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Uses of

Nanotechnology

on Surfaces for **Military Applications**

State of the Art Report

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State of the Art Report (SOAR)

Uses of Nanotechnology on Surfaces for Military Applications

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Mr. Nichols is the Scientific and Technical Advisor for the Homeland Defense and Security Information Analysis Center (HDIAC). Previously, he conducted applied health research for approximately seven years at ORAU in Oak Ridge, Tennessee, and also founded the Nanotechnology Studies Program, which evaluates the public health impacts of nanotechnology. Prior to working at ORAU, Nichols spent 10 years in various healthcare roles, including five years as a Hospital Corpsman in the U.S. Navy. He has published and presented on a variety of topics in the areas of emerging technologies, nanotechnology, public health, and risk assessment. Mr. Nichols is a member of the American Public Health Association and serves on the editorial board of Nano Research and Applications. His research primarily focuses on the impact of emerging technologies and advanced materials on public health. He has a bachelor's degree in philosophy and a Master of Public Health degree from the University of Tennessee and holds the Certified in Public Health credential.

Jason Davis, PhD

Dr. Davis is a health physicist at ORAU, where he supports dose reconstruction activities for the Energy Employees Occupational Illness Compensation Policy Act (EEOICPA) Program. He began his Health Physics career at Bechtel Nevada in 2003, where he analyzed worker dosimetry records in support of The EEOICPA Program He completed a bachelor's degree in Health Physics in May, 2005. In 2008, he transferred to the Nevada Test Site and began working as a radiological engineer, conducting data analysis and preparing procedures and reports to ensure compliance with federal, state, and local regulations. During this time, he maintained his graduate studies and graduated with a master's degree in Health Physics in May 2008. Since joining ORAU in 2009, Dr. Davis has supported the EEOICPA Program, which provides compensation for former workers who have developed cancer related to their work in the Manhattan Project. In addition, he has served as the subject matter expert for the Nuclear Regulatory Commission Annual Effluent Data report and as a quality reviewer for Defense Threat Reduction Agency/ Nuclear Test Personnel Review dose assessments. Dr. Davis has also lectured in and assisted in the development of technical health physics courses as part of the ORAU Professional Training Program. During his tenure at ORAU, he was awarded a PhD in Applied Health Physics in May 2014, and attained certification by the American Academy of Health Physics in November 2014.

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Mr. Ramsburg serves as Program Manager at the West Virginia University Innovation Corporation. He earned a bachelor's degree in electrical engineering from West Virginia University and an MBA from Duke University. His 20-year career has given him an extensive background in technology start-ups and high-tech small businesses. Mr. Ramsburg led the development of a multi-million dollar intellectual property portfolio for a start-up company in Virginia before returning to West Virginia to manage government contract research and development programs for various federal agencies, including the U.S. Department of Defense, the U.S. Department of Justice, and the U.S. Department of Homeland Security

Technical review was provided by **Dr. John Rumble,** president of R&R Data Services.

Acronyms and Abbreviations

APS ... Air plasma spray
ATPD ... Armor transparent purchase description
BC ... Bacterial cellulose
CA ... Contact Angle
CBRN ... Chemical/Biological/Radiation/Nuclear
CNT ... Carbon nanotube
DoD ... Department of Defense
DOE ... Department of Energy
D. tertiolecta ... Dunaliella tertiolecta
E. coli ... Escherichia coli
EBPVD ... Electron beam physical vapor deposition
ENM ... Engineered nanomaterials
HDIAC ... Homeland Defense and Security Information Analysis Center
HVAF ... High velocity oxy-fuel
HVOF ... High velocity air fuel
IR ... Infrared
LLDPE ... Linear low-density polyethylene
mm ... Millimeter
MRSA ... Methicillin-resistant staphylococcus aureus
MSZ ... Magnesia-stabilized zirconia
MWCNT ... Multi-walled carbon nanotube
nEM ... Nanoenergetic materials
NIR ... Near infrared
nm ... nanometer
NNI ... National Nanotechnology Initiative
PAN ... Polyacrylonitrile
PDA ... Polydopamine
PET ... Polyethylene terephthalate
PMC ... Polymer-matrix-composite
PP ... Pristine polypropylene
PVD ... Physical vapor deposition
R&D ... Research and Development
RAM ... Radar absorbing material
RFID ... Radio frequency identification
S. aureus ... Staphylococcus aureus
SOAR ... State-of-the-art Report
SWCNT ... Single-walled carbon nanotube
TBC ... Thermal barrier coating
UHMWPE ... Ultrahigh molecular weight polyethylene
UV ... Ultraviolet
UVP ... Ultraviolet protective factor
YSZ ... Yttria-stabilized zirconia

Elements/Alloys

Ag	Silver
$Ag_2M_oO_4$	Silver molybdate
AgNP	Silver nanoparticle
Al	Aluminum
Al_2O_3	Aluminum oxide
Al-NPs	Aluminum particles
Bi-YIG	Yttrium-iron garnet
CO_2	Carbon dioxide
CeO_2	Ceria
Cu	Copper
CuO	Copper oxide
H_2O_2	Hydrogen peroxide
H_2S	Dihydrogen monosulfide
H_2ZrF6	Hexafluorozirconic acid
$Ca_{10}(PO_4)6(OH)_2$	Hydroxyapatite
Fe_3O_4	Iron Oxide
MgO	Magnesium oxide
MoO_2	Molybdenum oxide
MoO_3	Molybdenum trioxide
MoS_2	Molybdenum disulfide
MSZ	magnesia-stabilized zirconia
Nb_2O_5	Niobium oxide
Ni	Nickel
NO_x	Nitrogen oxides
PBO	p-phenylene-2-2-benzobisoxazole
PIPD	polypyridobisimidazole
PMMA	Polymethyl methacrylate
SiO_2	Silicon dioxide
SO_2	Sulphur dioxide
Ti	Titanium
TiO_2	Titanium dioxide
YIG	Yttrium-iron garnet
ZnO	Zinc Oxide
Zr	Zirconium

Executive Summary

Nanotechnology is the manipulation of matter at an atomic level to produce new materials, referred to as engineered nanomaterials. Particles at this scale typically range in sizes from 1 to 100 nanometers (nm) in at least one dimension. A nm is one-billionth of a meter. To put this into perspective, DNA is 2 nm wide, and a human hair is approximately 50,000 nm wide. At this scale, the physicochemical properties of particles behave very differently than larger particles of similar composition. The characteristics of these particles make them highly desirable for certain applications. One of the most exciting developments of engineered nanomaterials is in surfaces used for military purposes.

The Department of Defense (DoD) is scheduled to spend more than $130 million on nanotechnology research in Fiscal Year (FY) 2017. The National Nanotechnology Initiative (NNI), a major federal nanotechnology research initiative, directly supports eight DoD research and development (R&D) organizations. The DoD has been a member of the NNI since its inception in 2000; however, the state of nanotechnology and its incorporation into defense strategy has changed over the past 16 years. Although the majority of nanotechnology research is still many years away from being commercialized for practical use, some current applications of engineered nanomaterials and some late-stage research show promise for enhancing the performance of military products.

Because surfaces almost exclusively dictate the functionality of an object and often can be modified with great success, nanotechnology and nanomaterials are increasingly important to the military. This state of the art report (SOAR) provides the DoD with an overview of some of the most promising new- and close-to-market nanotechnologies with military applications, along with a compendium of practical knowledge that can be used to develop a research strategy and streamline acquisition of new nanotechnologies and materials.

Three distinct categories of nanotechnology surface applications became clear during the research phase of this report, and the SOAR is organized around these categories: hard surfaces, soft surfaces, and nondurable goods.

- **Hard surfaces** refer to the outer portion of an object that is not normally pliable, such as the outside of vehicles, planes, ships, and weaponry. A significant amount of research and practical applications in this area have been related to developments in nanoceramics. Specialized coatings, such as superhydrophobics (water-repellent and self-cleaning) and anti-corrosives (prevention of weathering or decay) are desirable attributes for these surfaces.
- **Soft surfaces** generally refer to textiles, but also include hard and soft body armor. Major areas of research in this area focus on the development of smart fabrics that respond to the wearer's environment and on functionalization to make textiles flame resistant or capable of fighting microbial growth.
- **Nondurable goods** are applications that have short shelf-lives or require a significant amount of maintenance. Some applications in this area include biomedical products, such as bandages coated with nanoscale silver, and advanced lubricants for heavy machinery.

The information in this report generally applies to currently available products or late-stage research with the potential for commercialization within the next one to two years. In some cases, discussion regarding more advanced research that could be more than five years on the horizon is included to help frame the direction in which R&D appears to be heading.

The majority of research in this report was retrieved from a thorough search on relevant literature published over the past three years. An initial search retrieved more than 1,200 articles. The authors reviewed the list and selected the most appropriate literature for the topic. Subject matter experts were consulted regarding research and applications of nanotechnology for surfaces. In addition to the authors, information was solicited from Oak Ridge Associated Universities (ORAU), a 121-member university consortium based in Oak Ridge, Tennessee, and open source data from other institutions conducting nanotechnology research. Appendices A and B contain all of the information gathered from these sources.

