Then we cured them in the pre-heated oven at 120°C for 20 minutes. This process allowed a uniform film to form over the metal substrate.

Cooling: We cooled off the samples before testing on a cool monitor. Cooling helped the film to secure and settle over the substrate permanently.

Figure 4.4 left shows a bottle of P-48[^6] formulation prepared through the aforementioned process in Section 4.4.2. Figure 4.4 right shows a set of Q-panels ready with the coating by the same formulation to be tested under the cooling monitor (a pre-built cooling device).

![Figure 4.4](image-url)

4.6 Testing Device (Pre-Built testing equipment set-up):

Figure 4.5. Schematic diagram of thermal cooling assembly[^3]

Figure 4.5 shows a schematic diagram to design a cooling device using general physics heat laws.
Figure 4.6 left shows a schematic diagram of how the substrate to be tested rests on the copper block. Two input and output sensors are shown under the substrate. Figure 4.6 right shows the built thermal cooling device; at the center there is a copper block, which was protected by a thermal insulator (thermal sponge). On the right side there are sensors that flow heat into the block. The block then becomes heated and the object that sits over it is heated as well. The hot object then tries to cool off by a conduction and convection method. The thermal sponge, which works as an insulator, minimizes the heat loss by a conduction method. When our substrate is coated with molecular fan coating, a radiation process can cool this off. Our goal was to minimize the heat transfer process by a conduction and/or convection method rather than to maximize the radiation. The resultant temperature was carried out of the block by a sensor and was recorded by the Cosmol Multiphysics simulation software. These data then were stored in an Excel spreadsheet. An electrical heater (a heat source) heated the copper block. We set a certain voltage on the heater and a temperature monitor guided us to monitor the temperature.
4.7 Results and Discussion:

The experimental results of the temperature and voltage against time (1-120 minutes) all were stored in an Excel spreadsheet. From there we recorded the starting and final temperature to calculate the difference. Next, we found the % of efficiency with respect to the control (aluminum blank Q-panel). The data in Table 4.1 show the % of efficiency of the control and two substrates coated with MF-48 with a thickness of 37 and 50 μm, respectively. The results show the same % of efficiency for both samples. We found about a 16% cooling efficiency.

Table 4.2: Equilibrium temperature of MF-P48 coating with different Thickness and % Cooling efficiency with respect to Al-Control:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Voltage (V)</th>
<th>Starting Rm T (°C)</th>
<th>Ending Rm T (°C)</th>
<th>Initial T (°C)</th>
<th>Final T (°C)</th>
<th>Difference T (°C)</th>
<th>% Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-Thin-Control</td>
<td>52.65</td>
<td>19.1</td>
<td>20</td>
<td>21.6</td>
<td>55.7</td>
<td></td>
<td>---</td>
</tr>
<tr>
<td>MF-P48-37μm</td>
<td>52.51</td>
<td>18.3</td>
<td>18.2</td>
<td>19.7</td>
<td>46.8</td>
<td>8.9</td>
<td>15.97</td>
</tr>
<tr>
<td>MF-P48-50μm</td>
<td>52.62</td>
<td>18.1</td>
<td>18.2</td>
<td>20</td>
<td></td>
<td>8.9</td>
<td>15.97</td>
</tr>
</tbody>
</table>
A graphical presentation is shown in Figure 4.7 using the Table 4.2 data for all three samples (the control and the two coated panels with two thicknesses) to compare the cooling differences. The difference in temperature between the control and the MF-coated panel is 8.9°C. Both coated panels with a thickness of 37 µm and 50 µm generated 16% cooling efficiency.

4.8 Applications

4.8.1 Application: Heat Sink

Modern electronics that come in miniature sizes and with extreme complexity can generate a lot of heat. If this heat is ignored or left unchecked, this can damage or reduce the life span of the device itself. That is why we often see a metal object with fins, called a heat sink, comes with a PC or another electronic device. Inside the PC, a heat sink can be found with the CPU, graphics card, motherboard, power supply or some other places as needed. The smaller the
device is, the smaller the heat sink could be. Heat sinks can come in various shapes, sizes and thicknesses. But they all serve the same purpose, removing excess heat from a hot component, retaining its functionality, and improving its life span.

Figure 4.8: Variety of Heat Sinks for various purposes tested in Dr. Lin’s lab

In this section we discuss how different factors could impact the heat transfer and, thus, the cooling efficiency.

From Section 4.5, we know P-48\textsuperscript{[6]} MF formulation exhibits a decent molecular fan effect. Thereafter, we proceeded to test and apply heat sinks brought from China. We had a variety of heat sinks to test. Among them we tested seven types plus one control (eight in total). They are as follows:

1. Control – Silver Aluminum panel with tall fins
2. Bare – Black tall fins – Coated with MFC-1
3. Anodized – Black tall fin
4. Other special coating - black tall fins
5. Sand Blasted – black tall fins with MFC-1
6. Anodizing – Black short fin
7. Sand Blast – Black short fin with MFC-1

8. Double fin with alternate tall and short

**Note:** The formulation of MFC-1 resembles our P-48 formulation. Below is the picture after the coating and curing of the heat sinks.

Sand Blast is a process to spatter sand on the surface of the sample to make a rough surface. Sand blasting was done by the mechanic shop in the Physics and Chemistry Department at NIU. Before we started, we peeled off the label from the back of each sample; used a marker to label each one the same way it is named in the table. We ran heat dissipation measurements on them with the control run at the following conditions:

![Figure 4.9. Left: Seven types of heat sinks to be tested. Right: Alternate Tall and Short fins Heat Sink](image)

Figure 4.11 left displays all seven types of heat sinks ready to be tested with coating and curing. Figure 4.11 right gives a closer look at a heat sink with alternate tall and short fins.

Now they were ready to be tested to find their cooling efficiency. We did this testing using the device mentioned above.
Figure 4.10 left shows the entire cooling device with the coated heat sink on top of the copper block, which is protected by a thermal insulator. Figure 4.12 right shows the entire cooling assembly consisting of a heat source (heater), a cooling device and the computer attached to the device. This is our pre-existing cooling device built by our research group. Data were collected using Cosmol Physics software. This process was described in the previous section (4.4).

Application of thermal grease: We used thermal grease on the backside of each sample to be tested and over the copper block before we ran the experiment. When we set the sample, we made sure to press it hard enough over the copper block. This ensured us of not allowing any air pocket to develop during the experiment. More air underneath the sample could cause more heat to release by convection process. We tried to minimize any heat flow by conduction and convection but to maximize it by the radiation process.

### 4.8.2 Cooling Efficiency

Testing data from all eight types of heat sinks and their descriptions are tabulated below:

Voltage: 32.56 V, Time: 2 hours, With Board underneath the copper block as an *extra insulation*: 
Table 4.3: A 2 hours experimental result of all eight types of samples, at voltage 32V:

<table>
<thead>
<tr>
<th>Sample Types</th>
<th>Fins</th>
<th>ColorOf Coating</th>
<th>Starting Tmp $T_{\text{Air}}$ ($^\circ\text{C}$)</th>
<th>Final Tmp (Thermo Couple)</th>
<th>$T_{\text{C}} - T_{\text{Air}}$ ($^\circ\text{C}$)</th>
<th>Voltage (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1 Control</td>
<td>Tall</td>
<td>Silver</td>
<td>19.6</td>
<td>68.3</td>
<td>48.7</td>
<td>32.14</td>
</tr>
<tr>
<td>#2 MF C-1</td>
<td>Tall</td>
<td>Black</td>
<td>23.9</td>
<td>61.5</td>
<td>37.6</td>
<td>32.25</td>
</tr>
<tr>
<td>#3 Anodized</td>
<td>Tall</td>
<td>Black</td>
<td>20.1</td>
<td>61.6</td>
<td>41.5</td>
<td>32.14</td>
</tr>
<tr>
<td>#4 Other Special Coating</td>
<td>Tall</td>
<td>Black</td>
<td>19.5</td>
<td>61.5</td>
<td>42.0</td>
<td>32.12</td>
</tr>
<tr>
<td>#5 Sand Blast w/MFC1</td>
<td>Tall</td>
<td>Black</td>
<td>20.8</td>
<td>62.2</td>
<td>41.4</td>
<td>32.12</td>
</tr>
<tr>
<td>#6 Anodized</td>
<td>Short</td>
<td>Black</td>
<td>20.0</td>
<td>64.8</td>
<td>44.8</td>
<td>32.17</td>
</tr>
<tr>
<td>#7 Sand Blast w/MFC1</td>
<td>Short</td>
<td>Black</td>
<td>20.6</td>
<td>65.5</td>
<td>44.9</td>
<td>32.30</td>
</tr>
</tbody>
</table>
Figure 4.11. A comparison study of Cooling Efficiency of all seven Heat sinks with Voltage 32.56 V, Run Time 2 hours

Figure 4.11 is a graphical comparison of all heat sinks we tested. Among all, #2 Uniform surface with an MFC-1 sample showed the most and #7 Sand blast with short fins had the least cooling efficiency. The rest of the samples lay between #2 and #7. This graph also tells that heat sinks with tall fins dissipate more heat and thus cool faster than those with short fins. In all cases we wanted to see if MFC-1 always appeared below any other type. In other words, the MFC-1 had to show the best cooling efficiency. With many trials and experiments having been run in our group, MFC-1 was selected as the best formulation for this project. It is worth remembering our P-48\(^{[6]}\) formulation was comparable with the MFC-1.
4.8.3 Factors Impacting Cooling Efficiency (A through G)

Now we wanted to investigate how different factors could influence the cooling effect and how they impacted the resultant cooling performance. We chose different sections of coated surface area, voltage, thickness and mass and also compared single vs. double fins with alternate tall and short fins as different factors.

A. Testing with Variable Voltages: Keeping all other parameters constant (insulation, resistance, thickness, surface area, mass)

Table 4.4: A 2 hours experiment result at voltage 25V, 32V and 40V:

<table>
<thead>
<tr>
<th>Control</th>
<th>Anodized</th>
<th>MFC-1</th>
<th>Voltage (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_C - T_{Air} (^{\circ}C)$</td>
<td>$T_C - T_{Air} (^{\circ}C)$</td>
<td>$T_C - T_{Air} (^{\circ}C)$</td>
<td></td>
</tr>
<tr>
<td>34.2</td>
<td>29.2</td>
<td>28.6</td>
<td>25</td>
</tr>
<tr>
<td>48.3</td>
<td>41.1</td>
<td>41.6</td>
<td>32</td>
</tr>
<tr>
<td>73.6</td>
<td>64.5</td>
<td>63.9</td>
<td>40</td>
</tr>
</tbody>
</table>
Figure 4.12. A comparison study of Cooling Efficiency at different voltages 25V, 32V and 40V with run time 2 hours.

Note that the gap between control and anodized or MFC-1 increased consistently as the voltage became higher. This result verified that our cooling monitor testing device followed the general heat laws. We also identified that thermo couple temperature ($T_C$) reaches equilibrium at a lower temperature with a voltage drop. That is the lower the selected voltage, the lower the equilibrium temperature. From Figure 4.14, we saw the control found its equilibrium at $\sim70^\circ C$, $\sim40^\circ C$ and $\sim30^\circ C$ as the voltage dropped from 40V to 32V to 25V.
B. Testing with variable **Surface Area** (Control-bare, All coated, Vs. Partial Coating)

**Description of sample preparation:** All samples were tested with extra insulation.

#1 Aluminum control – all bare, no coating neither on top, nor on bottom

#2 Anodized – Surface was oxidized; top and bottom were completely coated

#3 MFC-1 –Uniform surface, coating was only on the top with the bottom left uncoated

#4 MFC-1_Square-Center – Coating was on top, but the bottom was coated only around a square-centered tape. The tape was then peeled off before testing.

Below is a set of heat sinks in Figure 4.15 showing the back-side of heat sink samples 1, 2 and 4: no coating on control on number 1, all coated on number 2, and only coated around the edge of an inside square on number 4. This center area was initially taped by scotch tape, sprayed with MFC-1 coating, and then the tape was peeled off before thermal cooling testing.

![Figure 4.13. #1 Control #2 Anodized –Uniform surface #4 Square-Center](image)
Find Cooling Efficiency at Voltage: 52 V; Time: 2 hours:

Table 4.5: A 2 hours experiment result at voltage 52V:

<table>
<thead>
<tr>
<th>Heat Sink Type</th>
<th>Description</th>
<th>Thermo-Couple Tem (°C)</th>
<th>Delta Tc (°C)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>Al Bare</td>
<td>73.8</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Anodized</td>
<td>All Coated</td>
<td>64.9</td>
<td>8.9</td>
<td>12.06</td>
</tr>
<tr>
<td>MFC-1</td>
<td>Bottom not coated</td>
<td>61.7</td>
<td>12.1</td>
<td>16.39</td>
</tr>
<tr>
<td>MFC-1 SquareCentered</td>
<td>Bottom-coated leaving a square area gap</td>
<td>58.8</td>
<td>15.0</td>
<td>20.32</td>
</tr>
</tbody>
</table>

Figure 4.14. A comparison study of Cooling Efficiency at voltage 52V; Run Time 2 hours
The results from Table 4.4 show that cooling efficiency is not necessarily higher if all of the surface area is coated with MFC-1. In fact, the last sample was coated except in a square around the center, which was then peeled off before the run time. That sample showed the highest cooling efficiency. This observation tells us that leaving a small surface bare allows the heat flow uniformly, generating more radiation. Thus the square-centered sample cooled off with higher efficiency (20.32%) versus MFC-1 (16.39%), whereas the all-coated anodized one shows 12% cooling efficiency. Figure 4.16 gives a graphical presentation of Table 4.4.

C. Testing with variable Insulation:

We continued cooling testing, checking with other factors like insulation. This time, we performed the same set at the same low voltage (~32 V), but without any insulator around the copper block (remove the wooden board under the copper block); if we removed the insulated padding around the copper block, there was too much drop in the equilibrium temperature. So, we kept a minimum of insulation around the copper block.

Testing Result With Insulation:

Table 4.6: Samples With Insulation at Voltage 32V, Run Time 2 hours

<table>
<thead>
<tr>
<th>Samples With Insulation</th>
<th>Ambient Temp $T_a$ (°C)</th>
<th>Thermocouple Temp $T_c$ (°C)</th>
<th>$T_c-T_a$ (°C)</th>
<th>Voltage (V)</th>
<th>Cooling Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1-Control</td>
<td>19.6</td>
<td>68.3</td>
<td>48.7</td>
<td>32.14</td>
<td>---</td>
</tr>
<tr>
<td>#2-MFC-1</td>
<td>23.9</td>
<td>61.5</td>
<td>37.6</td>
<td>32.25</td>
<td>22.79</td>
</tr>
</tbody>
</table>
Testing Result *Without Insulation:*

Table 4.7: Samples *Without Insulation* at Voltage 32V, Run Time 2 hours:

<table>
<thead>
<tr>
<th>SamplesWith Insulation</th>
<th>AmbientTemp T_a (°C)</th>
<th>Thermocouple Temp T_c (°C)</th>
<th>T_c-T_a (°C)</th>
<th>Voltage (V)</th>
<th>CoolingEfficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1-Control</td>
<td>21.2</td>
<td>52.7</td>
<td>31.5</td>
<td>32.33</td>
<td>---</td>
</tr>
<tr>
<td>#2-MFC-1</td>
<td>21.6</td>
<td>49.4</td>
<td>27.8</td>
<td>32.33</td>
<td><strong>11.75</strong></td>
</tr>
</tbody>
</table>

As an overall result, we achieved a 48.44% improved cooling efficiency by using the proper insulation.

![Heat Sink Curve With Vs Without Insulation](image)

Figure 4.15. A comparison study of Cooling Efficiency at voltage 32V and Run Time 2 hours

From Tables 4.6 and 4.7, we found that the same pair of samples (uncoated control and coated with MFC-1) run with additional insulation like a wooden board underneath the copper
block can improve cooling efficiency almost by a factor of two more than the same set run without the insulation. Both sets were run with the same parameters. The corresponding graph in Figure 4.17 depicts the comparison. We identified primarily two outcomes:

1. The gap between the top pair increases, which means with insulation, heat sinks dissipate heat more through radiation than conduction and convection. As soon as we took away the insulation, more heat escaped through conduction and convection and we had less thermal radiation as shown by the lower pair graphs.

2. We achieved higher cooling efficiency ~22.8% with insulation versus ~11.8% without insulation.

**D. Testing with Thicker samples at variable Voltages**

Aluminum *Thick* Square Panels Result at 61V:

Table 4.8: Thick Al samples, with Insulation at Voltage 61V, Run Time 2 hours:

<table>
<thead>
<tr>
<th>Samples</th>
<th>Voltage (V)</th>
<th>Air Starting Room T(°C)</th>
<th>Air Ending Room T(°C)</th>
<th>Cu Block Initial T(°C)</th>
<th>Cu Block Final T(°C)</th>
<th>Difference Final-Initial T(°C)</th>
<th>Cooling Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-Control</td>
<td>61.214</td>
<td>17</td>
<td>17.2</td>
<td>13.4</td>
<td>55.8</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Sample#1</td>
<td>61.305</td>
<td>17.5</td>
<td>17.3</td>
<td>16.3</td>
<td>50.9</td>
<td>4.9</td>
<td>8.78</td>
</tr>
</tbody>
</table>

Aluminum *Thick* Square Panels Result at 70V:

Table 4.9: Thick Al samples with Insulation at Voltage 70V, Run Time 2 hours:

<table>
<thead>
<tr>
<th>Thick Square Samples</th>
<th>Voltage (V)</th>
<th>Air Starting Room T(°C)</th>
<th>Air Ending Room T(°C)</th>
<th>Cu Block Initial T(°C)</th>
<th>Cu Block Final T(°C)</th>
<th>Difference Final-Initial T(°C)</th>
<th>Cooling Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-Control</td>
<td>70.43</td>
<td>17.6</td>
<td>17.5</td>
<td>14.4</td>
<td>67.4</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Sample#1</td>
<td>70.43</td>
<td>17.3</td>
<td>17.2</td>
<td>18.2</td>
<td>64.1</td>
<td>3.3</td>
<td>4.89</td>
</tr>
</tbody>
</table>
Comparison at different voltages for thick panels with MF coating:

We see Tables 4.7 and 4.8 that at a lower voltage, as low as at 61V, the equilibrium temperature of the thick panel is 50.9°C, whereas with the same at a higher voltage, as high as at 70V, the equilibrium reaches at 64.1°C. The downside is we lose cooling efficiency by 3.89%. This result again verifies the general principles of heat flow. Input heat is directly proportional to the square of input voltage as per equation (1), given below. Thus, as \( V \) increases, \( Q_{\text{in}} \) controlled by electricity increases, that impacts \( Q_{\text{out}} \) to rise.

Figure 4.16. Left: Heat flows through heat sink.\(^3\) Right: Heat flow of copper block controlled by voltage input.\(^3\)

Figure 4.17 shows a typical heat sink carrying heat with input temperature \( T_H \) and output temperature \( T_C \), where \( T_H < T_C \). Figure 4.19 shows a copper block heater (the red inner circle), which is heated by electricity through a power inlet. The temperature sensor carries the signal to a monitor, which records the rise in temperature at every second.

Voltage is directly proportional to resistance and current as per Ohm’s law in equation (2). Current is inversely proportional to resistance by the equation (3). Power watt is directly
proportional to the current and voltage by equation (4). We tested all general heat laws during our investigation, and our results abide by them.

\[
Q_{\text{in}} = W \cdot t = (I \cdot V) \cdot t = (V^2 \cdot t) / R \Rightarrow Q_{\text{in}} \propto V^2 \tag{1}
\]

Ohm’s law: \( V = I \cdot R \) \tag{2}

\( I = V / R \) \tag{3}

\( W = I \cdot V \) \tag{4}

Where,

- \( Q_{\text{in}} \): heat flow going into the heat sink (made by voltage)
- \( Q_{\text{out}} \): heat flow going out of the heat sink
- \( V \): voltage, \( I \): current, \( R \): resistance, \( W \): watt (Power), \( t \): temperature, \( Q \): heat, \( M \): mass, \( \Delta Q \): heat difference measured, \( \Delta t \): temperature difference

E. Testing with variable Thickness samples at constant Voltage

Aluminum *Thick Vs. Thin* Panels Result at 70V:

Table 4.10: Thick Vs. Thin Al samples with Insulation at Voltage 70V, Run Time 2 hours:

<table>
<thead>
<tr>
<th>Thick Square Samples</th>
<th>Voltage (V)</th>
<th>Air Starting Room T (°C)</th>
<th>Air Ending Room T (°C)</th>
<th>Cu Block Initial T (°C)</th>
<th>Cu Block Final T (°C)</th>
<th>Cooling Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thin</td>
<td>70.43</td>
<td>18.0</td>
<td>17.9</td>
<td>18.2</td>
<td>74.5</td>
<td>16.22</td>
</tr>
<tr>
<td>Thick</td>
<td>70.43</td>
<td>17.3</td>
<td>17.2</td>
<td>18.2</td>
<td>64.1</td>
<td>14</td>
</tr>
</tbody>
</table>

We can achieve, overall 14% more efficiency when we use a higher thickness object.

Heat transfer version in another form by Fourier’s Law:\(^5\):
\[ \frac{dQ}{dT} = h.A.(T(t) - T_{\text{env}}) \]  

\[ \Delta Q \propto A \]

\( h \): heat coefficient, \( A \): surface area of the object, \( T(t) \): temperature at time \( t \), \( T_{\text{env}} \): ambient temperature.

Equation (5) helps us to understand how energy (Joule) or heat generated is related to the surface area of the object. We can draw a relationship between them and find that the heat evolved is directly proportional to the surface area from which the heat is radiated. In this example, we are dealing with a thicker heat sink with a higher surface area and compared with a thinner one of the same type with less surface area. So heat generation is higher with the thicker samples. Therefore, more heat would radiate with the MF coating and dissipate away, resulting in reaching equilibrium at a lower temperature. Table 4.9 shows the comparison results of thin versus thick heat sinks. Thin sample reaches equilibrium at 74.4°C, whereas the thick one reaches at a much lower temperature (at 64.1°C), making it 14% more efficient in terms of cooling efficiency.

**F. Study with various Masses at constant voltage**

Heat transfer version in another form by

\[ \Delta Q = Q_{\text{in}} - Q_{\text{out}} = mc (\Delta t) \]  

Equation (6) shows heat flow is directly proportional to the mass. Therefore, a higher mass heat sink generates more heat than a lower mass object. Thus, excess heat will dissipate through molecular fan thermal cooling technology, resulting in a lower equilibrium temperature for the higher mass object. Table 4.10 tabulates the data to confirm the heat law equation (6).
Table 4.11: Heat sinks with different masses at Voltage 70V, Run Time 2 hours:

<table>
<thead>
<tr>
<th>Samples</th>
<th>Mass (g)</th>
<th>Voltage (V)</th>
<th>Air Starting Room T (°C)</th>
<th>Air Ending Room T (°C)</th>
<th>Cu Block Initial T (°C)</th>
<th>Cu Block Final T (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thin</td>
<td>16.60</td>
<td>70.43</td>
<td>18.0</td>
<td>17.9</td>
<td>18.2</td>
<td>74.5</td>
</tr>
<tr>
<td>Thick</td>
<td>88.40</td>
<td>70.43</td>
<td>17.3</td>
<td>17.2</td>
<td>18.2</td>
<td>64.1</td>
</tr>
</tbody>
</table>

G. Heat study with and without ISPR

ISPR stands for In-situ phosphatizing reagent. It helps to build a coating layer made of phytic acid, PM, $\gamma$-g, MTMO, TEOS and water. We used phytic acid (1:1) by weight ratio as a source of phosphate. $\gamma$-g (3-glycidoxypropyl trimethoxysilane), MTMO (mercapto silane or 3-mercaptopropanol), where mercapto is an –SH functional group), TEOS (tetra ethoxy silane) are all different sources of silanes, and PM (1-methoxy-2-propanol) is a solvent. This ISPR helped to form a metal-phosphate bond (M-O-P) over the metal substrate. ISPR offered an additional attribute like corrosion inhibition by forming a corrosion protective layer between the metal surface and the polymer top layer. Thus, this formulation acted in a dual role, heat dissipation by radiation (MF technique) as well as corrosion inhibition (ISPR).
Aluminum Thick Square Panels (control, no ISPR, with ISPR) at 70V:

Table 4.12: Thick Al samples with Vs. without ISPR at Voltage 70V, Run Time 2 hours:

<table>
<thead>
<tr>
<th>Thick Square Samples</th>
<th>Voltage (V)</th>
<th>Air Starting Room T (°C)</th>
<th>Air Ending Room T (°C)</th>
<th>Cu Block Initial T (°C)</th>
<th>Cu Block Final T(°C)</th>
<th>Delta T (°C)</th>
<th>Cooling Efficiency (%)</th>
<th>Overall Cooling Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-Control</td>
<td>70.43</td>
<td>17.6</td>
<td>17.5</td>
<td>14.4</td>
<td>67.4</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>No ISPR</td>
<td>70.43</td>
<td>17.3</td>
<td>17.2</td>
<td>18.2</td>
<td>64.1</td>
<td>3.3</td>
<td>4.89</td>
<td>28.83</td>
</tr>
<tr>
<td>With ISPR</td>
<td>70.43</td>
<td>17.3</td>
<td>18.0</td>
<td>17.9</td>
<td>63.1</td>
<td>4.3</td>
<td>6.38</td>
<td>28.83</td>
</tr>
</tbody>
</table>

We can achieve an overall 28.83% improved cooling efficiency by using ISPR.

4.9 Developing New Thermal Cooling Device

We wanted to develop a new thermal cooling device with the experience we attained from our previous heat dissipation study. The previously mentioned cooling device was built by our group during 2009. That assembly was based on general physics laws. They were all tested and proven practical. However, that previous cooling device was not designed following any certified standard scientific method. To satisfy industrial needs, now we wanted to develop a new cooling device following standard methods (American Standard Testing Method or ASTM).

Building a new device or any system needs well thought-out designing and planning. In our team of four members, we had one mechanical engineering student who helped with the designing using drawing software. Thus, we could identify which hardware parts we needed with the exact sizes. We had one software engineer who helped connect the mechanical designs with the proper software, so we could control and monitor the thermal cooling.
The tools we needed were brought from a local hardware store in DeKalb. They were assembled in our lab and tested with the same set of seven heat sinks we had tested with the cooling device mentioned in Section 4.6. We further tested its application using a conventional toaster oven and cell phones.

**Procedure:**

To develop the new system, we explored two standard methods: ASTM C1777 and ASTM D5470-06.

**I) Method I: Using Guarded Hot Plate Method (ASTM C1777 Testing Procedure):**

Here our purpose was to measure a steady state heat flux through conductive materials to minimize radial heat flow (heat loss or heat gain) and to measure thermal conductivity.

Thermal conductivity can be found as

\[ K = \frac{Q}{A} \left( \frac{\Delta T}{\Delta L} \right) \]  \hspace{1cm} (7)

Where:

*Heat Flux: Q/A; Thermal Gradient: ΔT/ΔL; K: Thermal conductivity*

Q: Amount of heat passing through a cross section A; A: Cross Section of the substrate

ΔT: Temperature Difference; ΔL: Distance Travelled along the substrate

**Design:** We studied the design from the standardized process ASTM C-1777 (Figure 4.17) and came up with some ideas how to built ours.
Assemblies:

The required tools with their functionalities are listed below for the ASTM C-1777 method

1. Guarded hot plate (metered section at the center) – Thermally isolated from a concentric primary guard by a definite separation or gap - Provides power by heat flow per unit time (Q/t)

2. Primary guard - Situated next to the guarded hot plate

- Provides the proper thermal condition to reduce the lateral heat flow within the apparatus
(3) Secondary guard - To reduce the lateral heat flow on both sides

(4) Top/bottom specimen - Two test specimens are sandwiched among the three units (top cold surface, rows of guards, bottom cold surface). Two pieces need to be identical in shape, size, thickness, area, and densities.