1. Introduction

1.1 Overview

Nanotechnology is the manipulation of matter on a scale of 1 to 100 nanometers (nm) in at least one dimension to create new structures and materials. These structures and materials are referred to as engineered nanomaterials (ENMs), because they are manufactured or altered in some way and do not typically exist in this form in nature. Nanotechnology is an emerging technology; therefore, much of the field currently operates in a research and development (R&D) environment in academia, government, and industry. However, as the consistency and scalability of nanotechnology research becomes more practical and reliable, the number of products benefiting the Department of Defense (DoD) and warfighters is increasing.

The DoD has been actively engaged in nanotechnology R&D since the National Nanotechnology Initiative (NNI) was founded in 2000 by the federal government. The NNI is a U.S. government R&D initiative involving 20 departments and independent agencies working together toward the shared vision of "a future in which the ability to understand and control matter at the nanoscale leads to a revolution in technology and industry that benefits society."[1] Funding support for nanotechnology R&D stems directly from NNI member agencies, and the NNI informs and influences the federal budget and planning processes through its member agencies. Cumulatively, NNI member agencies have spent nearly $24 billion since the inception of the NNI.[2] The proposed NNI budget for Fiscal Year (FY) 2017 is $1.4 billion, of which $131.3 million is slated for the DoD, representing a nearly 2% decrease from FY 2016.[3] Currently, eight DoD R&D organizations are directly funded to support basic and applied nanotechnology research (See Figure 1).

Each year the Homeland Defense and Security Information Analysis Center (HDIAC) develops state of the art reports (SOARs) on relevant and key topics for the DoD. One of the most relevant topics in the past 20 years has been nanotechnology, and this year, a primary focus is surface applications of nanotechnology. Figure 2 provides an overview of how nanotechnology surface applications can be applied to HDIAC's eight core areas. These applications range from coatings to textiles.

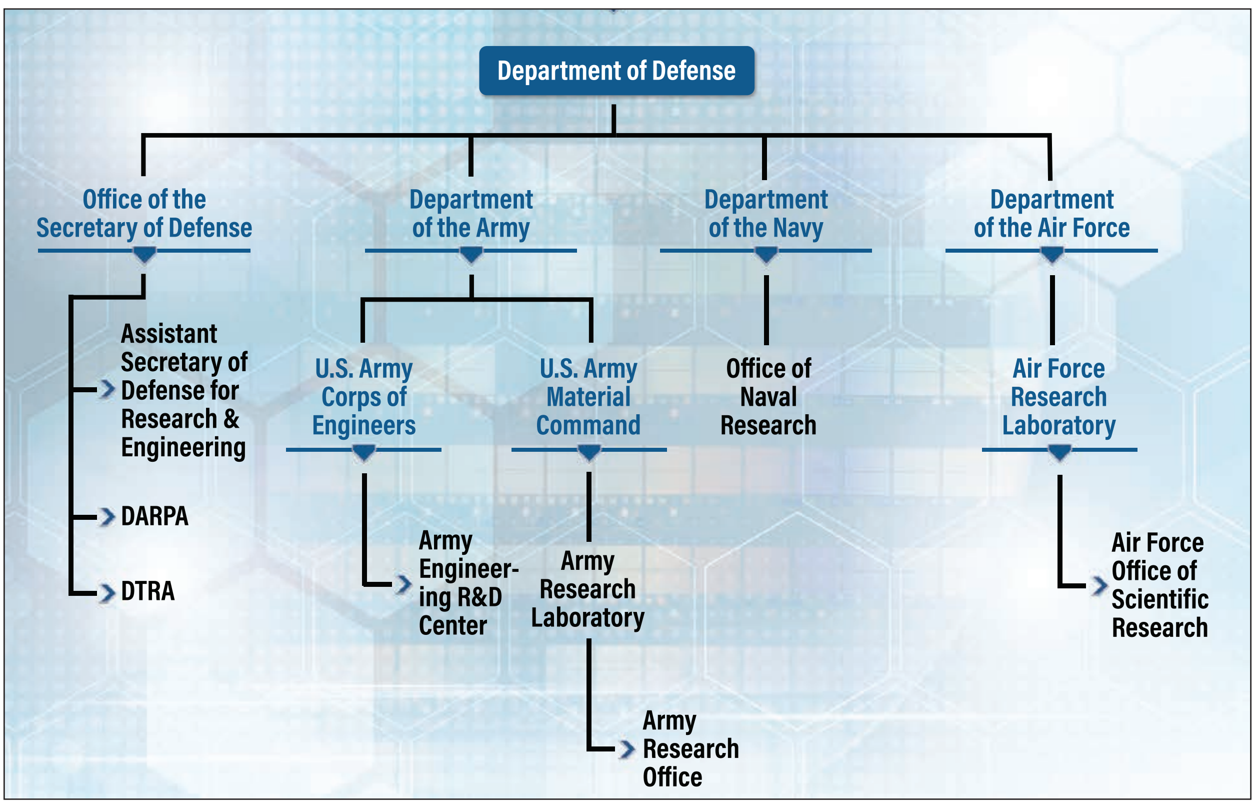

Figure 1: *DoD agencies that receive funding from the National Nanotechnology Initiative (in black).*

Alt. Energy	Biometrics	CBRN	CIP	Cultural Studies	HDS	Medical	WMD
• Fibers for power generation & storage • Smart fabrics	• Tattoos • Second-Skin	• Integrated sensors • Protective linings • Radiation resistant coatings	• Anticorrosive coatings • Radiation resistant coatings	• Smart textile fashion • Wearability	• Flame retardant coatings • Body armor • Radar absorbing materials	• Antimicrobial coatings • Wound dressing	• Protective linings • Radiation resistant surfaces

Figure 2: *Surface applications of nanotechnology in HDIAC's eight focus areas*

This report provides up-to-date information on some of the most exciting and anticipated uses of nanotechnology. The modification of surfaces is fundamental to engineering and technological innovation, because almost everything about a product or device can be affected by its surface functionality and interaction with the environment.

1.2 Methodology

The literature search and review for this SOAR encompassed a universe of thought revolving around practical concepts, methodologies, and products using engineered nanomaterials and nanotechnology techniques for surface applications that have direct relevance to military and defense practices. It is an overview of what is currently possible in regard to engineered nanomaterials and surfaces and is based on knowledge from subject matter experts, data from peer-reviewed literature, and other sources, including websites of reputable institutions and government agencies conducting nanotechnology research.

Because nanotechnology is a very broad and emerging field, certain parameters were established in order to provide the most relevant, up-to-date, and pragmatic information. The report focuses on methodologies and products developed and used within the past three years and research that may be commercialized or used on some practical level in the next one to two years. Where appropriate, less mature technologies or promising research is discussed to provide a glimpse of what may be on the horizon. The information is intended to describe the nanotechnology surface applications which are, or soon will be, available to enhance products used by the military. A fundamental understanding of nanotechnology will be beneficial to the reader.

Relevant peer-reviewed articles were identified by searching for specific keywords in the HDIAC database, to include:

- Engineered nanomaterials
- Surfaces
- Surface applications
- Coatings
- Textiles
- Nanocomposites
- Nanopolymers
- Nanoceramics

In addition, the literature search was limited to articles published in 2013 through 2016. Initially, more than 1,200 articles were identified. From this list, only the most relevant were retrieved and reviewed. In addition, websites of relevant institutions conducting research in the area of nanotechnology surface applications were reviewed for applicable research. These sites included:

- **Institute for Soldier Nanotechnologies**
- **Naval Research Laboratory/Institute for Nanoscience**
- **U.S. Air Force Research Laboratory**
- **U.S. Army Research Laboratory**
- **U.S. Army Corps of Engineers Engineer Research and Development Center**
- **Defense Advanced Research Projects Agency**
- **U.S. Department of Energy Nanoscale Research Centers**
    - Center for Functional Nanomaterials
    - Center for Integrated Nanotechnologies
    - Center for Nanophase Materials Sciences
    - Center for Nanoscale Materials
    - Molecular Foundry
- **International Institute for Nanotechnology at Northwestern University**

- **Manufacturing Innovation Institutes**
    - Advanced Functional Fabrics of America
    - Institute for Advanced Composites Manufacturing Innovation
    - Lightweight Innovations for Tomorrow
- **Intelligence Advanced Research Projects Activity**

A summary of the relevant research for surface applications being conducted at these institutions can be found in Appendix A.

HDIAC also collaborated with the University Partnerships Office at Oak Ridge Associated Universities (ORAU), which manages a university consortium of 121 PhD-granting institutions across the United States and in the United Kingdom. Six ORAU member universities provided research information relevant to this report (See Appendix B).

1.3 Structure of the Report

The information in this report is organized by types of nanotechnology surfaces applications for practical military use and is not meant to include all nanotechnology-enhanced surface applications. The three major functional areas are:

- **Hard surfaces** – Includes any surface consistent with weapons, vehicles (e.g., tanks), ships, and aircraft. Components of the surfaces including the base material used (i.e., nanoscale metals or nanoceramics) and surface modifications involving engineered nanomaterials.
- **Soft surfaces** – Includes surfaces consistent with the coverings of textiles, to include clothing, fabrics, smart textiles, and body armor.
- **Nondurable goods** – Includes other materials that can be applied to a surface and may affect the properties of surfaces, such as lubricants or coatings that require significant maintenance and have applications to military vehicles and operations.

The arrangement of this report centers on functionality; therefore, certain terms may appear in multiple sections, such as superhydrophobic coatings, and will be described as they apply to their respective uses or sections. This is because hard and soft surfaces rely on different techniques and contain different materials that affect the properties of coatings on their surfaces in unique ways. Nondurable goods are considered a separate section, because they may or may not be relevant to hard and/or soft surfaces and may have an expiration date when they lose effectiveness.

2. Hard Surfaces

The application of nanomaterials in hard surfaces has resulted in many benefits, such as adding new characteristics to the surface, improving physical properties of the surface, and functionalizing the surface. Hard surfaces refers to the outer portion of an object that is not normally pliable, such as the outside of vehicles, planes, ships, and weaponry. The following sections discuss some current and potential applications of various nanomaterial technologies. Some of these applications have reached maturity and many more are nearing commercial viability.

2.1 Nanoceramics

Ceramic materials have long been used in a variety of applications because of their unique properties compared to other materials. Ceramics are often used in electronics (due to their electrical and magnetic characteristics), in chemical processes and containers (due to their inert characteristics), and in various mechanical systems (due to their mechanical strength, resistance to bending and compression, and ability to maintain their strength at high temperatures). Bulk behavior of materials can be dramatically altered when constituted of nanoscale building blocks.[4] Nanoceramics are materials made up of nano-sized (less than 100 nm) ceramic particles.

Over the past 20 years, research conducted in academic, government, and private sector environments has resulted in significant advances in nanoceramics. Nanoceramics exhibit unique processing, mechanical, and surface characteristics, such as superplasticity, machinability, strength, toughness, and bioactivity due to their fine grain size, abundant grain boundaries, and controllable crystallinity.[5] Mechanical, magnetic, optical, and other properties of materials have been found to be favorably affected. Hardness and strength, as an example, can be greatly enhanced by consolidating ceramic materials from nanoscale particles. Ductility and superplastic-forming capabilities of nanophase ceramics have now become possible, leading to new processing routes that will be more cost-effective than traditional methods.[6]

2.1.1 Mechanical Applications

Nanoceramics have shown enhanced mechanical characteristics as particle size decreases. New nanoscale ceramics exhibit improved mechanical performance in applications requiring strong, hard, and abrasion-resistant materials. Metal-cutting, shaping, grinding, and sanding tools require materials which can remain intact through very harsh environments. Other nanoceramic materials, such as silicon nitrides and carbides, are used to make components for high-temperature applications, such as valves and turbocharger rotors. Nanoceramics also have been used successfully in heat shield tiles for the space shuttle and in rocket nose cones.

2.1.2 Electrical Applications

Because of various ceramics' electrical conducting, insulating, and semiconducting properties, which are particle-size dependent, nanoceramics exhibit unique characteristics. Some nanoceramics exhibit higher electrical resistance and dielectric constant than the same material with larger particle sizes. These traits make nanoceramic materials quite useful in circuit board fabrication and micro-electronics.

Some copper-oxide (CuO) based nanoceramics are superconductive at temperatures higher than the temperatures at which micro-sized copper compounds become superconductive. While superconductivity is not specifically a nano phenomenon, certain nanoscale copper oxides do exhibit this characteristic. Given that superconductivity requires extremely low temperatures, these higher temperature superconductors can reduce the cost of maintaining the required conditions in these applications.

2.1.3 Magnetic Applications

Ceramic materials, such as iron oxide-based ceramics and oxides of chromium, nickel, manganese, and barium, exhibit significantly enhanced magnetic properties when fabricated from nanoparticles. These magnetic nanoceramics show high resistance to demagnetization, making them useful in electric motors and generators. Nanoceramics also conduct high-frequency currents, unlike metal conductors, resulting in less power loss in transmission lines. Manganese zinc ferrites are used in magnetic recording heads, and ferric oxides are the active component in several magnetic recording media, such as recording tapes and computer diskettes.[7]

Iron oxide (Fe_3O_4) nanoparticles have garnered attention for applications in areas such as medical care and magnetic sensing. Magnetic iron oxide nanoparticles exhibit the finite size effect, or high surface-to-volume ratio, which enables higher adsorption capacity for metal particle removal in water. These nanoparticles have been used to remove heavy metals and metallic ions from contaminated industrial waste water.[8]

2.1.4 Biomedical Applications

Various ceramics have been in use to make medical implants for several years. The main requirements of these implants are to 1) enable/support new bone growth and 2) be biocompatible so the host body does not reject the implant. Ceramics are good for these applications because they are typically readily accepted by the body. Such ceramics are often used to make hip joints, dental caps and bridges, and various other implants. However, compared to conventional ceramics, nanoceramics have been shown to support better osteoblast adhesion and proliferation, alkaline phosphate synthesis, and concentration of extracellular matrix calcium.[9]

Other advanced ceramics, such as hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), which is the principal component of bones and teeth, has been used to repair bone fractures and as replacement material. Hydroxyapatite also is used on the surface of medical implants to improve the characteristics of friction, scratch resistance, and wear rate of commercially pure titanium (Ti) by increasing the microhardness, increasing the scratch resistance, and lowering the coefficient of friction.[10]

2.1.5 Anti-corrosion

Mild steel is a basic material used in countless products throughout industry because it is inexpensive; it is hard, yet weldable; and it is long lasting. However, mild steel is not resistant to corrosion and must be protected by painting or otherwise coating it in some way. These paints, coverings, and coatings often wear off over time and must be reapplied to ensure the mild steel remains in good condition. However, nanoceramics can be applied in new ways that embed the particles into the surface and improve the surface of the steel without altering its internal composition. A recent study observed that thermodiffusion of $Cr_{1.3}Fe_{0.7}O_3$ ceramic nanopigments into the surface of mild steel showed excellent performance as a corrosion inhibitor.[11]

2.2 Superhydrophic Surfaces

Superhydrophobic surfaces are defined as surfaces that have a water contact angle (CA) larger than 150°, which causes water droplets to bead up as shown in Figure 3. These surfaces exhibit characteristics that are quite useful in many applications and have been commercialized in the form of coatings and sprays. While the coatings offer excellent superhydrophobic characteristics, they require an extra step or multiple steps to be applied to the surface of interest and often require re-application after a peri-

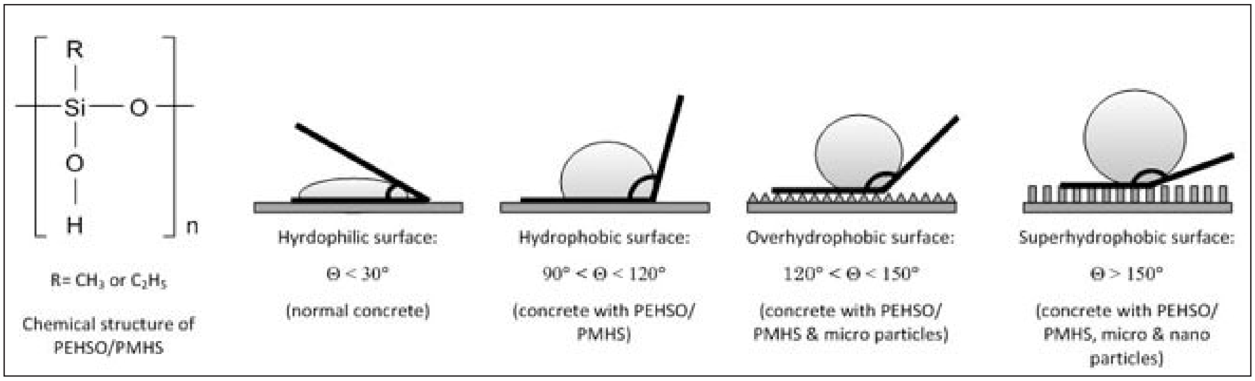

***Figure 3:** Contact angle of hydrophobic surfaces*[12]

od of time. Therefore, there has been a lot of effort to incorporate superhydrophobic characteristics into the surface itself.

Superhydrophobic materials cause liquids to run off and not stick to the surface, taking dirt and small surface debris with it. These surfaces are useful in the following applications:

- **Water-proofing** for clothing and tents
- **Self-cleaning surfaces**, such as windshields or housing materials
- **Anti-corrosive surfaces** – the internal electronics of cellular phones are often coated to protect them from corrosion
- **Anti-icing** for airplane surfaces
- **Friction reduction** for boat hulls
- **Anti-bacterial** for hospital walls and floors

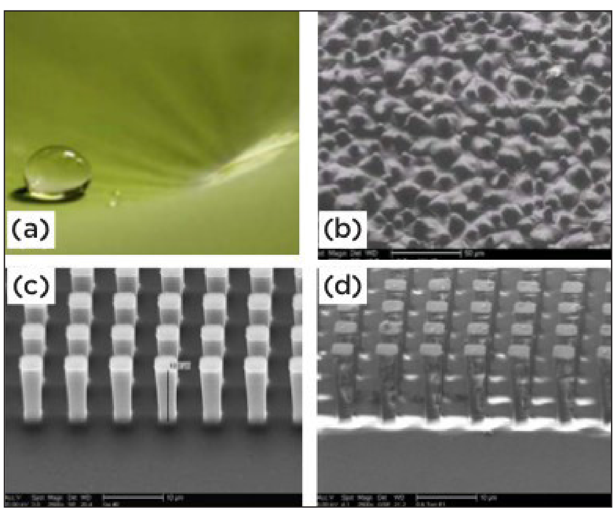

***Figure 4:** Superhydrophobic materials in nature and manmade. **(a)** Superhydrophobic nature of a lotus leaf surface; **(b)** scanning electron microsocope (SEM) image of the surface of an Idaho National Laboratory (INL) made molded polymer with surface features similar to that of hte lotus leaf; **(c)** SEM images of silicon pillars. **(d)** SEM image of INL-made molded polymer pillars. The image height in (b), (c), and (d) is -175 micrometers (µm). Images courtesy of Idaho National Laboratory (released).*

The U.S. Department of Energy (DOE), Energy Efficiency & Renewable Energy Laboratory, in partnership with Idaho National Laboratory and General Electric Global Research, completed a project to fabricate structured surfaces for enhanced boiling, condensation, and water repellency. The result of the project was fabrication of surfaces with nanoscale and microscale features, as shown in Figure 4.