(5) Top/bottom cold surface plates
  - To maintain the temperature in the chamber from over heating
  - The size of the cold surface assemblies is the same as the hot surface assemblies (including the primary guard)

(6) Insulation - All around the main components

  Note: It is important to have space between each guard to allow the heat transfer

(7) The entire assembly is to be set on a sturdy flat base.

Comparison of current versus new device:

It is good to summarize the characteristics and compare the components between two devices. The attributes are listed below in Table 4.13.

Table 4.13: The comparison study between two devices:

<table>
<thead>
<tr>
<th>Previously Built Cooling Device</th>
<th>Newly Built Testing Device</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Guard (Primary or Secondary)</td>
<td>Presence of Primary and Secondary Guard</td>
</tr>
<tr>
<td>No Isothermal Cold Surface Assemblies</td>
<td>Isothermal Cold Surface Assemblies</td>
</tr>
<tr>
<td>Some insulation, not all around the device</td>
<td>Insulation all around the Device</td>
</tr>
<tr>
<td>Open Air Device</td>
<td>Controlled Environmental Chamber</td>
</tr>
</tbody>
</table>

Our purpose was to measure thermal impedance and to calculate the apparent thermal conductivity for thermally conductive electrical insulation materials ranging from liquid compounds to hard solid materials. Thermal conductivity applies only to homogeneous materials. Some terms to be aware of for better understanding for the method ASTM D5470-06 are listed in Table 4.14 given below.

Table 4.14. Some terminologies for heat study for the method ASTM D5470-06:

<table>
<thead>
<tr>
<th>Term</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apparent thermal conductivity</td>
<td>(λ - W/m.K): The time rate of heat flow, under steady condition, through unit area of a heterogeneous material, per unit temperature gradient in the direction of perpendicular to the area</td>
</tr>
<tr>
<td>Average temperature</td>
<td>(T-K): The area’s weighted mean temperature</td>
</tr>
<tr>
<td>Composite</td>
<td>Materials made up of definite parts contributing to the properties of the combination</td>
</tr>
<tr>
<td>Homogeneous material</td>
<td>A material in which relevant properties are not a function of the position within the material</td>
</tr>
<tr>
<td>Thermal impedance</td>
<td>(θ – (K.m²)/W): The total opposition that an assembly (material, material interfaces etc.) presents to the flow of heat</td>
</tr>
<tr>
<td>Thermal interfacial resistance</td>
<td>(contact resistance-Rİ): Temperature difference: ΔT required to produce a unit of heat flux (Q/A) at the contact planes between the specimen surface and the hot and cold surfaces in contact with the specimen</td>
</tr>
<tr>
<td>Thermal resistivity</td>
<td>(λ⁻¹ - (m.K)/W); K is in Kelvin) Reciprocal of thermal conductivity where thermal conductivity is k=(Q/A)/(ΔT/ΔL)</td>
</tr>
<tr>
<td>Area of specimen</td>
<td>(A - m²)</td>
</tr>
<tr>
<td>Thickness of specimen</td>
<td>(d – m)</td>
</tr>
<tr>
<td>Time rate of heat flow</td>
<td>(Q – W or J/s)</td>
</tr>
<tr>
<td>Heat flux</td>
<td>Q/A or q (W/m²)</td>
</tr>
<tr>
<td>Thermal impedance</td>
<td>(temperature difference per unit of heat flux – θ- (K.m²)/W)</td>
</tr>
</tbody>
</table>
Design:

The design suggested by the method ASTM D5470-06 is given in figures 4.18 left and right. This method applies some pressure from the top. Also note that if heat flow meter bars are used on both the hot and cold surfaces, guard heaters and thermal insulators are not needed.

Figure 4.18. Left: Test stack using the Meter Bars as calorimeter; Right: Guarded Heater suggested by ASTM D5470-06
Specifications to remember for the method ASTM D5470-06:

1. Electric heaters must be combined with a guard heater along with high quality insulation to limit heat leakage away from the primary flow through the specimen.
2. The test surfaces are to be smooth within 0.4 microns and parallel to within 5 microns.
3. Heat sources are either electrical heaters or temperature-controlled fluid circulators.
4. The thermal conductivity of the bar material is recommended to be greater than 50 W/m.K.
5. Contact pressure on the specimen will be applied perpendicularly to the test surface while maintaining the parallelism and the alignment of the surface.
6. Pressure can be controlled and maintained either by linear actuators, lead screws, pneumatics or hydraulics.

Significance and Use:

This standard ASTM D5470-06 is useful for measuring the Thermal Impedance of a few material types such as:

Type I: Viscous Liquids (grease, paste)
Type II: Viscoelastic Solids (gels, soft and hard rubbers)
Type III: Elastic Solids (ceramics, metals, and some type of plastics)

Studying both ASTM C-1777 and ASTM D5470-06, we summarized some features to be included in the device we were building.

Hardware: All hardware components were bought from a local hardware store (DeKalb, IL). Some were obtained from out of state vendors. Figure 4.19 displays our newly built cooling device. This device has special feature like applying pressure from top as discussed in method.
ASTM D5470-06. The pressure-setting device could control variable pressure with the assistance of a red lever. The black tip above the sample touches the sample controlled by the pressure from top, making sure of absolute tightness, to get rid of any air between the sample and the copper block. Since air is a medium and heat can be lost from the heat sink by convection method through air. We also spread some thermal paste uniformly under the sample, ensuring no air pocket remained at the contact of the heat sink and the copper block. The square shaped sample, in this case an aluminum heat sink, was placed over a square shaped copper block of the exact same area as the heat sink, ensuring no heat loss. The sample and the copper block both were surrounded first by a thermal sponge (grey) and then by a cork (porous material). Both served as insulators. The copper block was kept over a porous cork insulator, which was placed over a wooden thick block. The copper block was embedded inside two layers of insulators, which served as a primary and a secondary guard as described in the method ASTM C-1777. The deep wooden block was purposely chosen to serve as the thermal insulator all the way at the bottom, as discussed in the method ASTM D5470-06. Figure 4.20 (left) shows a Voltage/Current controller and (right) a Monitor with software respectively to control and monitor heat change.
Outcome of the experiments using the newly built device is summarized below:

(1) We were able to conduct and repeat similar testing
(2) Results obtained were compatible with the old device
(3) The entire device was dismantled and shipped to China with all of the parts
The device was re-assembled and tested at the conference in China.

Developing New System for Application: Phone as testing objects: **THERMAL ENVIRONMENT**

**TEST SYSTEM: HEAT DISSIPATION OF MOLECULAR FAN FOILS** (**CHEM NOVA TECHNOLOGIES INC., NOV. 2016**)

**Concept of system**

This test system provides the thermal environment with controlled-temperature air convection. The analyzer is able to run direct thermal monitoring and data collection from various electronic devices and materials. The heat and thermal property of the integrated electronic device are conveniently measured under various temperatures. The wide window of a convection oven provided convenient observation of the test subjects inside.

![Diagram of application schematic view for testing objects (Phone)](image)

Figure 4.21. Application schematic view for testing objects (Phone)
Components needed for testing for application purpose:

To develop a new system for application, first we need to plan, design and accumulate all list of components. They are described below:

1. Oven with full convection heating
2. Temperature controller
3. Thermocouple sensor
4. Data log unit, TC 08 USB device, up to 8 channels
5. Data collection computer

Setup Instructions

1. The controller and the oven are connected with a cable through the hole on the right surface of the oven. This establishes control over the oven. The port to be connected for the cable is 6.
2. The oven and the controller are plugged into the power supply with the voltage connector and the adapter, respectively.
3. The temperature sensor for the Omega temperature controller is connected to terminal 2 and 3. Terminal 2- red wire and terminal-3 with the white wire. The DC 12V power cable into terminal 7 and 8.
4. Then connect terminal 5 and 7 for DC input for relay in oven.
5. The only connections on the right side input side is the temperature sensor and all the remaining are on the right side block.
6. Plug in the TC- 08 device to the computer and open the logging software to power on the device. You should see a green light on the top of the device.
7. The thermocouples (J type) are connected into the TC-08 using the connector pins, which are yellow.

8. The instrument is now ready to use.

A complete connection for the controller should look something like this:

![Connection Diagram](image)

Figure. 4.22. USB device attached with a computer

**Procedure**

1. The temperature at oven body setting will be safety limit of maximum heating. You can set to any value. However a reasonable safe limit will be desirable, for example let us assume 300 F.

2. Now the timer should be set which cuts off the oven after some time. Let us say 120 minutes.

3. At the temperature control device, select the SP1 temperature to the desired control temperature. Let us say 40 °C.
4. Once the value of SP1 is entered, the oven starts to heat and it will take approximately 12-15 minutes to maintain the temperature very accurately by less than a degree difference.

5. Meanwhile take the desired device, such as a mobile phone, and connect the sensors wherever required – screen, battery or any other test subject and location. Note the channel connected for each device

6. Open the logging software and click new settings:

**Software instruction manual:**

![Recording settings](image1)

Use the required settings for sampling and others.
Click OK---→ Then select the channels that have the plugged into the ports.

Select the channel -→ and click Edit.

Click Apply. And then click OK
Then you will see the below
7. Similarly add all the channels connected and you will see them on the main screen.

8. Then click new data and give a file name to save in PLW format

9. Then click on the record button to start recording. Then you can pause or save or stop the recordings.

10. Once the recording starts, please open the CPU temperature app and put the phones in the oven. Make sure that it is visible from outside.

11. Since the temperature in the oven is different, heating will take place.

12. Note down manually the values of CPU on specific time intervals based on the logging software.

13. Wait for around 5 minutes at each temperature so that it reaches equilibrium.

14. Then increase the SP1 by not more than 10 degrees and note down the CPU values. Please note that the logging software is still running and recording the values of the screen and battery for both the mobile phones.
15. After attaining equilibrium and reach no more than 55°C on the phones because it can cause damage to the cell phone.

16. Then stop the recording and save the file as a .csv format to observe the readings.

17. Open the .csv file and insert heading for each channel where they were connected.

**Result of Phone Testing:** The left side phone is uncoated and the right side phone is coated.

1. **At Room Temperature:**

![Figure 4.23. Phone testing at 25°C](image)

2. **At 35°C:**

![Figure 4.24. Phone testing at 35°C](image)
3. At 450°C:

Figure 4.25. Phone testing at 450°C

18. Use a spreadsheet or any calculation software, MS Excel, to input the CPU values and plot the graphs. The Excel sheet should look something like below.

Figure 4.26. Display of result (data and graph) on Spreadsheet
4.10 Discussion:

The comparison of the testing results between the existing and the newly built cooling device are quite compatible, within a 10-15% range. We also tested cell phone batteries that were wrapped with the copper coil sprayed by our molecular fan coating (P-48\(^{[6]}\)). The phones were attached by wires connecting through the toaster oven to the USB device attached to a computer. As the toaster was heated, the phones started becoming hot and the temperature was displayed on the cell phone monitor. The mechanism was controlled by a special software code for Androids. Our software engineer used his skills to develop the code. We kept the two cell phones side-by-side, one with the regular battery and the other one with the copper foil with the MFC coating around it. With increasing the heat in the toaster oven, we observed the temperature change on the display monitor. Every degree of temperature change was read by another software that came with the USB port and was recorded on a spreadsheet as shown in Step 18.

All of the above-mentioned planning, designing, testing every step were guided by our project manager and my co-advisor. The entire project took about three months from planning to shipping. The entire assembly was disassembled, packed and shipped to China for demonstration at an industrial exhibition. Our project manager reassembled and demonstrated the entire cooling procedure at the conference.

4.11 Conclusion:

Hereby we can conclude about our heat dissipation study: We have developed an effective molecular fan coating (MFC). MFC efficiently dissipates heat away from a hot object through radiation. MFC exhibits good thermal efficiency. A new cooling device was successfully
built to conduct the cooling performance of heat sinks as per the standard scientific method.

We were able to use MFC in real world application.

4.12 Future Work:

In the near future, we plan to continue working on the same project to look into two more aspects:

1. Thermal resistance of coated and uncoated sample calculation.

2. Kinetic study of heat flow (Newton’s law of cooling).
4.13 References:


CHAPTER 5
SYNTHESIS AND CHARACTERIZATION OF CU-DOPED OXIDE BASED NANOCOMPOSITES, WITH WHITE ZINC OXIDE (ZNO) AND BLACK GRAPHENE OXIDE (GO)

Abstract: Copper-doped reduced graphene oxide (rGO) and zinc oxide (ZnO) nanocomposites were synthesized via facile thermal decomposition methods. Our goal was to enhance thermal conductivity and improve thermal efficiency of the nanomaterials such as graphene (Black) and zinc oxide (White) by doping a right stoichiometric amount of conducting material, such as copper, silver or nickel. Spectral analysis (FTIR) helped us to identify C-O bonds in GO/rGO and presence of copper (LIBS). We observed the circular shaped nanostructures of ZnO and cubes, rectangle and nanorod type of structures while doping with a higher Cu to Zn molar ratio. We intended to investigate the conduction nature of the nanocomposites. In the future, these nanocomposites can be used in coating technology for radiative cooling, such as molecular fan, and possibly to produce nanofluids and thermal paste.

5.1 Introduction

Nanostructures possess a large number of surface atoms per unit volume. As the size of the structures becomes continuously smaller, the ratio of the surface atoms to the interior atoms changes dramatically. When a cube is successively divided into smaller cubes, more atoms are exposed on the surface. For example, an iron cube with a 1 cm³ dimension, the percentage of surface atoms would be only $10^{-5}$ %. When the same cube is further divided with an edge of 10 nm, the percentage of surface atoms increases by 10%. In such a cube of iron with a 1 nm³,
every atom becomes a surface atom. Thus, the dramatic change in the ratio of surface atoms to the interior atoms in nanostructures and nanomaterials can explain why the nanometer scale objects are expected to illustrate greater changes in terms of the physical and chemical properties.