Another similar surface characteristic useful in many military and industrial applications is oleophobic materials, which repel oils. Researchers at Aalto University in Finland developed surfaces that cause oil to move away from a drop point in a direction based on the asymmetric geometrical pattern on the surface. These types of engineered geometrical nanosurfaces make powerless fluid transport systems and oil contamination self-removal applications possible.[13]

The superhydrophobic hybridization of concrete uses superhydrophobic additives in the material to keep water from penetrating the surface (even when small cracks form) and deteriorating the concrete from within.[14]

2.3 Other Applications

2.3.1 Transparent Armor

Armor Transparent Purchase Description (ATPD) 2352, revision P1, was issued in July 2008 to create a new standard for transparent armor aimed at improving battlefield performance, maintenance costs, equipment survivability, and general durability based on data collected from performance of transparent armor in the battlefield.[15] These new, more stringent standards prompted nanoparticle research efforts to develop materials that could meet all the requirements for ballistic impact, transparency, thermal-mechanical stress, sand abrasion, and many other characteristics.

The first material to meet the requirements of ATPD

2352 was a glass-ceramic filled with 65%, by volume, nanocrystals of about 70 nm and smaller in size. This material was able to meet the higher standards while being 20% to 50% lighter than the incumbent soda-lime based transparent armor.[16]

2.3.2 Gas-Sensing

Zinc Oxide (ZnO) is a stable compound which is very sensitive to many types of gas. However, its operating temperature is high (400° to 500° C), and its gas selectivity is poor. There is a lot of on-going research to overcome these shortcomings using various additives and catalysts to reduce ZnO operating temperature and to improve its gas selectivity.[17]

Other nanoparticles are being used in sensing toxic gases. A low-cost chemical sensor made of groups of single wall carbon nanotubes (CNT), individually wrapped with supramolecular polymers, was developed to sense trace amounts of electrophilic chemical substances, such as diethylchlorophosphate. The electrical conductivity of the material increases up to 3,000 times when exposed to electrophilic toxic gases.[18] These nanoscale toxic gas sensors were integrated with the near-field communication technology on a cell phone to both power and read the sensors wirelessly.

2.3.3 Stronger Concrete

Concrete is one of the most widely used building materials in the world because of its strength and durability. However, these properties of concrete can be enhanced using nanoparticles to alter the structure within the material as it forms. Addition of nanosilica leads to densifying of the micro and nanostructure and results in improved strength by filling the pores between large fly ash and cement particles at nanoscale.[19]

2.3.4 Magneto-optics

Bismuth-substituted yttrium-iron garnet (Bi-YIG) films and Bi-YIG nanoparticles doped polymethyl methacrylate (PMMA), or Bi-YIG doped acrylic glass (Plexiglass), are used in various applications due to their magneto-optic characteristics.[20]

- **Sensor** – device that detects changes in magnetic field and current strength. Magneto-optic sensors are used in high-voltage network testing, monitoring, precision measurement, remote control, telemetry, and automated control systems.
- **Recording** – magneto-optical recording combines the advantages of magnetic disk and CD-ROM. It is used in applications requiring large-scale real-time data collection, recording, storage and analysis.
- **Modulator** – device that modulates light beams by rotating the polarization plane of the incident light through a magneto-optical medium. This type of modulator is used in infrared detectors chopper, infrared radiation pyrometer, television signal transmission, distance measuring devices, optical detection, and transmission systems.

The yttrium iron garnet (YIG)-tuned filter is a filtering device, which uses a YIG ball as the oscillator to select specific frequencies through resonant coupling. The filters exhibit very high frequency range (3 – 40 GHz) and adjustable 3 dB bandwidth of 5 – 70 MHz, making them useful in broadband microwave communications, millimeter-wave receivers for tracking, and pre-selecting radio frequency signals.[21]

3. Soft Surfaces

3.1 Functionalization of Textile Surfaces

A growing development in textile technology is the integration of nanomaterials into fabrics[22] (See Figure 5). Textile attributes, such as softness, durability, breathability, and water repellency can be enhanced through nanomaterial finishing of fabrics made of

Figure 5: *Representative applications of nanotechnology in textiles*[26]

Table 1: Nanotechnology in Textile Industries	
Application in Textile	**Nanomaterial Used**
Electro conductive and antistatic	Carbon black, Carbon nanotubes (CNT), Cu, Polypyrrole, Polyaniline
Increase durability	Al_2O_3, SiO_2, CNT, ZnO, Polybutylacrylate
Antibacterial	Ag, Chitosan, SiO_2 (as matrix),TiO_2, ZnO
Self-cleaning/ dirt and water repellent	CNT, Fluoroacrylate,SiO_2 (as matrix), TiO_2
Moisture absorbing	TiO_2
Improved staining / reduce fade	Carbon black, Nanoporous hydrocarbon on Nitrogen coating, SiO_2 (as matrix)
UV protection	TiO_2, ZnO
Fire proof	CNT, Borosiloxane, Montmorillonite (nano clay), Sb_3O_2
Controlled release of active agents, medicinal products or fragrances	Montmorillonite (nano clay), SiO_2 (as matrix)

Table 1: *Finishing applications and nanomaterials used in textile industries.*[27]

natural and synthetic fibers to achieve desirable functional properties[23] (See Table 1). Nanoparticles have outstanding surface properties compared with traditional additives and materials[24] and possess large surface area and high surface energy that ensure better affinity for fabrics.[25] Many functional applications can be gained from synthetic and natural fibers through surface functionalization with nanomaterials (See Table 2).

Several methods of applying engineered nanomaterials to fabrics have been developed; however, three stand out when applying nanomaterials to textiles:

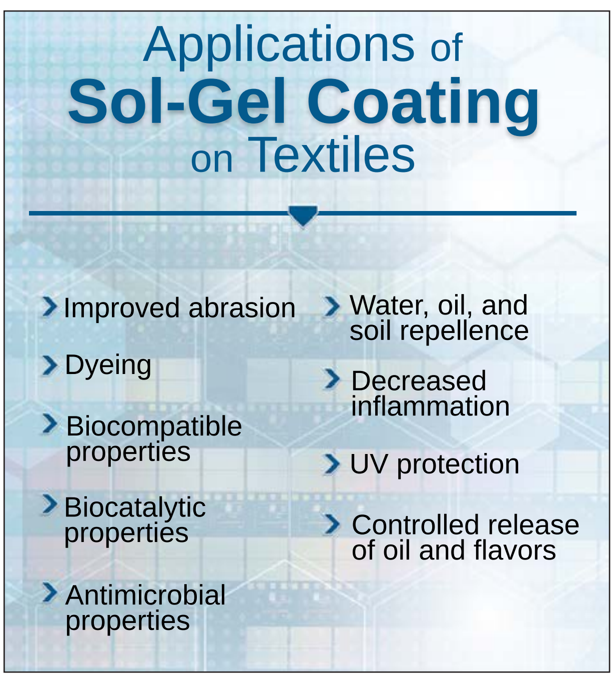

Figure 6: *Applications of sol-gel coating on textiles*[36]

physical vapor deposition (PVD), sol-gel method, and electrospinning.

PVD is a type of thin-film deposition technique in which a thin layer of coating is deposited on a substrate. A solid material is transformed into a vapor and then transferred onto the surface of a substrate, forming a uniform coating layer.[29] Three methods of PVD exist: vacuum evaporation, sputter coating, and ion implantation. Each differs in the energy contained in their depositing materials, with vacuum evaporation having the lowest and ion implantation having the highest.[30] The applied energy is influential in interactions of coating materials and substrates and the growth of the film.[31]

The sol-gel method is a type of chemical solution deposition commonly used in materials science and ceramics engineering to fabricate metal oxides.[32] This method uses a chemical solution (sol) that acts as the precursor for a network of particles (gel).[33] The sol eventually converts into a gel-like system that can be deposited as a thin film on polymeric substrates using dip coating or spin coating.[34,35] Coatings developed through the sol-gel technique have a variety of applications on textiles (See Figure 6).