For an example, nano gold can exhibit a plasmon effect, but bulk gold cannot. As gold particle size changes from macro to micro to nano, the color of gold (Aurium) can change from yellow to orange to pink to green. As the particle size changes from centimeter size to nanometer size, not only does the surface area increase, but the surface energy also increases seven orders of magnitude ($10^7$). Thus, the smaller the particle size is, the higher the surface area can be achieved, which leads to more surface reactivity. One nanometer is a billionth of a meter, i.e., $1 \text{nm} = 10^{-9}\text{m}$.

Figure 5.1 demonstrates the scale difference in the various object sizes, starting from earth ($10^7\text{m}$) to an orange ($10^{-1}\text{m}$) and, finally, a bucky-ball or Fullerene ($10^{-9}\text{m}$).
The total surface energy increases with the overall surface area, which is strongly dependent on the dimension of the material. A sodium chloride cube with a side of 0.77 cm has a total surface area of 3.6 cm² and surface energy of 7.2x10⁻⁵ J/gm.¹ Whereas, a sodium chloride cube of side 10⁻⁷ cm (1 nm) can achieve a total surface area of 2.8x10⁷ cm² and surface energy of 560 J/gm.¹ Due to the huge surface area, all nanostructured materials possess huge surface energy. Thus, they become thermodynamically unstable or metastable.¹ This property leads to a challenge for material scientists to overcome the surface energy and to prevent agglomeration during the fabrication process. More details are given in the Introduction chapter.

In this project, we wanted to synthesize some new materials (nanocomposites) based on oxide-based nanomaterials. With a trace amount of doping or impurities, nanomaterials can show enhanced performance. In this project, we wanted to study how doped nanomaterials behave differently than their pristine component. For this purpose, nanomaterials needed to be chosen carefully. We selected two kinds of nanomaterials to start with as substrates, one white and the other one black. We picked zinc oxide, a well-known semiconductor, from the white category and graphene from the black category. We tried to dope the oxides with highly conductive materials such as copper (mostly) and silver (some). During our synthesis process, we incorporated dopant (copper or silver) as the zinc oxide was synthesized. We called them copper or silver doped zinc oxide, copper doped graphene oxide (GO) or copper doped reduced graphene oxide (rGO), respectively.

Graphene, being the thinnest (one atom thick) and hardest black nanomaterial, was selected for its excellent electrical, optical, mechanical properties. It provides a high specific surface area, which is most desirable for fabrication of nanocomposites. Graphene can be
uniformly dispersed with high frequency sound waves (sonication). Thus, it can act as a good nanocontainer or substrate.

![Graphene](image)

**Figure 5.2 Graphene²**

Zinc oxide nanoparticles (10-30 nm) was chosen as the white nanomaterial for being a good semiconductor with a wide band gap (~3.37 eV) and due to its good electron mobility, optical, magnetic properties. ZnO exhibits high catalytic efficiency and a strong absorption capacity. ZnO is also demanding for its antibacterial properties, which is why it is used in ointments.

For our interest, zinc oxide worked as an excellent substrate or nanocontainer because it is easily dispersed and stabilized nanomaterial. When copper or silver ion is incorporated with zinc oxide, those metal ions can replace Zn²⁺ ions in its lattice structure (Wurtzite). Figures 5.3(a) and 5.3(b) display two possible structures of zinc oxide: wurtzite and zinc-blend, respectively.

![ZnO - Wurtzite structure](image)

**Figure 5.3. Left: ZnO - Wurtzite structure¹³; Right: ZnO – Zinc Blende structure¹³**
5.2 Previous Work

Zinc oxide is an attractive nanomaterial and has previously been used to conduct different studies for various purposes by many research teams. Among them, the most common study was to see its photocatalytic activity. For example, to study ZnO as a promising photocatalyst to see the extent of photocatalytic degradation influenced by dopant by Labhane et al.⁴ For this purpose, zinc oxide was synthesized by a co-precipitation method.⁴

Another group investigated the luminescence properties of ZnO films with Cu as a luminescence activator to try out its luminescence application.⁵ Here, fabrication of Cu-doped ZnO film was performed by employing a magnetron-sputtering process.⁵ In Dr. Lin’s lab, we synthesized and studied a new type of nanomaterials in two ways through a solvo-thermal method and a precipitation method. We discuss each process and its outcome in detail. We wanted to study their properties, try to incorporate them into emulsion coating, and measure thermal performance. In the future, we want to investigate their optical properties and find the best way for possible application.

5.3 Objective

Our goal is to enhance the thermal conductivity of zinc oxide (ZnO) and reduce (GO/rGO) by doping with a popular conducting material, such as copper or silver using stoichiometry. To do so, we needed to find the nanostructures and the behavior of the newly synthesized material. Therefore, proper characterization of the nanocomposites was necessary. We primarily used TEM to detect the nanostructure, SEM for morphology study, EDX for
elemental composition, and powder XRD to find crystal lattice information. We also investigated the extent of thermal radiation by running a heat dissipation study using cooling monitor. From the results of our analysis, we determined if we could apply these nanocomposites into coating technology for radiative cooling purposes, such as molecular fan. We also wanted to explore other possible applications in the areas of nanofluid and thermal paste.

5.4 Experimental

5.4.1 Materials

All chemicals were purchased from Sigma Aldrich and used as received without further purification. We needed zinc acetate dihydrate as a solute, copper (II) acetate monohydrate as a dopant, anhydrous ethanol as a solvent and dimethylethanolamine (DMEA) as a sol stabilizer and pH controller. Figures 5.4 (a), (b), (c) and (d) show all the main chemicals needed to synthesize the copper doped zinc oxide.

![Figure 5.4(a)](image-url)
Zinc acetate dihydrate
Zn(CH₃COO)₂·2H₂O
MM: 219.50 g/mol

![Figure 5.4(b)](image-url)
Copper(II) acetate monohydrate
Cu(CH₃COO)₂·H₂O
MM: 199.65 g/mol

![Figure 5.4(c)](image-url)
Anhydrous ethanol
CH₃CH₂OH
MM: 46.07 g/mol

![Figure 5.4(d)](image-url)
N,N-Dimethylethylamine
C₄H₁₁N
MM: 73.14 g/mol

Figure 5.4(a)                   Figure 5.4(b)                      Figure 5.4(c)                   Figure 5.4(d)
5.4.2 Synthesis Procedure

Zinc acetate dihydrate was ground into a fine powder by mortar and pestle. It was then dissolved into the solvent DMEA/Ethanol mixture with a magnetic stirrer with low heat. The zinc acetate mixture was transferred into a two neck round bottomed flask and set under a reflux system. Next we added the copper(II) acetate monohydrate slowly into the flask through the second neck. We covered it and let the reflux run for two hours at 70°C and then let it age overnight. A deep blue solution was received and dried in a oven at 130°C for 16 hours. At this point, copper doped zinc oxide was formed, which was still in a gel type consistency. Now we needed to make it into a dry powder to conduct all testings for characterization. The blue gel was then heated up between 216-220°C under an electrical heating coil bath set at 50V and with an argon gas flow continuously blowing in the flask at low pressure until the blue gel started bubbling and slowly turned into a grayish white dry solid. The solid obtained in this procedure was then collected and ground into a fine powder for characteristic tests and applications. We needed to carefully observe the heating process, so it would not become over burned. We purposely used argon gas rather than oxygen to avoid any oxide formation of copper. Figure 5.5 gives a pictorial description of the entire procedure step-by-step.
5.4.3 Sample Run

Table 5.1 below tabulates the measurements of all runs with a different amount of copper acetate but a fixed amount of zinc acetate (2.2 g) for each run. In the last row, the calculated mole ratio is displayed.
Table 5.1 Samples prepared with Zn$_{1-x}$Cu$_x$O nanoparticles by solvo-thermal method

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc acetate dihydrate (g)</td>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
</tr>
<tr>
<td>Anhydrous ethanol (g)</td>
<td>99.1</td>
<td>99.1</td>
<td>99.1</td>
<td>99.1</td>
<td>99.1</td>
</tr>
<tr>
<td>DMEA (g)</td>
<td>0.90</td>
<td>0.90</td>
<td>0.90</td>
<td>0.90</td>
<td>0.90</td>
</tr>
<tr>
<td>Copper (II) acetate monohydrate (g)</td>
<td>2.00</td>
<td>1.50</td>
<td>1.00</td>
<td>0.50</td>
<td>0.40</td>
</tr>
<tr>
<td>Mole-Ratio (Cu/Zn)</td>
<td>3.35</td>
<td>2.52</td>
<td>1.68</td>
<td>0.84</td>
<td>0.67</td>
</tr>
</tbody>
</table>

We also repeated the same synthesis procedure with respect to weight ratio. Table 5.2 shows the measurement in terms of weight percent. Here the amount of copper acetate also varied with fixed amounts of zinc acetate (2.2 g) for each run. It also displays the measurements in mole ratio.

Table 5.2 Atomic% of samples prepared with Zn$_{1-x}$Cu$_x$O nanoparticles by solvo-thermal method

<table>
<thead>
<tr>
<th>Cu-doped Sample</th>
<th>1(At.%)</th>
<th>2(At.%)</th>
<th>3(At.%)</th>
<th>4(At. %)</th>
<th>5(At. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc acetate dihydrate (g)</td>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
</tr>
<tr>
<td>Anhydrous ethanol (g)</td>
<td>99.1</td>
<td>99.1</td>
<td>99.1</td>
<td>99.1</td>
<td>99.1</td>
</tr>
<tr>
<td>DMEA (g)</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>Copper (II) acetate monohydrate (g)</td>
<td>0.02</td>
<td>0.04</td>
<td>0.06</td>
<td>0.08</td>
<td>0.10</td>
</tr>
<tr>
<td>Mole Ratio (Cu/Zn)</td>
<td>0.01</td>
<td>0.02</td>
<td>0.03</td>
<td>0.04</td>
<td>0.05</td>
</tr>
</tbody>
</table>
Table 5.3 summarizes the amount of copper acetate and its corresponding mole ratio with respect to zinc acetate, where the amount of zinc acetate remained fixed (2.2 g). Preparation of Zn$_{1-x}$Cu$_x$O nanoparticles at 212$^\circ$C by solvothermal process is summarized in Table 5.3.

Table 5.3 Sample runs (Atomic% and mole ratio) for Zn$_{1-x}$Cu$_x$O nanoparticles by Solvothermal

<table>
<thead>
<tr>
<th>Cu-doped Sample (At. %)</th>
<th>Amount of Copper Acetate (g)</th>
<th>Mole Ratio (Cu:Zn)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>2</td>
<td>0.04</td>
<td>0.02</td>
</tr>
<tr>
<td>3</td>
<td>0.06</td>
<td>0.03</td>
</tr>
<tr>
<td>4</td>
<td>0.08</td>
<td>0.04</td>
</tr>
<tr>
<td>5</td>
<td>0.10</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Figure 5.6 Copper doped zinc oxide - Products of Solvothermal method in wt%

Figure 5.6 displays the dry products in vials with the Zn$_{1-x}$Cu$_x$O nanoparticles (1-4 wt.%), or (x=0.00, 0.002, 0.04, 0.06, 0.08). ZnO is white, and the rest change from light brown to darker brown.
5.4.4 Characterization

The products obtained by the solvo-thermal method were characterized by a series of procedures: transmission electron microscopy (TEM), scanning electron microscopy (SEM), and powder x-ray diffracton (XRD) to find the material structure, morphology, elemental analysis, and lattice orientation. The products obtained by the precipitation method were also characterized by the same procedures. Furthermore they were analyzed by Fourier transmission infrared spectroscopy (FTIR) to find a comparative study of the functionalities. In this section we display the results from each analysis.

**TEM** (Solvo-thermal Method):

Figure 5.7. Left: 0.01g Cu, core-shell type structure; Middle: 0.05g Cu, spherical shape; Right: 0.50g Cu, rods and cube like shape

Figure 5.7 (left and middle) shows the spherical shapes of pristine zinc oxide with no impurities. As we started from lower amount (0.01g) of copper acetate as dopant, we saw same spherical shapes but a core shell type of structures was predominant (Figure 5.7 left). As the amount of copper acetate slowly increased (0.05g), the core shell structure diminished but the overall spherical shapes remained prevalent (Figure 5.7 Middle). With an even higher amount of copper acetate (0.50g or higher), the spherical shapes completely disappeared and new geometric shapes arose, like a distinct rod, cube or rectangular prism (Figure 5.7 Right). In either synthesis
method, solvo-thermal or precipitation method, we found spherical shapes for pristine zinc oxide, and as the dopant amount increased, shapes took on the form of monoclinic shapes as shown in Figure 5.8.

**TEM (Precipitation Method):**

![TEM Image](image1)

Figure 5.8. Left: hexagonal/cubical shaped Cu-doped ZnO (1.07 wt. %); Right: spherical shaped pristine ZnO nanoparticles;

![Hexagonal Close Packed ZnO](image2)

Figure 5.9. Hexagonal Close Packed ZnO (Theoretical)

![Monoclinic Bravais lattice](image3)

Figure 5.10. Left: Monoclinic Bravais lattice; Right: Monoclinic Crystal (Theoretical)
In crystallography, the monoclinic crystal system is one of the seven crystal systems. Vectors of unequal lengths can describe a crystal system such as the orthorhombic system. They form rectangular prisms with a parallelogram as its base. Thus two vectors meet at right angle (perpendicular), while the third one meets the other two vectors at an angle other than 90 degree. These crystal structures are shown in Figure 5.11. Remembering these crystal structures and looking at the shapes obtained from TEM images, there are two possibilities here forming copper oxides as monoclinic crystals as cuprous oxide [Cu(I)O] with a band gap 2.137 electron volt (Figure 5.11) and cupric oxide [Cu(II)O] with a band gap 1.2 electron volt (Figure 5.12).

In each kind, cubical or rectangular shapes are expected in monoclinic crystal structures. Figure 5.9 shows the hexagonal close-packed structure of zinc oxide, and 5.11 left and right
show the cubical structures of the cuprous oxide unit lattice structure and monoclinic Bravis lattice structures. Thus, shapes obtained from TEM result in Figure 5.7 (Right) give us hint, why they are cubical in shape. Additionally, 1.07% copper-doped zinc oxide, obtained from the precipitation method, shows the existence of hexagonal shapes besides the cubical in Figure 5.8 (Left). The reason could be due to the hexagonal close pack base structure of zinc oxide (Figure 5.9) into which copper ion finds its place.

**FTIR (Solvo-Thermal Method)**

![FTIR of Cu-doped ZnO by Solvo-Thermal Method](image)

Figure 5.13: FTIR of the sample A, B and C

In Figure 5.13, the FTIR finds frequency at ~500 cm\(^{-1}\) is due to Zn-O stretching, frequency between 615-675 cm\(^{-1}\) is due to Cu-O formation, frequency between 1480-1580 cm\(^{-1}\) is due to O-H bending, and frequency at ~3400 cm\(^{-1}\) is due to O-H stretching frequency, respectively.\(^{[4]}\)
XRD (Solvo-Thermal Process):

Figure 5.14. Left: XRD of pristine zinc oxide; Right: XRD of 0.1g copper doped zinc oxide

Figure 5.15. Left: XRD of 0.2g copper-doped zinc oxide; Right: XRD of 0.3g copper-doped zinc oxide

The XRD plots show all products obtained from the solvo-thermal method are crystalline and comply with literature data shown in Figure 5.11. Copper oxides can be formed by heating copper in air at around 300 - 800°C, where the reaction: \(2 \text{Cu} + \text{O}_2 \rightarrow 2 \text{CuO}\)

But our reaction temperature is 216-220°C in an argon environment. Even so there oxygen remains in the reaction flask. During the heating process, some copper can react with oxygen and form into copper oxides. Thus in XRD, we expected to see elemental copper, copper (I) and copper (II). Therefore both cuprous and cupric oxides are possible options to be seen in
XRD, besides elemental copper. From the literature (Figure 5.16), we found possible peak positions of elemental copper at 43°; copper (Cu\(^{1+}\)) in cuprous oxide form at 29°, 37°, 42°, 61.5°; and copper (Cu\(^{2+}\)) in cupric oxide formed at 33°, 36°, 38°, 54° and 68°. These peaks are also shown in our XRD results, which further establishes our successful synthesis to prepare new material copper-doped zinc oxide. This testing confirms the presence of Cu, O and Zn in the unit lattice, as per JCPDS data (01-075-1533). The peaks found at 32, 35, 37 degrees belong to ZnO planes (100), (022), (101), respectively. The peak shown at 38 degrees is due to the elemental copper plane (101). ZnO peaks are also supported by the literature data shown in Figure 5.17.

![Figure 5.16: XRD of elemental copper, cuprous oxide and cupric oxide](image)
EDX: Elemental Analysis: (Solvo-Thermal Method)

We wanted to see which elements were present in the product sample of the new material we prepared. Therefore, we conducted an elemental analysis on the EDX. The results for 0.1g copper acetate sample are given in Figure 5.18. We found only copper, zinc and oxygen were detected as individual elements. The very first peak shown was due to the presence of carbon found in the carbon tape on the substrate.
Like the XRD, the EDX testing confirmed the presence of Cu, O and Zn in the sample. EDX also determined the amount of each element in weight percent. We saw that the amount of Cu decreased and the amount of zinc increased as it moved from the high end of the copper acetate to its low end. The 0.3g sample does not follow this trend due to some processing errors. With a very low amount of copper acetate, neither Cu nor Zinc was identified, like in the samples 0.05g, 0.025g and 0.0125g.

Table 5.4 EDX report of elemental analysis

<table>
<thead>
<tr>
<th>Amount of Cu (g)</th>
<th>Mole Ratio (Cu/Zn)</th>
<th>Elements (Wt.%)</th>
<th>Elements (Atomic%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>O</td>
<td>Cu</td>
</tr>
<tr>
<td>2</td>
<td>1.047</td>
<td>6.72</td>
<td>73.50</td>
</tr>
<tr>
<td>1.5</td>
<td>0.785</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>1.0</td>
<td>0.523</td>
<td>12.04</td>
<td>29.40</td>
</tr>
<tr>
<td>0.5</td>
<td>0.262</td>
<td>10.79</td>
<td>39.21</td>
</tr>
<tr>
<td>0.5 (w/ Industrial ZnO)</td>
<td>0.262</td>
<td>16.38</td>
<td>2.01</td>
</tr>
<tr>
<td>0.4</td>
<td>0.209</td>
<td>18.44</td>
<td>11.18</td>
</tr>
<tr>
<td>0.3</td>
<td>0.157</td>
<td>13.54</td>
<td>37.17</td>
</tr>
<tr>
<td>0.2</td>
<td>0.104</td>
<td>12.82</td>
<td>6.96</td>
</tr>
<tr>
<td>0.1</td>
<td>0.052</td>
<td>15.57</td>
<td>1.85</td>
</tr>
</tbody>
</table>

Notice that the Wt.% of Cu decreased, while that of the Zn and O increased, as predicted.
SEM analysis provided the morphology of the copper doped zinc oxide. Figure 5.19 left gives a close look at the zinc oxide prepared by the solvo-thermal method. We found definite rod like structures with hexagonal shapes. Figure 5.19 right shows the SEM image of the copper doped zinc oxide sample with a higher agglomeration at a higher concentration. These morphologies are supported by the literature results shown in Figures 5.20 left and 5.20 right. \[14\] Literature study was done under high resolution SEM. Thus, we were able to see each sharp edge
and corner distinctly. Individual SEM images of all other samples are not given here. But they all comply with the literature results.

The SEM with a higher amount of copper doped samples did not turn out very well, as some of them were not ground properly before SEM or the particles had a large grain size.

5.5 Application: Molecular Fan Nanocoating

The molecular fan technology was discussed in the Introduction and in Chapter 4 (Heat Dissipation Study) in great detail.

Due to the kinetic energy of the molecules, they acquired a quantized lattice motion that absorbed energy from the heat source and became excited, resulting in faster vibrations. Well-dispersed nanomaterials can achieve active molecular functional groups with quantized lattice motions that can act as a selective emitter displaying an enhanced emissivity for dissipating heat. We used this principle to prepare our formulation for the heat dissipative coating. We also wanted to keep in mind the heat law given in equation (1),

$$\frac{dq}{dt} = \varepsilon \sigma A T^4$$  \hspace{1cm} (1)

Equation (1) shows, the heat produced (Q) is directly proportional to the emissivity (\(\varepsilon\)) and surface area (A) of the hot object and to the magnitude of four of the temperature (T).
We prepared the water-based formulation for coating that included a polymer binder or resin, solvent, co-solvent, cross linkers, additives and nanomaterials. Table 5.5 gives an estimated measurement.

Table 5.5 Individual component, amount and functionalities to prepare heat dissipative coating with nanocomposites

<table>
<thead>
<tr>
<th>Material/Chemical</th>
<th>Percentage</th>
<th>Purpose / Property</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin/acrylate</td>
<td>20-25%</td>
<td>Acrylic copolymer resin</td>
</tr>
<tr>
<td>Well–dispersed nanomaterials</td>
<td>0.1-0.5%</td>
<td>Radiative emission/ High thermal conductivity/ Delectric/ High Surface Emissivity</td>
</tr>
<tr>
<td>Solvent</td>
<td>50-60%</td>
<td>Diluent for viscosity/pH adjustment</td>
</tr>
<tr>
<td>co-solvents</td>
<td>10-15%</td>
<td>Matting agent for gloss reduction</td>
</tr>
<tr>
<td>Self crosslinkers</td>
<td>(0.5-2 wt%),</td>
<td>Crosslinked polymer for resistance properties</td>
</tr>
<tr>
<td>Additives</td>
<td>1-2%</td>
<td>Surfactants/Wetting agent/Defoamer/Coalescing agent for film formation</td>
</tr>
</tbody>
</table>

We made several attempts to formulate the coatings with all of the samples of copper doped zinc oxide. Figure 5.21 shows a few.

Figure 5.21 Molecular Fan coating with copper doped zinc oxide
5.6 Result and Discussion

5.6.1 Zn_{1-x}Cu_xO nanoparticles (copper doped zinc oxide) by Solvo-Thermal Method

The results of the heat dissipation study are tabulated in Table 5.4. We saw 0.10g of the copper acetate sample with a mole ratio of copper to zinc 0.17 achieved the highest cooling efficiency at 23.14%. Note that the cooling efficiency of the 0.20g copper acetate sample with mole ratio of copper to zinc 0.34 was undetermined.

Table 5.6 Sample runs of Solvo-Thermal (mole ratio and cooling efficiency):

<table>
<thead>
<tr>
<th>CuAcetate.H_2O (g)</th>
<th>Mole-Ratio (Cu/Zn)</th>
<th>Cooling Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0125 ~0.01</td>
<td>0.02</td>
<td>18.03</td>
</tr>
<tr>
<td>0.0250 ~0.03</td>
<td>0.04</td>
<td>17.52</td>
</tr>
<tr>
<td>0.0500 ~0.05</td>
<td>0.08</td>
<td>19.63</td>
</tr>
<tr>
<td>0.1000 ~0.10</td>
<td>0.17</td>
<td>23.14</td>
</tr>
<tr>
<td>0.2000 ~0.20</td>
<td>0.34</td>
<td>-----</td>
</tr>
<tr>
<td>0.3000 ~0.30</td>
<td>0.50</td>
<td>20.38</td>
</tr>
<tr>
<td>0.4000 ~0.40</td>
<td>0.67</td>
<td>22.48</td>
</tr>
<tr>
<td>0.5000 ~0.50</td>
<td>0.84</td>
<td>19.34</td>
</tr>
<tr>
<td>1.0000 ~1.00</td>
<td>1.68</td>
<td>18.32</td>
</tr>
<tr>
<td>1.5000 ~1.50</td>
<td>2.52</td>
<td>19.12</td>
</tr>
<tr>
<td>2.0000 ~2.00</td>
<td>3.35</td>
<td>18.47</td>
</tr>
</tbody>
</table>
Figure 5.22 A graphical representation of cooling efficiency of copper doped zinc oxide

Figure 5.15 gives a graphical representation to check how the cooling efficiency varied with different %weight ratios. We saw the slope was very steep at the low end between 0.01 to ~10 wt.%. Between 10-20 wt.%, the cooling efficiency stayed in peak, after 20 wt.%, it started to drop. At 30 wt.%, we found a minima and again cooling efficiency rose between 30-40 wt.%. At 40 wt.%, we found maxima and a little after cooling efficiency continuously dropped. Thereafter, we determined the maximum cooling efficiency is ~15 wt.%.

We see from Table 5.4 that with an increasing amount of copper at the low scale 0.01g to 0.10g, cooling efficiency rose from 18.03% to 23.14%. However after that it slowly dropped, even with the additional amount of copper. With 0.40g copper, it gave a slight boost, but beyond that the cooling efficiency steadily fell. This is due to loading effect.

When lattice molecules become saturated with active vibrational modes, they do not further excite at a higher energy level. Thus, there is no excess energy to release as radiation. Therefore, no further cooling effect was observed at the molecular level.
As the copper amount slowly increased, the zinc ions (Zn$^{2+}$) in zinc oxide were replaced by copper ions (Cu$^{1+}$ or Cu$^{2+}$). When the loading amount was complete, zinc ions in the lattice molecule were no longer replaced by copper ion. At this point the zinc oxide lattice was saturated. Figure 5.16 shows the saturation of the zinc oxide lattice on all samples made by the solvo-thermal process.

The highest cooling efficiency achieved in this method was 23.14% with 0.10g of copper acetate with mole ratio (Cu/Zn) 0.17.

When lattice molecules become saturated with active vibrational modes, they do not further excite at a higher energy level. Thus, there is no excess energy to release as radiation. Therefore, no further cooling effect was observed at the molecular level.

As the copper amount slowly increased, the zinc ions (Zn$^{2+}$) in zinc oxide were replaced by copper ions (Cu$^{1+}$ or Cu$^{2+}$). When the loading amount was complete, zinc ions in the lattice molecule were no longer replaced by copper ion. At this point the zinc oxide lattice was saturated. Figure 5.23 shows the saturation of the zinc oxide lattice on all samples made by the solvo-thermal process.

The highest cooling efficiency achieved in this method was 23.14% with 0.10g of copper acetate with mole ratio (Cu/Zn) 0.17.
5.6.2 Investigation of cooling efficiency: Results affected by different factors

In this section we wanted to summarize our work based on our observations in the heat dissipation studies.

A. When doping was done in the 10th scale, thermal efficiency increased with decreasing Cu amounts (Table 5.7).

<table>
<thead>
<tr>
<th>Cu-doped Sample</th>
<th>Thermal Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5g</td>
<td>19.64</td>
</tr>
<tr>
<td>0.4g</td>
<td>22.48</td>
</tr>
<tr>
<td>0.1g</td>
<td>23.14</td>
</tr>
</tbody>
</table>

B. When doping was done in the 100th scale, thermal efficiency increased with increasing Cu amounts (Table 5.8).
Table 5.8 Thermal Efficiency (B)

<table>
<thead>
<tr>
<th>Cu-doped Sample</th>
<th>Thermal Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2At.% (0.04g)</td>
<td>20.00</td>
</tr>
<tr>
<td>3At.% (0.06g)</td>
<td>20.29</td>
</tr>
<tr>
<td>4At.% (0.08g)</td>
<td>20.95</td>
</tr>
<tr>
<td>5At.% (0.10g)</td>
<td>23.14</td>
</tr>
</tbody>
</table>

C. Heat Dissipation Study by Cooling Monitor:

![Graphical presentation of cooling monitor](image)

Figure 5.24 Graphical presentation of cooling monitor

Figure 5.24 gives a graphical presentation of the cooling performance obtained from the thermal cooling device (described in Chapter 1 and Chapter 4). We saw bare aluminum substrate reached at equilibrium at about 137°C, whereas aluminum panels coated with molecular-fan
active nanoparticles of copper doped zinc oxide reached to equilibrium much faster. In this comparison study, we also noticed 0.1g copper cools off with highest efficiency, next followed 0.4g, and 0.5g being the least efficient. We crosschecked the loading effect here as well.