Electrospinning is one of the most exciting new developments regarding nanomaterials in textiles. Doshi and Reneker first reported the electrospinning process in 1995, but the process has grown in popularity.[37] It is a technique that enables the uniform coating of nanofibers onto different substrates. A thick polymer solution is sprayed through a nozzle while high voltage is applied to the nozzle and a metallic board below. The electrical field converts the polymer into fibers that are deposited onto the board

Substrate	Functional Applications
Cotton	• Electrically Conducting fiber • Antistatic carpets, filters, antimicrobial heating pads • Fastness performances to washing, light exposure and dry rubbing • Electrical and physical properties • Improving electrical property by novel covering methods • Electromagnetic properties of coated fabric with UV-protection • Military applications and conductivity behavior of the fabric
Wool	• Conducting fiber • Electrical and physical properties • Electrical and thermal properties of the fabric • Coating yarns with low electrical resistivity
Silk	• Conducting Fiber • Improving electrical property by novel covering methods • From apparel to technical issues
Polyester	• Resistivity of conductive polymer • Gas sensing capabilities • EMI, SE, DC conductivity of fabric • Dielectric characteristics of coated textile using frequency • Flame retardancy • Conductivity and stability • Coating property and electrical behavior • Strain sensor
Nylon	• EMI and SE Shielding • Fire retardant • Absorption of microwave radiation in coated textiles

Table 2: Fabrics and Functional Applications

Table 2: *Fabrics used for deposition/incorporation of polymer and its composites for functional applications*[28]

to achieve an interconnected, membrane-like web of fibers (mat).[38] This process allows the diameter of the fibers to be controlled and adjusted.[39] Electrospinning provides numerous advantages compared with other methods, including simplicity, effectiveness, low-cost, quickness, and involvement in a wide-range of applications[40] (See Table 3).

A variety of textile nanocoatings, including CNTs, zinc oxide (ZnO), titanium dioxide (TiO_2), silicon dioxide (SiO_2), aluminum oxide (Al_2O_3), and silver (Ag) have been commercialized in developed countries.[42] Although surface functionalization of nanomaterials, particularly in textiles, shows much promise, industry trends in functional nanomaterials for textiles are still sluggish. The sol-gel method currently appears most feasible, particularly for large-scale applications, as thin-film deposition and electrospinning are still challenging for industrial scale products.[43] However, applications of electrospinning will be more important for smart textiles, biosensors, and metal surfaces once the technology improves and becomes more practical for commercial use.[44]

3.2 Surface Coatings for Textiles

A coating is a covering that is applied to the surface of an object to improve surface properties of the substrate, and, in other cases, to form an essential part of the finished product.[45]

3.2.1 Antibacterial Applications

Certain metals and metal oxides, such as copper (Cu), Ag, and titanium dioxide (TiO_2) have been used for many years as antimicrobial agents. These materials continue to be of interest in fighting bacteria, particularly in medical applications (hospital linens, bandages, and dressings), where they can be used to battle antibiotic resistant bacteria, such as methicillin resistant *staphylococcus aureus* (MRSA), or to reduce the growth of bacteria, in general. In addition, these metals also are used in active gear, including athletic clothing and socks, where their presence keeps bacterial colonies at bay and helps reduce odor and the spread of disease. In addition to metals, other materials, such as certain polymers and biomaterials, including chitosan, have become popular antimicrobial agents and show promise in reducing the growth of bacteria on surfaces, including bandages and dressings.

All antimicrobial finishes have one characteristic from each of the following categories:[46]

- **Biocidal** (agents that kill bacteria and fungi) OR **biostatic** (inhibit organism growth)
- **Leaching** (gradual or persistent release into surroundings and act as a poison) OR **bound** (fixed to a surface and act as a barrier to control organism growth)
- **Poor** (nanomaterials easily removed by laundering in a short period of time) OR **good** (typically bound nanomaterials that do not rinse off easily during laundering)

Table 3: Electrospun Nanofibers Fabrication		
Antibacterial Applications		
Antibacterial Agent	**Polymeric Precursor**	**Antibacterial Tests**
Ag NPs (from $AgNO_3$ reduction)	Poly(acrylic acid) (PAA) /cyclodextrin	*L. plantarum*, 2012
Ag NPs (from aqueous solution)	Poly(vinyl alcohol) (PVA)	*S. aureus* and *E. coli*, 2010; 2011
Ag NPs (by seed mediate growth method)	Poly(vinyl pyrrolidone) (PVP)	*S. aureus*, *K. pneumoniae*, and *E. coli*, 2011
Ag NPs (in ethanol solution)	Poly(vinylidene fluoride) (PVDF)	*S. aureus* and *K. pneumoniae*, 2010
Ag NPs (from $AgNO_3$ reduction)	Poly(vinyl alcohol) (PVA) and chitosan	*E. coli*, 2012
Ag NPs (from $AgNO_3$ reduction)	Polyvinyl alcohol (PVA) /regenerated silk fibroin	*S. aureus* and *E. coli*, 201
Ag NPs (from $AgNO_3$ reduction)	Poly(acrylonitrile) (PAN)	Not tested, 2005, 2003. *E. coli*, 2012
Ag NPs (from $AgNO_3$ reduction)	Nylon 6	*B. cereus* and *E. coli*, 2011
Quatemary ammonium salts	Diblock copolymers with polyacrylates	*S. Aureus* and *E. coli*, 2008
Triclosan	Poly(lactic acid) (PLA), cyclodextrin	*S. aureus* and *E. coli*, 2013
Chlorhexidine	Cellulose acetate	*E. coli* and *S. epidermidis,* 2008
Other Applications		
Active Agent	**Polymeric Precursor**	**Application**
Mupirocin (antibiotic)	Poly-L-lactic acid	Drug release, 2008
Tetracycline hydrochloride (antibiotic)	Poly(lactic acid) (PLA), poly(ethylene-co-vinyl acetate) (PEVA); poly(l-lactid-co-e-caprolactone)	Drug release, 2002, 2009
Fluoroquinolone antibiotics	Poly(l-lactide-co-d, l-lactide) and coPLA/poly (ethylene glycol)	Drug release, 2012
Ampicillin (antibiotic)	Poly(methyl methacrylate)-nylon 6	Drug release, 2013
Gentamycin sulfate (antibiotic)	Polycaprolactone	Drug release, 2006
Iodines	Poly(vinyl pyrrolidone) PVP)	Wound dressing, 2007 [143]
AG NPs	Gelatin; poly(vinyl alcohol)	Wound dressing mats, 2007, 2008
CoS NPs; AG_3PO_4	Poly(acrylonitrile) (PAN)	Water treatment, photocatalyst, 2013
CdO, ZnO, TiO_2 (photocatalytic)	Poly(vinyl alcohol)	Water treatment, 2012, 2010
Collagen; Cell adhesive peptides	Poly(L-lactid acid)-co-poly(e-caprolactone); poly(B,L-lactic-co-glycolic acid) (PLGA)	Tissue engineering, 2006, 2005
Hydroxyapatite, PLGA	Poly-L-lactic acid; PLGA	Tendons/ligaments/bones tissue engineering, 2006, 2007
Boronic acid NPs	Polyamide 6	Flame retardant, 2012, 2014

Table 3: *Summary of some of the most relevant works classified by applications, indicating polymer precursor and the loaded active agents for electrospun nanofibers fabrication*[41]

Many conventional antimicrobial agents are used effectively for minimizing pathogenic growth (See Table 4); however, a major challenge is leaching of the agent from the fiber. Nanomaterials offer a potential solution in that particles on the nanoscale can be more strongly bound to fibers than traditional bulk antimicrobial agents, and they can be more effective against antibiotic resistant bacteria. It is unknown whether the antimicrobial effectiveness is due to the size of the nanoparticle itself or the dissolution of the component atoms.

A variety of nanostructured materials with good antimicrobial activity have been used for textile surface modification (See Table 5); however, Ag is by far the most common. Silver ions denature proteins and lead to cell death because of a reaction that occurs with nucleophilic amino acid molecules in proteins.[48] Cotton is the most common fabric to which Ag nanoparticles are applied. Silver is effective against *Staphylococcus aureus* (*S. aureus*) after 20 washings when applied to cotton fabric,[49] and 98% effective against *Escherichia coli* (*E. coli*) when hydrogel silver nanocomposite is grafted onto cotton.[50] Davidovic et al. have shown that, in addition to *S. aureus* and *E. coli*, Ag is effective against *Candida albicans*.[51] However, the addition of increasingly higher concentrations of Ag does cause cotton to yellow.[52,53]

Nanoscale Ag applied to silk has been reported to be 97% effective against *S. aureus* and 99% effective against *E. coli* after 50 washings by using an *in situ* synthesis technique to produce Ag nanoparticles directly onto the silk fibers.[54] Perhaps the most common application of Ag on cotton is for improved wound dressings. Several products that use Ag nanoparticles on cotton bandages are already found on the market, including Acticoat, Actosorb, Aquacel, Contreet Foam, and Urgotul.[55] In fact, Ag nanoparticles are so effective in reducing bacterial growth that Paladini discovered Ag-treated cotton gauze with 0.5 wt/v %Ag solution is just as effective as the gauze treated with 4 wt/v %Ag solution against *S. aureus*.[56]