![Aluminum Q-panels with MF coating ready to be tested on cooling monitor](image)

Figure 5.25. Aluminum Q-panels with MF coating ready to be tested on cooling monitor

Aluminum Q-panels are silver colored. When coated and cured, they became brownish. Figure 5.25 shows one set of coated Q-panels are ready to be tested.

**D. Thickness**: Thermal efficiency increased with increasing thickness. Tables 5.7 and 5.8 show two samples of each kind of coating with different thickness. The better cooling performance occurred between 50-75 μm. Table 5.9 compares % Efficiency of the same composition (0.3g) but with two thicknesses.

<table>
<thead>
<tr>
<th>0.3g Cu-doped ZnO</th>
<th>Thermal Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Al_ZnO-Exp</strong></td>
<td>15.33</td>
</tr>
<tr>
<td>40 (μm)</td>
<td>17.88</td>
</tr>
<tr>
<td>52 (μm)</td>
<td>20.36</td>
</tr>
</tbody>
</table>
Table 5.10 Comparing % Efficiency of D (1.5g)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thermal Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5g Cu-doped ZnO</td>
<td></td>
</tr>
<tr>
<td>Al·ZnO-Exp</td>
<td>1.33</td>
</tr>
<tr>
<td>67 (μm)</td>
<td>19.53</td>
</tr>
<tr>
<td>72 (μm)</td>
<td>22.8</td>
</tr>
</tbody>
</table>

Table 5.10 compares % Efficiency of the same composition (1.5g) but with two thicknesses.

E. The *shiny surface* radiates less heat as per Table 5.11.

Table 5.11 % Thermal Efficiency of shiny versus non-shiny surfaces

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thermal Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1g (Gloss-cut)</td>
<td>23.14</td>
</tr>
<tr>
<td>0.0125 (Shiny)</td>
<td>1.03</td>
</tr>
</tbody>
</table>

5.6.3 Silver doped zinc Oxide, Zn$_{1-x}$Cu$_x$O nanoparticles by solvo-thermal method

We performed the same synthesis process and testing procedure with silver doped zinc oxide. We used silver acetate instead of copper acetate in the same stoichiometric ratio. We prepared silver doped zinc oxide with two different amounts: 0.1g and 0.0125g of silver acetate (Figure 5.26). Figure 5.26 shows the Q- Panels with Ag-doped ZnO nanocoating after being
cured before Heat Dissipation testing. Figure 5.27 left shows the dry products of copper and silver doped zinc oxide powder obtained from the solvo-thermal method.

Figure 5.26 Q-Panels with Ag-doped ZnO after being cured before Heat Dissipation testing

Figure 5.27 Left: Copper doped and silver doped zinc oxide powder; Right: Copper doped and silver doped Zinc oxide coating on Q-panels

5.6.3.1 Heat Dissipation Study of Ag-doped ZnO

Figure 5.28 below shows a graphical presentation of the cooling efficiency of silver doped zinc oxide. We found silver doped zinc oxide has better cooling efficiency than undoped zinc oxide.
5.6.4 Conclusion (Solvo-Thermal Method)

From the experimental analysis we can say that Cu-doped ZnO or Zn$_{1-x}$Cu$_x$O is synthesized successfully. ZnO nanomaterial can enhance its thermal conductivity by doping with the right amount of conducting material (Cu, Ag). The optimal doping amount found is below the 0.15 mole ratio (Cu:Zn) with maximum loading capacity. We were able to develop a water-based coating with good heat dissipation efficiency. The heat dissipation performance shows a cooling efficiency ~19-23%.

For application, this new material can be used in molecular fan nanocoating.

5.6.5 Future Work (Solvo-Thermal Method)

In the future, we want to focus on the following fields.

1. Developing nanofluids.
2. Developing thermal paste.

4. Try to dope zinc oxide with other conducting material (Ni, Co).

5.7 Copper-doped Zinc Oxide by Precipitation Method

5.7.1 Synthesis Procedure:

Chemicals needed here were zinc sulfate (ZnSO\(_4\).7H\(_2\)O), sodium carbonate (Na\(_2\)CO\(_3\)), and copper sulfate (CuSO\(_4\).5H\(_2\)O). We used them in stoichiometric ratios. We synthesized them in three steps.

**Solution 1:** We mixed 9g of Na\(_2\)CO\(_3\) with 85 ml of water and dissolved it under low heating and constant stirring.

**Solution 2:** Then we mixed 2g of ZnSO\(_4\).7H\(_2\)O in 15 mL H\(_2\)O. Dissolved it under low heating and constant stirring.

**Solution 3:** We added a-0.24Wt.% Cu into Solution 2 while it was being stirred on low heat. We continued stirring for 20 minutes to obtain a mixture of 0.24% Cu-doped ZnO.

We repeated the above steps to obtain 0.35% and 1.07% Cu-doped ZnO.

Finally, we added Solution 3, drop wise, into Solution 1 until the PH reached ~11. We continued stirring under a low heat for another 10 minutes until the precipitate developed. We separated the precipitate by filtration under vacuum, continuously washing the precipitate with DI water until the PH reached 7. We air-dried it overnight under vacuum. Then we heated the ppt. at 500°C for 3 hours and cooled it at room temperature.

We repeated the above steps for b (0.35%) and c (1.07%) to obtain Zn\(_{1-x}\)Cu\(_x\)O nanoparticles (x=0.00, 0.24, 0.35, 1.07).
Table 5.12 tabulates the mole ratio against copper, the actual amount copper and the particle size of the four runs. The first run is blank or pure zinc oxide (0.0%). Samples a, b and c are three doped samples prepared with 0.24%, 0.35% and 1.07% of copper. Obtained products are shown in Figure 5.29.

Table 5.12 Mole ratio and particle size of Zn$_{1-x}$Cu$_x$O by precipitate method

<table>
<thead>
<tr>
<th>Sample (At.%)</th>
<th>Amount of Cu (g)</th>
<th>Mole Ratio (Cu/Zn)</th>
<th>Particle Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>o – 0.00%</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.32-1.16</td>
</tr>
<tr>
<td>a – 0.24%</td>
<td>0.0042</td>
<td>0.0024</td>
<td>0.41-1.24</td>
</tr>
<tr>
<td>b – 0.35%</td>
<td>0.0061</td>
<td>0.0035</td>
<td>0.06-0.21</td>
</tr>
<tr>
<td>c – 1.07%</td>
<td>0.0186</td>
<td>0.0107</td>
<td>0.32-1.93</td>
</tr>
</tbody>
</table>

Figure 5.29. Zn$_{1-x}$Cu$_x$O nanoparticles (x=0.00, 0.24, 0.35, 1.07), obtained products from precipitate process

Table 5.10 shows the mole ratio based on the amount of copper introduced into the zinc oxide substrate. This table also displays the particle size using the Scherrer equation shown below. This was derived using the diffraction angles obtained from XRD. XRD allowed us to determine the size of the particles in our sample, for which we took the angle measurement 2θ, divided by 2 to get θ and used that in Scherrer equation:
\[ D = \frac{K\lambda}{B \cos \theta} \tag{2} \]

where, \( D \) is the average crystalline diameter, \( B \) is the full width half max (FWHM) of a diffraction peak, \( \theta \) is the diffraction angle and \( K \) is the Scherrer’s constant. Equation (1) gives us an estimated size of the particle rather than an accurate one. Acceptable value of \( K \) is taken as 0.9-1.0. We found the average particle size was in a very small range, 0.32 to 1.93 m.

5.7.2 Characterization:

**Transmission Electron Microscopy (TEM):**

![TEM Image](image)

Figure 5.30: Sample b – 0.35% Cu-doped ZnO

The distinct cubical shapes of the nanoparticles observed in TEM image in Figure 5.30 were found just like in the solvo-thermal method. This similarity supports the existence of the monoclinic crystals of copper in our sample.
In Figure 5.31, FTIR found Zn-O stretching between 400-415 cm\(^{-1}\).\(^4\) All other peaks appeared due to the attributes of new material formation of the copper doped zinc oxide nanoparticles. If we notice closely, on the blue line there is only one peak at \(~400\) cm\(^{-1}\), which is for pure Zn-O stretching. But little after at \(~450\) cm\(^{-1}\), which is shown in all of the others (a, b, c), is due to the appearance of Cu-O stretching. The absorption peak between 1450-1590 cm\(^{-1}\) is due to O-H bending, 837-881 cm\(^{-1}\) is possibly due to some peroxide formation (Zn-O-O-Cu), and 1090-1420 cm\(^{-1}\) is undetermined.\(^4\)
EDX (Elemental Composition)

Figure 5.32. Elemental analysis of cu-doped ZnO from precipitation method

Note that in Figure 5.32, EDX could not detect the Wt.% of Cu for the precipitation method. EDX only found zinc and oxygen. This is due to the particle size obtained in a very small range, as mentioned in Table 5.5 as well as a very trace amount of copper introduced into the zinc oxide matrix, which is below the machine’s detection limit.
XRD:

Figure 5.33 Cu-doped ZnO Peaks from precipitation method

Figure 5.34 Copper peaks from JCPDS card 36-1451 \[^{15}\]
Figure 5.35 Cu-doped ZnO peaks from literature\textsuperscript{[16]}

Figure 5.36 XRD of elemental copper from literature\textsuperscript{[17]}

All products obtained by the precipitation method, such as pristine zinc oxide and Zn\textsubscript{1-x}Cu\textsubscript{x}O, are crystalline in nature. Figure 5.33 shows the XRD peaks are found at 2-theta positions 32, 34.6, 37.7, 47.8, 57, 63, 66.6, 68.2, 69.3, 73, and 78 degrees that correspond to the planes (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (002), respectively\textsuperscript{[16]}. These peaks all belong to ZnO peaks meeting the standard JCPDS card 36-1451,
shown in Figure 5.34 and 5.35. Peaks found at 38.4 and 47.8 degrees are due to the elemental copper planes (111) and (202), also in accordance with literature values shown in Figure 5.36.\textsuperscript{[15-17]}

**Heat Dissipation Studies (Precipitation Method)**

Table 5.13: Cooling efficiency of cu-doped ZnO by precipitation method

<table>
<thead>
<tr>
<th>Samples</th>
<th>Equilibrium Temp (°C)</th>
<th>Thermal % Efficiency</th>
<th>Thickness (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0 Wt. %</td>
<td>108.2</td>
<td>21.02</td>
<td>70</td>
</tr>
<tr>
<td>0.24 Wt. %</td>
<td>109.2</td>
<td>20.09</td>
<td>63</td>
</tr>
<tr>
<td>0.35 Wt. %</td>
<td>110.6</td>
<td>19.27</td>
<td>39</td>
</tr>
<tr>
<td>1.07 Wt. %</td>
<td>111.5</td>
<td>18.39</td>
<td>54</td>
</tr>
</tbody>
</table>

![% Cooling Efficiency](image)

Figure 5.37 Cooling efficiency drops in precipitation method

We found thermal efficiency (%) dropped in the precipitation method (Table 5.9 and Figure 5.32). This is due to the trace amount of copper present in zinc oxide matrix and the average particle size being extremely small (0.32-1.93 nm), as shown in Table 5.9, which is not sufficient to saturate zinc oxide lattice. Therefore, cooling efficiency decreased even with the increasing amount of copper. Figure 5.37 shows the steady fall of the cooling performance.
Figure 5.38 Cooling efficiency graphical presentation of precipitation method

Figure 5.38 shows pristine ZnO and sample ‘a’ have the most thermal performance and ‘b’ and ‘c’ have the least in the small range of difference.

5.7.3 Conclusion (Precipitation Method)

Zn_{1-x}Cu_xO nanoparticles (x=0.00, 0.24, 0.35, 1.07) were synthesized successfully by a facile method (the precipitation method) with the assurance of the results from FTIR and XRD. The doping concentration was below 1 At.%. A water-based coating was developed with freshly prepared nanocomposites. The cooling efficiency obtained was ~13% - 21%. As an application, this product also could be used in molecular fan. However, we obtained better results from the solvo-thermal procedure.
5.7.4 Future Work (Precipitation Method)

We want to perform the following analysis as the next steps:

1. Improve developing coating with higher thermal efficiency
2. Disperse and stabilize in base fluids
3. Find the zeta potential (nanofluid)
4. Measure band gap using DRS (diffuse reflectance spectroscopy)
5. Develop thermal paste
5.8 References


15. Das, S., Dutta K. and Pramanik, A.; “Morphology control of ZnO with citrate”. 
*CrystEngComm*, **2013**, 32. DOI: 10.1039/C3CE40822A.

16. Copper peaks from XRD. *JCPDS card 36-1451*.


CHAPTER 6. POROUS SILICA BASED NANOCOMPOSITES

Part I: Synthesis of Mesoporous Silica/Carbon Nanocomposites

6.1 Introduction

Porous materials have drawn great attention and interest in material science and industry for the last several decades (since 1990s) due to their high potential in various applications, such as template making, catalysis, molecular separation, electronics, adsorption technology, gas sensors, and above all provoking new challenges in the research field such as drug-delivery or weaponry.

In this project we wanted to synthesize mesoporous carbon/silicon oxide nanocomposites by the sol-gel process and apply that into formulation to study cooling performance.

The mesoporous form of material is a relatively new development in nanotechnology. In 1990, a Japanese research group first developed a technique to synthesize mesoporous nanoparticles (MSN). Later it was named MCM (Mobile Composition of Matter) by the Mobile Corporation Laboratories. In 1997, another research team at the University of California at Santa Barbara synthesized mesoporous silica and named it SBA-15 and SBA-16 (Santa Barbara Amorphous with pore size 4.6 to 30 nm, arranged in hexagonal array). Since then mesoporous silica has been growing fast to meet the escalating demand in various applications in medicines, biosensors, imaging and thermal energy storage.
The most common form of mesoporous silica is MCM-41$^{13}$ and SBA-15$^5$. In this project we tried to follow both techniques. We learned that MCM-41 comes in a regular arrangement of cylindrical mesopores with pore size 2 nm to 6.5 nm diameters, forming a one-dimensional pore system. It has distinct characteristics of pore distribution, large surface to pore volume ratio. The pore size or diameter can be finely tuned by reaction conditions and type of surfactant used. However, MCM-41 is not a stable material as it is made of poor degrees of cross-linking of silicates units.