Titanium dioxide (TiO_2) and zinc oxide (ZnO) nanoparticles are also commonly used for antimicrobial treatment. Nanoscale TiO_2 is highly stable, long-lasting, and effective against a broad spectrum of pathogens, because it is self-cleaning, antibacterial, and protective against ultraviolet (UV) light.[58] It decomposes common organic materials, such as bacteria and viruses. Irradiation by light induces redox reactions at the surface, generating highly active oxygen species that can oxidize organic compounds of cells.[59] On the other hand, ZnO also shows antimicrobial activity, is lower in cost than silver, and is also UV blocking like TiO_2.[60] Shaheen et al. found that ZnO applied with an amine material in low concentrations to cotton fabric was more effective than higher concentrations against *S. aureus* and *E. coli* and was still effective (90% for *S. aureus* and 87% for *E. coli*) after 20 washings.[61] An *in situ* approach for synthesizing ZnO particles onto cotton fibers showed that antibacterial activity is dose-dependent.[62] Combining TiO_2 and ZnO also appears to have positive antibacterial results. A TiO_2/ZnO nanocomposite applied to nylon/cotton blend was effective against *S. aureus* and resisted leaching after repeated washings.[63]

Table 4: Conventional antimicrobial agents, applications, and challenges			
Antimicrobial Agent	**Effective Against**	**Applications For**	**Challenges**
Quaternary ammonium compounds	Bacteria (Gram-negative and gram-positive), fungi, viruses	Mulitiple textiles	Leaching, poor wash durability
N-halamines	Bacteria, fungi, viruses	Cellulose, polyamide and polyester fibers	Poor durability, limited effectiveness
Chitosan	Bacteria, fungi	Cellulose and cellulose/polyester fibers, and wool	Durability, wash resistance
Halogenated phenols	Bacteria (antibiotic-resistant), fungi, viruses	Cellulose fibers, non-woven textiles	Wash durability, widespread use could lead to resistant microorganisms
Polybiguanides	Bacteria (antibiotic-resistant)	Cellulose fibers	Reduced antimicrobial effectiveness through interaction with dyes

Table 4: *Conventional antimicrobial agents, applications, and challenges*[47]

Table 5: Nanoparticles used for Antibacterial or Antifungal agents		
Antibacterial Agent	**Fabrics**	**Antibacterial or Antifungal Tests**
Silver-tricalcium phosphate NPs (Ag/TCP)	Polyamide	*E. coli* and *S. sanguinis*, 2011
Silver nanoparticles	Polyester	*E. coli* and *S. aureus*, 2010
Silver nanoparticles	Polyester and polyamide	*E. coli* and *S. aureus*; laundering durability pretreatment corona 2008
Silver nanoparticles	Polyester and polyamide	*C. albicans*; laundering durability pretreatment: corona, 2009
Silver nanoparticles	Polyester	*E. coli* and *S. aureus*; laundering durability pretreatment: radio frequency (RF) plasma, 2010
Silver nanoparticles	Polyester	*S. aureus*, *S. epidermidis*, *P. aeruginosa*, and *C. albicans*, 2008
Silver ammonia complex	Polyamide	*E. coli*; laundering durability pretreatment: glutaraldehyde (GDA), 2010
Silver ammonia complex	Polyamide	*E. coli* and *S. aureus*, 2012
Silver ammonia complex	Polyamide	*E. coli* and *S. aureus*; laundering durability, 2014
Silver nanoparticles	Polyamide	*E. coli* and *S. aureus*, 2015
Silver nanoparticles (in situ synthesis)	Polyester	*E. coli* and *S. aureus*, 2013
Copper nanoparticles (in situ synthesis)	Polyamide	*S. aureus*, 2013
TiO_2 nanoparticles	Polyester/wool	*E. coli*, 2011
TiO_2 nanoparticles	Polyester	*E. coli* pretreatment oxygen and argon plasma, 2010
TiO_2 nanoparticles	Polyester	*E. coli* Pretreatment: corona/air RF plasma, 2011
SiO_2 nanoparticles	Polyester	*E. coli* and *S. aureus*; laundering durability binder: acrylate polymer, 2013
ZnO nanoparticles	Cotton/Polyester	*E. coli* and *M. luteus*, 2014
Ag/ZnO composite nanoparticles	Cotton/Polyester	*E. coli* and *M. luteus*, 2014
Silver-doped silica-complex nanoparticles	Polyester	*E. coli* and *S. aureus*, 2014
Chitosan and silver-loaded chitosan nanoparticles	Polyester	*S. aureus*, 2011
Mixture Of silver and TiO_2 nanoparticles	Polyester	*E. coli*, *S. aureus* and *C albicans*, 2011
Silica sols with silver nanoparticles	Polyamide	*E. coli*; laundering durability, 2010
Gold nanoparticles	Polypropylene	*E. coli* and *S. aureus*; laundering durability pretreatment: air plasma treatment, 2013
Silver nanoparticles	Polypropylene/polyethylene	*E. coli*, *Klebsiella pneumoniae*, and *S. aureus*, 2005

Table 5: *Summary of the types of nanoparticles used for antibacterial or antifungal activity.*[57]

In addition to silver and metal oxides, other nanoscale materials also show promising results for antibacterial activity. Chitosan has been used in dressings for many years and has been effective against bacteria. Certain polymers also demonstrate antibacterial activity. Velmurugan, et al. demonstrated that gold nanoparticles synthesized onto silk, cotton, and leather showed effective antibacterial activity against *Brevibacterium linens*.[64]

Nanomaterials have proven to be a promising solution to many of the challenges of traditional antimicrobial finishings. Techniques, such as the sol-gel process, have enabled antibacterial nanomaterials to adhere to fibers much more effectively, reducing the potential for leaching after repeated washings.[65] This works particularly well for binding metal oxides to cotton. Additionally, electrospinning has been used effectively to produce certain fibers with antimicrobial activity. Stanley et al. used electrospinning to produce polyacrylonitrile (PAN) fibers embedded with a porphyrin-based cationic photosensitizer and created a nonwoven textile that was effective against several pathogens, including *S. aureus*, *E. coli*, *Enterococcus faecium*, *Acinetobacter baumannii*, *Klebsiella pneumonia*, human adenovirus, and vesicular stomatitis virus.[66] A method for developing ZnO nanoparticles using ultrasonic waves was demonstrated by Abramova et al., and these particles were more effective against *E. coli* compared with industrially produced ZnO nanoparticles.[67]

3.2.2 Flame Retardant Applications

Many synthetic and natural fibers are prone to combustion. Fire retardant fabrics become more resistant to fire after a chemical treatment or through the use of manufactured fireproof fibers.[68] To improve the usability in extreme environments and minimize safety concerns, fabric made with fibers that can melt or catch fire are often covered with flame-retardant coatings. An efficient flame retardant system has multiple components, including particle morphology, chemical nature of the particles, concentration of the particles, and distribution of the particles onto the fabric.[69] Using nanomaterials for these coatings has become more common. (See Table 6) Many current flame retardant coatings use halogen-coatings additives;[70] however, many nanomaterials have become good alternatives, because they require a smaller amount of particles to produce similar flame-retardant effects.[71]

3.2.3 Superhydrophobic Applications

A superhydrophobic coating repels water to the point that no drop ever reaches the surface of the textile. Superhodrophobicity describes a surface that presents water CAs higher than 150° and is known as the lotus effect,[73] named after the lotus leaf where this phenomenon is seen in nature. Water beads up on lotus leaves and picks up particles of dirt as it rolls off,[74] making lotus leaves self-cleaning as well as water-repellent. This phenomenon has been recreated using nanomaterials (See Table 7). Suprhydrophobicity depends on surface chemistry and morphology,[75] including low-surface energy materials and a specific surface topography based on a dual-size surface roughness.[76]

Three basic requirements needed to create a superhydrophobic surface are:[78]

Table 6: Flame Retardant Applications

Type of Fabrics	Deposition Process	Type of Nanoparticles
Polyester and cotton/polyester blend	Impregnation process	Globular octalpropylammonium (POSS) nanoparticles. 2015
Cotton/polyester blend	Pad-dry-cure method	Zinc oxide (ZnO) nanoparticles (an average particle size of 30 nm), 2013
Polyester	Layer-by-layer assembly	Silica (SiO_2) colloidal nanoparticles (<10 nm average thickness), 2011
Polyester and cotton/polyester blend	Impregnation process	Mixture of silica (SiO_2) globular (spherical particles with an average size of 150 nm) and hydrotalcite (HT lamellar nanoparticles, 2012
Polyamide and polyester	Layer-by-layer assembly	Titanium dioxide (TiO_2) nanoparticles, thickness film (approx. 500 nm), 2015
Polyester	Layer-by-layer assembly	Multi-walled carbon nanotubes (MWCNTs) (an average diameter of 9.5 nm and an average length of 1.5 µm), 2012

Table 6: *Types of nanoparticles for flame retardant applications and corresponding deposition techniques used for specific types of fabrics*[72]

- Water droplets should have a high static contact angle
- Droplets should not be strongly attached to a surface and should easily move at low inclination
- Adhesion between dust and a solid surface should be lower than the adhesion between dust and water

Cotton is one of the most common materials to which superhydrophobic coatings are applied. Patra et al. report that nanowhiskers added to cotton fibers create a "peach fuzz" effect in which water remains on top of the whiskers, because the spaces between the whiskers are smaller than a drop of water but larger than individual water molecules.[79] Xue, et al. prepared superhydrophobic cotton textiles by coating silica nanoparticles with functional groups on microscale natural cotton fibers followed by hydrophobization.[80]

A modified Cassie and Baxter equation can be used to describe the wetting behavior of a water droplet on a hydrophobic cotton textile surface:[81]

$$\cos\theta_{CB} = r_f f \cos\theta_0 + f - 1$$

Where:

- θ_{CB} is the observed water CA on a rough, porous surface
- θ_0 is the intrinsic water CA on corresponding smooth surface
- f is the fraction of the projected area of the solid surface wetted
- r_f is the surface roughness of the wetted area

This equation accounts for local surface roughness on the wetted area.