To create porosity, we must use surfactants that form micelles in the synthesis process. These micelles are necessary because they form templates that develop mesoporous framework. Different types of mesoporous material would require different kinds of surfactants. For example, MCM-41 used CTAB (cetyltrimethylammoniumbromide), a quaternary ammonium surfactant, (Figure 6.1 left). In this experiment we used SDS (sodium dodecyl sulfate, Figure 6.1 right) and SDBS (sodium dodecyl benzene sulfonate, Figure 6.2 left). Figure 6.2 right shows a schematic diagram of a micelle of oil in aqueous suspension. Herein it displays how hydrophobic long hydrocarbon tail is spun inside and has interactions with oil (blue); however, the hydrophilic head group (red ball) comes on the surface in contact with water phase (pink). The same scenario happens when water and oil are immiscible. With the help of a surfactant, we can expect to have a better-dispersed emulsion.
Figure 6.1. Left: CTAB\[14\]; Right: SDS\[14\]

Figure 6.2. Left: SDBS\[14\]; Right: A schematic diagram of a lipid micelle\[14\]

Surfactants are substances that lower surface tension or the interfacial tension between two liquids, or between a liquid and a solid or gas. There are many kinds shown in Figure 6.3. Some common surfactants are Triton-X, which is neutral; SDS and SDBS are anionic, whereas CTAB is cationic. Surfactants can also be amphoteric (characteristics of zwitterion), as in phospholipids, where there is a phosphate anion and amine or ammonium cation, together make it zwitterionic. Also some surfactants are nonionic.

Figure 6.3 Different categories of surfactants with hydrophobic head and hydrophilic tail\[14\]

These surfactants can act differently under different circumstances. They may act like
detergents, wetting agents, emulsifiers, foaming agents, or most interestingly as dispersants. When a surfactant acts as detergent, its work ethic is fascinating. It is made up of a polar hydrophilic head group and a nonpolar hydrophobic long tail. Micelles are dynamic structures that are made up of these detergent molecules. These molecules dissolve in water. If the concentration can be kept slightly higher than a critical micelle concentration (CMC), the detergent aggregates and forms special rod-like structures called micelle. Often they group as a hexagonal array, like shown in Figure 6.4 below.

![Figure 6.4 A schematic diagram of Micelle Formation](image)

At first surfactants form rod-like micelles that eventually align into hexagonal arrays. When a silica species is added to the reaction, silica covers the rods of micelles. Next, silicon atoms are bridged by oxygen atoms, forming the siloxane bond (Si-O-Si) by the condensation of silanol groups. At the end, the organic templates become oxidized and disappear.
6.2 Synthesis Outline

We took a bottom-up approach (sol-gel technique), suggested by Dr. Lin from the Department of Chemistry at NIU, IL. The pathway used to create porous materials in this experiment followed a two-step sol-gel process, where hydrolysis followed by condensation took place. Polymerization is carried out in an aqueous solution by adding catalysis and a precursor/source of silica (TEOS – tetra ethyl ortho silicate or tetra ethoxy silane).

6.2.1 Sol-Gel Science

A sol-gel process involves the formation of sol (a stable suspensions of colloidal particles) and gel (a porous 3-dimensionally inter-connected solid network that expands in a stable fashion through a liquid medium, only limited by the size of the container). During the sol-gel process, the molecular weight of the oxide product constantly increased, eventually forming a high viscous gel. The first step for this method was selecting the right precursor for the wanted material.
6.2.2 General Trends of Sol-gel process

Tetraethyl ortho silicate (TEOS) first is hydrolyzed. Then alcohol condensation or water condensation takes place, followed by hydrolysis, shown in Figure 6.5.

![Figure 6.5 The general trend of sol-gel process](image)

6.2.3 Sol-Gel Chemistry

Acidic condition: Under the acidic condition, the first step is hydrolysis. This is a fast process. The second step is condensation. This is a slow process and is a rate-determining step.

Basic condition: Under the basic condition, the first step is hydrolysis. This is a slow process. The second step is condensation. This is a fast process.
6.2.3.1 Mechanism (Acidic Condition)

Acidic catalyzed hydrolysis mechanism is an SN2 type in nature. Here protonation of alkoxide makes the silicon atom a strong electrophile, leading to an attack of water molecules with its active site of the oxygen atom. Leaving groups are $H^+$ and ROH, resulting an O-Si-O, oxo-bridge (Siloxane bond). Figure 6.6 shows the reaction scheme for acid catalyzed hydrolysis and condensation of a silicon alkoxide precursor.

![Figure 6.6. The Hydrolysis of sol-gel process under acidic condition](image)

6.2.3.2 Mechanism (Basic Condition)

In a base catalyzed hydrolysis mechanism (Figure 6.7), a hydroxyl group (-OH ion) attacks the alkoxide. In the first step, a nucleophilic -OH anion comes from a water molecule. A hydroxyl anion then attacks the silicon atom. $S_{N}2$-Si reaction involves a replacement of an
alkoxy group (-OR) by a hydroxyl group (-OH).

Figure 6.7 The reaction scheme of a base catalyzed sol-gel reaction.

6.3 Synthesis Procedure

We prepared two sets of chemicals. They are described in Set I and Set II.

Set I: Prepare carbon source

In Set 1, we prepared a solvent by mixing 10 g water with 6.6 g ethanol and 1.0 g of 1 molar HCl. We weighed them in a small beaker over the balance and labeled it Solution 1. The beaker was covered and set over a magnetic stirrer for 10 minutes. After that we added 4.4 g of P123 and kept it over a magnetic stirrer for 1 hour. P123 is a carbon source.

Set II: Prepare silicon source

In Set 2, we mixed 20 g TEOS (Tetra Ethyl Ortho Silicate) and 6 g furfuryl alcohol in a beaker. We labeled the beaker Solution 2. We kept the mixture covered and set over a magnetic-
stirrer for 1 hour. TEOS is a silicon source. After 1 hour, we added Solution-2 into Solution-1, drop by drop.

Aging – We allowed the mixture to settle for 4 days (wrapped, undisturbed in a cabinet).

Curing – We dried the mixture in the hood at 90 °C for 3 days. After 3 days, black particles (monoliths) were observed.

Annealing - Next we annealed at 550°C for 5 hours in the tube oven in an argon atmosphere.

Product - Freshly obtained dark black product was used. We crushed the product in a mortar pestle to obtain a fine powder of mesoporous silica.

6.4 Formation of Mesoporous Silica/Carbon (MSC) Nanocomposites

Figure 6.8 A schematic route of formation Santa Barbara Amorphous (SBA)

To synthesize Mesoporous Silica-Carbon (MSC), we followed the similar route as shown in Figure 6.8.
**Carbon source (Surfactant)** – P123 (a tri-block polymer (ethylene glycol)-propylene glycol – ethylene glycol) – was comprised of two parts, a nonpolar hydrophobic tail and polar hydrophilic head turning toward the aqueous solution, enriching the surface and resulting in a reduction of surface or interface energy (thermodynamically favorable).

With the surfactants dissolving into a solvent making a solution, the surface energy of the solution decreased rapidly but linearly with a constant rise in concentration until it reached C.M.C. (critical micelle concentration). After that surface energy remained constant with a further increase in the surfactant concentration.

**Silicon source (Precursor)** – TEOS (Tetraethoxy silane, an organosilane)

It is the precursor that leads the reaction toward the formation of either colloidal particles or polymeric gels.

We also prepared other samples by the same formulation with higher factors (2, 3, 4 etc.). All samples were used for spectroscopy analysis: The ratio of TEOS/P123 = 5, 2.5, 1.25.
**Prepared Samples:** We attempted to prepare three sets of samples with different amount of carbon source. Figure 6.9 below shows three sets of samples prepared with 4.1g, 8.2g and 16.4g of P123 respectively.

![Three samples prepared in different ratio: a (left), b (middle) and c (right); Left: a - 4.1g P123; b - Middle: 8.2g P123; c - Right: Sample 16.4g P12](image)

Three samples were prepared with carbon to silicon ratio 1.02, 1.30 and 2.36 respectively.

<table>
<thead>
<tr>
<th>Ratio of TEOS/P123</th>
<th>1.25</th>
<th>2.5</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ratio of C/Si</td>
<td>1.02</td>
<td>1.30</td>
<td>2.36</td>
</tr>
</tbody>
</table>

**6.5 Characterization of Mesoporous Silica-Carbon (MSC)**

**6.5.1 SEM (Morphology Study)**
We like to compare our result obtained from SEM with the similar result from literature. Figure 6.11 below is expected mesoporous silica obtained from the literature where we notice clear porosity. From our experimental result we saw porous structure developed in Figure 6.10 bottom right, but not so clearly observed. This is due to the difference in resolution between two SEM machines. Figure 6.10 top right looks a little granular. Experimental morphology of MSC in Figure 6.10 bottom right is similar to that of expected one in Figure 6.11. Ours was densely populated.
6.5.2 FTIR Study of Mesoporous Silica-Carbon (MSC):

Figure 6.12: Experimental FTIR of MSC
In Figure 6.12, the experimental FTIR found the functionality of mesoporous silica-carbon (MSC) with an absorption peak at 1080 cm\(^{-1}\). Literature on the IR spectrum (Figure 6.13) verifies the MSC’s functionality. The absorption band in the range of 1000-1080 cm\(^{-1}\) relates to the Si-O-Si stretching mode from the literature. We also found the Si-O-Si stretching mode in the same region in our experimental study (Figure 6.13). Therefore, we can say for sure our work gives the right MSC product.
6.5.3 X-Ray Diffraction (XRD) Study:

![X-ray Diffraction](image)

Figure 6.14. Left: Experimental result of XRD; Right: Literature value of XRD

The XRD results (Figure 6.14 left) tell us that the MSC obtained is amorphous in nature. The broad reflections at 2θ position ~23 and 43 can be assigned to the amorphous carbon for fresh mesoporous silica, as found in the literature (see Figure 6.14 right). Its peak at 400 corresponds to the unit lattice plane (111).
6.5.4 Heat Dissipation Study Of Mesoporous Silica/Carbon (MSC) Nanocomposite

A cooling device built in the lab determined the cooling efficiency. The data was recorded and stored by the cooling monitor. The result is tabulated in the Table 6.2 and displayed in Figure 6.15.

Table 6.2 Three Samples of silica/carbon nanocomposites with cooling performance

<table>
<thead>
<tr>
<th>Ratio</th>
<th>1.25</th>
<th>2.5</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔT (°C)</td>
<td>26</td>
<td>26.3</td>
<td>27.5</td>
</tr>
</tbody>
</table>
Our heat dissipation study of three samples with silica to carbon ratios of 1.25, 2.5 and 5 gives the equilibrium temperatures of 26\(^0\)C, 26.3\(^0\)C and 27.5\(^0\)C, respectively. As the ratio of TEOS to P123 increased, the equilibrium temperature increased, so the block temperature difference between the control and sample increased, even with small differences, as shown in Table 6.2. Thus, lower the ratio, the better the cooling performance is for silica/carbon nanocomposites.

6.6 Conclusion

A facile method has been developed using a sol-gel technique to synthesize mesoporous carbon/silicon oxide based nanocomposites. We used a P-123 [poly(ethylene glycol)-block-poly(propylene glycol)-block-poly (ethylene glycol)] as an organic surfactant and TEOS (tetra ethoxy silane) as an inorganic precursor to form inorganic/organic mesoporous composites. XRD indicated the nanocomposites found are amorphous in nature. The morphology study shows porous formation of silica. A silicate framework (Si-O-Si bond) was also confirmed by the FT-IR study.

6.7 Application:

Mesoporous Silica-Carbon (MSC) can be used in a wide field of study. Some of them are listed below:

*Catalysis – MSC is heavily used as a catalysis due to its large surface (7700m\(^2\)/g) and pore volume (up to 70%).

Drug delivery and bio-sensing application - Due to porosity, the biocompatibility of materials
with a high surface area and pore volume can be carried by MSC to transport to the right organ or cells.

*Template* – Mesostructured silica materials can serve as templates due to their controlled morphology, pore size, ordered pore structure, high surface area and large pore volume. Ex – mesoporous carbon can be obtained for use as electrodes for electrochemical capacitors, using the above template.

*Electronics/Gas Sensor* – Cube like mesoporous silica film can improve the characteristics of surface photo voltage (SPV) sensors due to the physical adsorption of the target gas nitric oxide (NO) or nitrogen dioxide (NO₂) into the mesoporous layer, which works as an insulator layer in metal-insulator semiconductor (MIS) devices.

*Current Application* – Mesoporous silica-carbon constantly challenges the material science research field. In this research, we like to explore application of MSC nanocomposites into polymer coating.

**Part II: Measurement of Heat Dissipation Using Mesoporous Silica-Carbon Nanocoating**

Heat dissipation coating is fabricated to transfer excess heat away from the substrate it is applied to. By removing this heat, we can improve a substrate’s thermal efficiency, which allows increased protection and longevity. By lowering heat transfer, we can reduce the operating temperature. This feature offers more efficiency and performance gain of the components that need to dissipate the rapid growth of heat, such as computers, cell phones, watches, automobile
engines, radiators, transmission coolers, etc. Table 6.3 below gives a list of the chemicals used in our formulation and their functionalities/purpose:

Table 6.3: Chemicals used in our MSC formulation and their functionalities

<table>
<thead>
<tr>
<th>Chemicals Needed for Formulations</th>
<th>Functionalities</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cymel 303, 385</td>
<td>High viscous cross linker (nitrogenous)</td>
</tr>
<tr>
<td>Neocryl A 6085</td>
<td>Water based polymer</td>
</tr>
<tr>
<td>SDBS</td>
<td>Surfactant (Dispersant)</td>
</tr>
<tr>
<td>Q2 – 5211</td>
<td>Additive</td>
</tr>
<tr>
<td>TS – 100</td>
<td>Filler to avoid bubbles on the Q-panel while spraying</td>
</tr>
<tr>
<td>Mercapto</td>
<td>Helps with surface adhesion with metal</td>
</tr>
<tr>
<td>BYK 348</td>
<td>Surfactant</td>
</tr>
<tr>
<td>Tego</td>
<td>Defoaming agent</td>
</tr>
<tr>
<td>DSX 1550</td>
<td>To make the coating more viscous/sticky (Thickener)</td>
</tr>
<tr>
<td>DPnB</td>
<td>(Di-propylene glycol butyl ether) – works as solvent with water</td>
</tr>
<tr>
<td>ZnO</td>
<td>Helps to get good radiation</td>
</tr>
<tr>
<td>HBN</td>
<td>Allows to dissipate heat more</td>
</tr>
<tr>
<td>R 706 (TiO2)</td>
<td>Conductive, corrosion inhibitor</td>
</tr>
</tbody>
</table>
**Procedure:**

**Part-1 (Make nanomaterial dispersion):**

In a small glass beaker, 15g of Water, 0.5g of SDBS, 0.1g of ZnO and 0.225g white mesoporous silica (MS) were measured.