Superhydrophobic coatings have been applied to polyester and cotton using the dip-pad-cure process.[82] Recently, a chitosan and polyalanine polymer nanocomposite was used as a multifunctional finishing agent on polyester fabric by conventional pad-dry-cure process and soft *in situ* chemical polymerization.[83]

3.2.4 Photocatalytic and UV Blocking Applications

Inorganic semiconductor oxides, including TiO_2, ZnO, SiO_2, and Al_2O_3, are more preferred as UV light-blockers than organic materials because they are non-toxic and chemically stable when exposed to high temperatures and UV light.[84,85] Nanoscale TiO_2 and ZnO provide better protection against UV light compared with microscale particles of TiO_2 and ZnO because they absorb and scatter UV radiation more efficiently,[86] and ZnO nanoparticles block a broad range of UV wavelengths.[87,88] Shaheen, et al. recently demonstrated that ZnO loaded onto cotton provided an adequate ultraviolet protective factor (UPF) after 15 washings.[89] In addition to coating fibers with metal oxide UV blocking agents, photocatlytic agents can be integrated directly into the fiber through the melt-electrospinning process. Karahaliloglu, et al. created a nanocomposite nonwoven fabric using pristine polypropelene (PP) and nanoscale Ti particles.[90] Melt-electrospinning has been shown to be more effective at creating photocatalytic thin fibers of polypropelene compared with chemical binding methods.[91] However, there are some limitations to the melt-electrospinning process regarding the manufacture of thin, photocatalytic fibers. Titanium as a photocatalyst is heavily dependent on pH, or the acidity or basicity of an aqueous solution, and the photocatalytic efficiency decreases as the concentration of dyes in the fabric increases.[92]

Table 7: Superhydrophobic Applications

Type of Fabrics	Deposition Process	Superhydrophobic Surface
Polyester	Pad-dry-cure method	Alkaline hydrolysis and fluorocarbon layer, 2011
Polyester	Dip-coating	Silver nanoparticles and fluorination, 2012
Polyester	Dip-pad-cure process	Silica (SO_2) nanoparticles and fluropolymer, 2015 and 2014
Polyester	Spin-coating	Silica (SO_2) nanoparticles and fluorosilanization, 2012
Polyester	Electroless deposition	Zinc oxide (ZnO) nanoparticles, 2013
Polyester	Solution or vapor deposition	Zinc oxide (ZnO) nanoparticles and octadecyltrimethoxysilane (ODS), 2013
Cotton/polyester	Pulse laser deposition	Zinc Oxide (ZnO) nanoparticles, 2011
Polypropylene	Solvent swelling method	Swollen of the polymeric chains, 2015

Table 7: *Summary of the type of nanoparticles or nanomaterials used for superhydrophobic surfaces*[77]

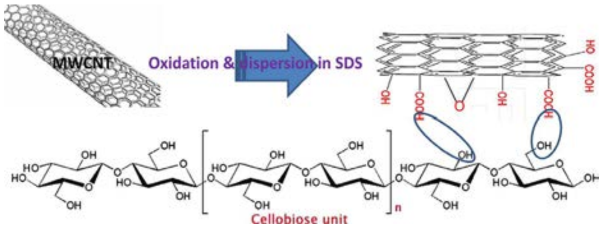

Figure 7: *Interaction of MWCNTs with cellulose/cotton fabric structure through glycosidic linkages*[103]

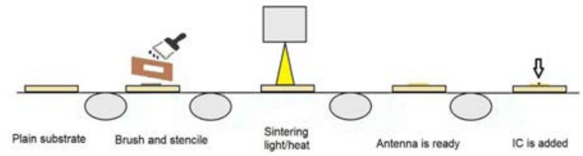

Figure 8: *Brush painting process*[106]

3.3 Smart Textiles

Smart textiles are textile products such as fibers, filaments, and yarns, together with woven, knitted or nonwoven structures, which can interact with the environment/user.[93] The integration of electronics into textiles is known as electronic textiles, or e-textiles, a term often used interchangeably with smart fabrics or smart textiles. Smart textiles are wearable structures that have properties, such as sensing, communicating, and storing power. They enable continuous interaction among device, user, and the environment, and have use in military applications, among others.[94] Smart textiles integrate a high level of intellignece and can be divided into three groups:[95]

- **Passive smart textiles** – only able to sense the environment/user based on sensors
- **Active smart textiles** – reactive sensing to stimuli from the environment, integrating an actuator function and a sensing device
- **Very smart textiles** – able to sense, react, and adapt their behavior to the given circumstances

Nanotechnology-based coatings offer a new dimension to finishing procedures for textiles, particularly smart textiles, because of their size-related properties and high surface area-to-volume ratio, which result in enhanced characteristics compared with larger particles.[96]

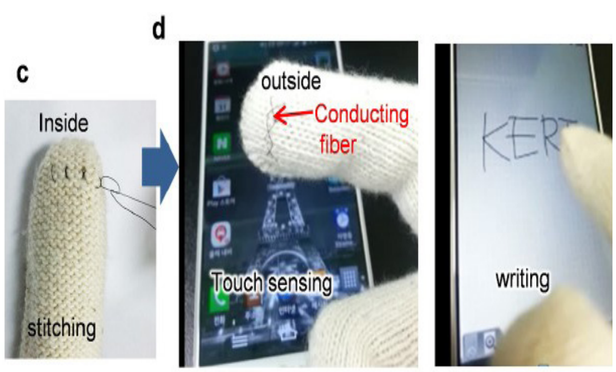

Figure 9: Conducting composite fiber was stitched into the glove showing touch screen sensing and writing with the glove stitched with the conducting composite fiber[107]

Sensors are one of the key features for smart fabrics, and nanomaterials allow parts of the fabrics themselves to be sensors, instead of incorporating separate sensors into the material. CNTs are one of the best nanomaterials for conductivity, because they exhibit high sensitivity and fast response time at room temperature.[97] They also have a very high aspect ratio with unique electrical and thermal properties, which makes them highly desirable for use in the preparation of lightweight and flexible electrothermal materials.[98] Andretta et al. describe how CNTs can be fashioned into sensing units and incorporated into clothing to be used as sensors for toxic chemicals. Chemicals induce perturbations of the nanotube conductance sending a signal to a host server.

Wang et al. describe a method of using a wearable fabric sensor made of multi-walled carbon nanotubes (MWCNTs) that can detect strain and temperature difference on the wearer.[99] A review of similar techniques shows that several products already exist on the market that provide real-time biological monitoring, such as pulse and respiratory rate using devices made of carbon nanotubes stitched into fabric.[100] Functionalized MWCNTs were used by Rahman et al. to produce a conductive cotton textile using a dipping-drying coating method.[101] In this particular case, the textile was used as a lightweight, flexible electrothermal heating element. Multi-walled CNTs easily enter into the interwoven structure of cotton fabric and irreversibly wrap around cellulose fibers to create a three-dimensional porous structure, which results in the creation of numerous electrical carrier paths[102] (See Figure 7).

In addition to CNTs, Ag is another nanomaterial commonly used in smart textiles. A technique develop by Virkki was used to incorporate radio frequency identification (RFID) tags onto a nanosilver base painted onto fabric[104] (See Figure 8). The brush-painted Ag tags had a range of 8 meters. Because silver is an

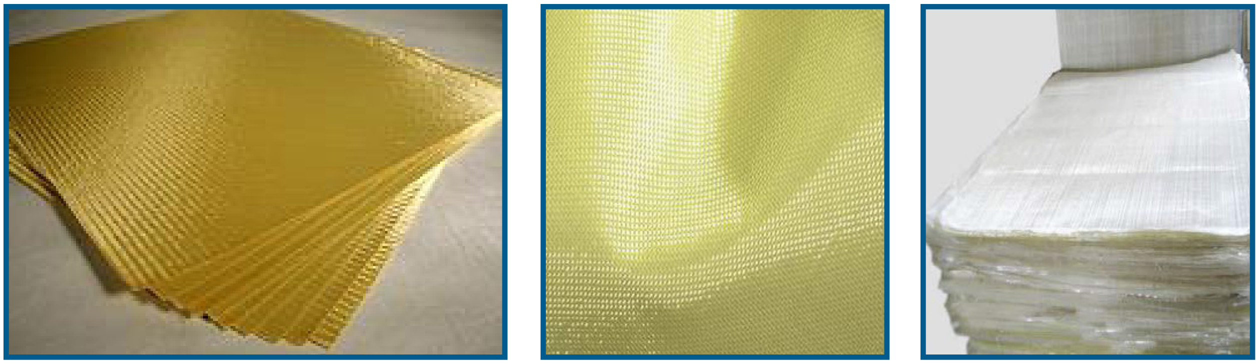

Figure 10: *UD aramid fabric treatment with nanotechnology* ***(a)****, Aramid fabric (Argus)* ***(b)****, and UD UHMWPE fabric polyethylene treated with nanocomposite* ***(c)****.*[112]

electrical conductor, it can also be used to send signals in fabrics. Han, et al. developed a composite wire of Ag nanowires and multi-walled CNTs that was stitched into a glove and allowed for interaction with a smart phone[105] (See Figure 9). This setup has applications in situations where protective gear is necessary, but still allows for functional use of touch-screen electronic devices.