Using a needle sonicator at the maximum level (10), sonicate water and SDBS first for 5 minutes to get the matrix ready. Then add the nanomaterials a little at a time to better disperse. Sonicate for 10 minutes more until uniform dispersion is achieved.

**Part-2 (Prepare polymer binder or carrier):**

In a large plastic beaker, 22g of Neocryl A-6085, 1.75g of Cymel 303, 0.15g of Q2-5211, 1.5g of TS-100 were measured. They were grind with metal beads by a mechanical grinder at pressure 70 psi for 15-20 minutes. This helps to break down bigger particles into smaller. Part-1 was then added into Part-2. Grinding was continued for further 20 minutes.

**Part-3 (Prepare solvent):**

In a beaker 5.65g of Water and 4.75g of DPnB were measured. They were stirred with a small magnetic stir bar, keeping over an electrical magnetic stirrer for 10 minutes. Part-3 was then added into Part-2. Grinding process was further continued together (Part-1 + Part-2 + Part-3) for additional 30 minutes.

**Part-4 (Additives):**

The following additives were added drop-wise into the above mixture (Part-1 + Part-2 + Part-3):

- Mercapto – 25 drops
- BYK 348 – 2 drops
- Tego – 4-5 drops
- DSX 1550 – 2-4 drops
Grinding was continued for additional 30 minutes. Next, strain and store the above prepared formulation in a plastic container with a lid. Table 6.4 below shows the collected data using meso carbon/SiO2 under a cooling monitor with different formulations.

Table 6.4 Mesoporous Carbon/Silica Formulations for heat dissipation study on cooling monitor

<table>
<thead>
<tr>
<th>Different polymer based Nanocoating with Meso SiO₂</th>
<th>Input voltage (V)</th>
<th>Input Current (Amp)</th>
<th>Al Q-panel (sample coated) Tc (°C)</th>
<th>Input Watt (W)</th>
<th>Al Q-panel (not coated) T (°C)</th>
<th>ΔT = T-Tc (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20120606-Zno-white meso SiO₂-65µm, SDBS, cymel-303, Neocryl A-6085</td>
<td>56.57</td>
<td>0.39</td>
<td>100.4</td>
<td>21.92</td>
<td>126.30</td>
<td><strong>25.90</strong></td>
</tr>
<tr>
<td>20120607-Zno-white meso SiO₂-60µm, SDBS, cymel-385, Neocryl A-6085</td>
<td>56.68</td>
<td>0.39</td>
<td>102.3</td>
<td>22.1</td>
<td>127.05</td>
<td><strong>24.75</strong></td>
</tr>
<tr>
<td>20120611-Zno-white meso SiO₂-50µm, SDBS, cymel-385, Neocryl A-6102</td>
<td>56.14</td>
<td>0.40</td>
<td>103.3</td>
<td>22.31</td>
<td>127.85</td>
<td><strong>24.55</strong></td>
</tr>
<tr>
<td>20120615-No ZnO-white meso SiO₂-50µm, SDBS, cymel-385, Neocryl A-6085</td>
<td>56.84</td>
<td>0.39</td>
<td>103.10</td>
<td>22.10</td>
<td>127.03</td>
<td><strong>23.93</strong></td>
</tr>
<tr>
<td>20120618-ZnO-Cymel-385, Neocryl A-6085-60µm, No SDBS, No white meso SiO₂</td>
<td>57.10</td>
<td>0.39</td>
<td>102.80</td>
<td>22.14</td>
<td>127.19</td>
<td><strong>24.39</strong></td>
</tr>
</tbody>
</table>
Note: Mesoporous SiO$_2$ shows a better cooling efficiency with a thickness of 65 µm, formulated with Neocryl A-6085 as a polymer, cymel-303 as a cross linker, SDBS as a surfactant, and Zinc oxide as a nanomaterial.

**Heat Dissipation**

**Graphical representation of mesoporous silica with different strength of cross linkers (Cymel 303 and Cymel 385):** shown in Figure 6.16 below

![Figure 6.16. Thermal performance for two type of cross linkers](image)
Figure 6.17 shows the transparent Q-panel after spraying, since there is no white HBN. Here discoloration starts at 330°C within the first 2 minutes during annealing with white ZnO and AC 2403 but no SDBS nor HBN in the formulation. During high temperature annealing, the color change occurs when our formulation does not have any HBN or SDBS.

Conclusion

Heat dissipation was successfully measured. Our data show that mesoporous carbon/silica nanomaterials possess good cooling efficiency when incorporated with ZnO, SDBS, Cymel 303 and Neocryl A-6085, and at a thickness of 65 µm, it shows higher efficiency. Our formulation can be used for industrial use.
Part III: Molecular Fan, Heat Dissipation and Application of Nanocoating Heat Management-Molecular Fan

Heat management is a consistent rising problem as the technology is becoming smaller and smaller. Molecular fan is an application of a thin-layered nanocoating for heat sinks to enhance the cooling effect and thereby reduce the excess heat produced during the operation of a system.

Molecular Fan-Experimental

Different carbon products like carbon nanotube (CNT), carbon black, nano-diamond powder (NDP), graphene or non-carbon products like hexagonal boron nitride (HBN) can be dispersed in an acrylate resin, and the resulting nanocomposite can be coated on a blank aluminum panel. Next, the cooling effect of the molecular fan is studied with an appropriate temperature monitoring system. We collected data from the average of the last 30 minutes run out of 5000, compared the heat measurement with a blank sample, and observed the heat difference with multiple samples.
Table 6.5 Temperature difference data between the coated and uncoated Al-panel with various nanomaterials measured by radiator cooler:

<table>
<thead>
<tr>
<th>Different Nano Materials</th>
<th>Sample - Temp for Q-Panel with coating (°C)</th>
<th>Control - Temp for Q-Panel without coating (°C)</th>
<th>ΔT (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R706 (TiO₂) -30 µm (8/16/2012)</td>
<td>108.8</td>
<td>134.19</td>
<td>25.39</td>
</tr>
<tr>
<td>CNT-30 µm (8/23/2013)</td>
<td>103.6</td>
<td>131.61</td>
<td>28.01</td>
</tr>
<tr>
<td>Graphene (8/2/2012)</td>
<td>105.2</td>
<td>131.64</td>
<td>26.44</td>
</tr>
<tr>
<td>White-BaSO₄ -30 µm (10/11/2012)</td>
<td>107.1</td>
<td>133.63</td>
<td>26.53</td>
</tr>
</tbody>
</table>

Note: From the tabulated data in the Table 6.5, Carbon nanotubes show a higher Cooling Efficiency at 30µm thickness.

Table 6.6 Cooling Efficiency with hexagonal boron nitride, with and without the Presence of thickener DSX:

<table>
<thead>
<tr>
<th>Nano materials</th>
<th>Input (V)</th>
<th>Input (A)</th>
<th>T1 for Sample (°C)</th>
<th>Input Watt (W)</th>
<th>T1 for Q-Panel (°C)</th>
<th>ΔT (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO, HBN, Cymel - 385-70 µm (6/23/2013)</td>
<td>57.39</td>
<td>0.39</td>
<td>103.2</td>
<td>22.47</td>
<td>128.46</td>
<td>25.26</td>
</tr>
<tr>
<td>ZnO, HBN, Cymel- 385-70 µm -3 (6/23/2012)</td>
<td>56.88</td>
<td>0.39</td>
<td>103.2</td>
<td>22.16</td>
<td>127.27</td>
<td>24.07</td>
</tr>
<tr>
<td>ZnO, HBN, Cymel- 385, no DSX (6/27/2012)</td>
<td>57.43</td>
<td>0.39</td>
<td>105.9</td>
<td>22.33</td>
<td>127.92</td>
<td>22.02</td>
</tr>
</tbody>
</table>
Note: ZnO and HBN when treated with Cymel 385 show decent cooling efficiency at a 70 µm thickness.

Table 6.7 Cooling efficiencies of various combinations of MSC nanoparticles at different thickness.

<table>
<thead>
<tr>
<th>Nanomaterials</th>
<th>Input Volt (V)</th>
<th>Input Current (A)</th>
<th>T1 for sample (°C)</th>
<th>Input Watt (W)</th>
<th>T1 for Q-Panel (°C)</th>
<th>ΔT (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RC (ZnO, HBN, R706)-white-40um (8/9/2012)</td>
<td>57.69</td>
<td>0.39</td>
<td>104.5</td>
<td>22.52</td>
<td>128.67</td>
<td>24.17</td>
</tr>
<tr>
<td>RC-white-1-25um (8/16/2012)</td>
<td>58.53</td>
<td>0.40</td>
<td>109.1</td>
<td>23.29</td>
<td>131.64</td>
<td>22.54</td>
</tr>
<tr>
<td>RC-white-1-40um (8/16/2012)</td>
<td>59.56</td>
<td>0.41</td>
<td>112.7</td>
<td>24.25</td>
<td>135.29</td>
<td>22.59</td>
</tr>
<tr>
<td>RC-black-1-60um (8/19/2012)</td>
<td>60.48</td>
<td>0.41</td>
<td>108.5</td>
<td>24.60</td>
<td>136.64</td>
<td>28.14</td>
</tr>
<tr>
<td>RC-white-4-10g-30um (8/16/2012)</td>
<td>59.70</td>
<td>0.40</td>
<td>108.80</td>
<td>23.96</td>
<td>134.19</td>
<td>25.39</td>
</tr>
<tr>
<td>RC-ZnO-5% ISPR-55um (9/5/2012)</td>
<td>58.57</td>
<td>0.40</td>
<td>106.1</td>
<td>23.28</td>
<td>131.06</td>
<td>24.96</td>
</tr>
</tbody>
</table>

The above Table 6.7 tabulates the cooling efficiency of various combinations of MSC nanoparticles at different thickness. Row six shows the result using 5% In-Situ Phosphatizing Reagent (ISPR).

Note: Among all the above combination of nanomaterials, RC-black exhibited the highest cooling efficiency at 60 µm thickness.

Conclusion

Molecular fan is an excellent nanoscale thermal technique to dissipate heat. A thin film of a variety of nanomaterial coatings can be successfully used for molecular fan. A graphene based molecular fan showed best cooling effect; however, a carbon
nanotube showed a higher cooling efficiency at 30µm thickness. Our heat dissipation technique surely can help to cool down any kind of today’s technology – small or large.
6.8 References


Chapter 7
Conclusion and Future Work

7.1 Conclusion

We have studied and provided a wide view of nanomaterials, how to handle and how to use them to prepare coatings for various purposes such as heat dissipation and corrosion protection. We are currently in the process of learning about corrosion protective coating for hot spring water carrier metals and their alloys and UV shielding coating as well.

We have developed facile methods of synthesizing new nanomaterials that exhibit good mechanical and optical properties. We have successfully synthesized porous materials like mesoporous silica. We were also able to synthesize zinc oxide based nanomaterials with dopants such copper and silver. Each of them was characterized to understand its properties and incorporated into an emulsion coating to study the molecular fan effect and observe thermal performance.

We used knowledge of previous research in our group to develop coatings for corrosion inhibition on magnesium alloys (AZ91) and heat dissipative coating for heat sinks (P-48[6]). We explored each field with various aspects at a length and with great details. Our results were quite successful, and we were able to apply them in real world applications (3C industries) according to industry standards. Each work is individually explained with full details in the previous chapters in this dissertation. We are looking forward to progressing in our future work.
7.2 Future Work

7.2.1 Hot Spring Water Corrosion Project

This project is an extension of a corrosion inhibition project that was described in Chapter 3. In this project we wanted to use the experience from Chapter 3 and apply that to develop an appropriate corrosion protective layer for metal alloys that carry hot spring water. Special care and caution are needed for carrying hot water with a content of sulfur. In our lab, we did some preliminary work by mimicking hot water in a flask and refluxing our coated metal substrates for different lengths of time (30 minutes, 1 hour, 2 hours …10 hours) in a 5% sulfuric acid solution at 60\(^\circ\)C. We were quite successful with our initial attempt. Now we want to extend our work on a bigger project in this field following industry standards.

7.2.2 UV and NIR Cut Coating

In the near future, we want to study optically transparent ultraviolet (UV) and near infrared (NIR) light cut coating for solar control application. Some UV cut coating research was performed earlier. We have formulated UV shielding coatings using zinc oxide (ZnO) and titanium oxide (TiO\(_2\)) nanoparticles fillers that showed about 60-70% UV absorption and visible transparency each. In this project, we used NIR absorbing Cs\(_x\)WO\(_3\) nanorods with uniform particle size distribution that was synthesized by our group. We wanted to further extend our work by employing different resins and different amount of nanomaterials to achieve better performance. Our goal is to achieve a 90% UV absorption and visible transparency.
7.2.3 6% CNT emulsion coating

Making a 6% CNT emulsion coating is challenging, as the stoichiometric amount of CNT needs to be uniformly dispersed minimally as 5 ml of solvent and incorporate that into an emulsion coating to achieve a steady colloidal suspension. We initiated this project but have not made much progress yet. We want to explore a new area in nanocoating application with a 6% CNT.