3.4 Body Armor

One of the most promising, yet underdeveloped nanomaterials area in textiles, is body armor applications. Body armor now typically comes in two forms—soft and hard. Soft armor is made of layers of a strong, flexible fabric comprised of high performance fibers. Commonly used fibers are:[108]

- S-glass
- Aramids (Kevlar 29, Kevlar 49, Kevlar 129, Kevlar KM2, Twaron)
- Highly oriented, ultra-high molecular weight polyethylene (Dyneema, Spectra)
- p-phenylene-2-2-benzobisoxazole (PBO) (Zylon)
- polypyridobisimidazole (PIPD) (M5)

These fibers are characterized by low density, high tensile and compressive strength, high modulus, high rupture strain, resistance to thermal degradation, and high-energy absorption capacity.[109] When a projectile strikes the fabric, the fibers stretch and absorb the energy and redistribute it throughout the material. Although soft armor provides maximum flexibility and movement, it provides relatively poor protection to high velocity projectiles, especially at close distance.

Hard armor is much more rigid than soft armor, but it provides greater protection, especially to high velocity ammunition. Current approaches include stacking plates of ceramic, steel, or Ti against a ballistic fabric backing. When the projectile strikes the plate, the energy is absorbed resulting in localized deformation of the hard surface.[110] Because of these stiff plates, hard armor limits wearer movement and performance.

Currently, the most feasible way of improving body armor with nanomaterials is by incorporating them into existing products as reinforcement, rather than by developing entirely new products manufactured completely with nanomaterials. In regards to soft armor, Abdulghaffar evaluated three fabrics, as shown in Figure 10: (a) UD aramid (heat-resistant and strong synthetic fiber) fabric bonded with stitches, treated with an undisclosed nanomaterial and woven in a diagonal orientation with two layers of fibers; (b) woven Argus aramid sheet fabric encapsulated in a thermoplastic coating; and (c) UD ultrahigh molecular weight polyethylene (UHMWPE) fiber fabric made as a unidirectional construction in which the fibers lie parallel to each other and were treated with a nanocomposite material.[111] Based on mechanical testing, he postulated the ideal configuration of the three materials would be 6 layers of UD aramid fabric in front, 12 layers of UHMWPE in the middle, and 6 layers of the Argus aramid fabric in the back.

The key mechanism that ensures that soft armor works is friction between the fibers, especially in woven fabrics. There must be some slippage to accommodate the projectile and distribute the force across the fabric, but the fibers cannot completely separate and pull out. Currently used fibers can only handle so much force before the fibers give way. A recent project supported by the Army Research Office suggests that growing ZnO nanowires on aramid fibers (Kevlar KM2) (See Figure 11) improves inter-yarn friction and delays the failure of the tows during

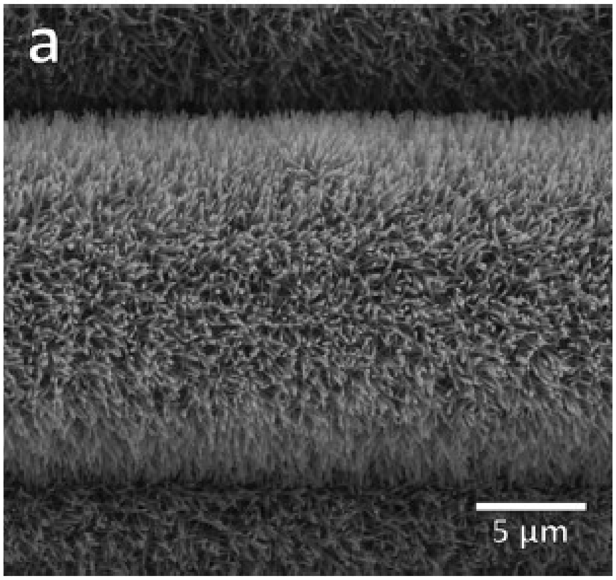

Figure 11: *Morphology of ZnO nanowires synthesized on aramid fabric*[115]

pullout tests.[113] Hwang et al. demonstrated that the aramid fabric with ZnO nanowires had 23 times higher absorbed energy and 11 times higher peak load compared with bare aramid fabrics.[114]

Because hard armor relies on the ability of a material to deform slightly to absorb the kinetic energy of a projectile, either thicker plates or stronger, tougher plates are needed for improved performance. Maximum maneuverability is the key when designing body armor, so even though hard armor provides greater protection than soft armor, it is not nearly as flexible. One of the current issues of hard armor plates is that thicker, more protective plates are heavy. The enhancement of ceramics shows the most promise of improving hard armor, as demonstrated by a completed program at the Army Research Laboratory.[116] Grain size is known to play a key role in strength and hardness of ceramics, thus creating and using smaller particles in armor should improve its toughness. Apart from manufacturing smaller ceramic particles, the addition of nanomaterials to existing products may help to increase strength without adding additional weight. Huang et al. demonstrated this concept by developing a material comprised of nanoscale zirconia (zirconium dioxide)-toughened alumna stabilized with 15% yttrium that displayed much greater hardness and toughness compared with controls.[117] In addition, studies have shown that incorporating as little as 4% of volume of CNTs into ceramics, such as alumina and silicon carbide, can improve fracture toughness by 94%.[118,119]

Future developments for improving soft and hard armor may lie in the use of carbonaceous nanomaterials, such as CNTs and graphene and in biomimicry. CNTs are an encouraging material for body armor given their incredible physical properties and dramatic energy absorption capacity versus other existing ballistic fibers.[120] There are three approaches for using CNTs in body armor:[121]

- Incorporating CNTs into polymer-matrix-composites (PMCs), metals, or ceramics to enhance their hardness or toughness and erosion resistance
- Using neat or composite fibers of CNTs, in the form of woven or non-woven fabric, for achieving exceptional ballistic performance
- Reinforcing the armor grade fibers, such as Kevlar, UHMWPE, or PBO, with CNTs to improve their elastic modulus and energy absorption capacity

Given cost and scalability, realistic expectations favor the reinforcement of the commonly used armor grade fibers with CNTs and the integration of CNTs into metals and ceramics. However, some encouragement for creating CNT fabric for use in armor is displayed by Miralon (Nanocomp Technologies, Inc.), which is a CNT fabric that can be combined with traditional aramid and polyethylene materials to create a lighter-weight, thinner, and more flexible vest (http://www.nanocomptech.com/armor). Another potential breakthrough in lightweight, highly strong materials is graphene. Recently, Lee et al. have shown that multi-layer graphene sheets provide a high level of protection even to a supersonic projectile.[122] Their measurements show that graphene is 10 times better than steel at absorbing the energy of a penetrating projectile; however, large scale production of graphene still remains several years away.

Biomimicry is the design and development of materials based on similar structures found in nature. The possibilities for improving hard body armor lie with studying the structures of seashells, specifically aragonite and nacre.[123,124] Furthermore, it may be possible to blend natural and synthetic materials to create even more energy absorptive materials.[125] Although some of the newer materials and techniques would revolutionize body armor, evidence suggests they are still five to 10 years away from commercialization.

4. Nondurable Goods

4.1 Coatings

Nanotechnology applications in coatings have shown remarkable growth in recent years. Use of nanomaterials has the potential to address many performance challenges presented by the vast range of products and structures that integrate coatings. Coatings play one or more of three key roles in these applications by:

- Improving the product's aesthetic appeal
- Protecting the substrate from a wide range of abuses, such as scratches, impact, corrosion, long term weathering, and bio-fouling
- Providing specialized functionality, such as conductivity, insulation, water repellency, and heat reflection to the product.

Nanotechnology has opened up exciting possibilities in the latter two roles to improve performance attributes of coatings and the associated products.[126]

4.1.1 Anti-corrosive

Aluminum alloys are widely used in the marine industry, unfired welded pressure vessels, and transportation equipment. These alloys are prone to corrosion and wear and, as a consequence, have limited service life. Protection of aluminum and its alloys from corrosion is a key requirement for many engineering applications. Sol-gel derived thin films are being investigated as environmentally compliant alternatives for chromate-based conversion coatings, whose strong oxidation properties make them potentially carcinogenic. Hybrid sol-gel nanocomposites have been found to increase the corrosion resistance of aluminum alloys.[127]

Epoxy coatings are frequently used to reduce the corrosion of metallic substrates subject to aggressive electrolytes by acting as a physical barrier layer against the ingress of a deleterious species and by serving as a reservoir for corrosion inhibitors to aid the metal surface in resisting oxidation. The usual epoxy coatings are susceptible to damage by surface abrasion, wear, and cracking. Defects appearing on coating surfaces can act as pathways, accelerating the ingress of water, oxygen, and chloride anions onto the metallic substrate.

Epoxy coatings can be enhanced by the incorporation of nanosized inorganic filler particles, dispersed within the epoxy matrix, to form an epoxy based nanocomposite. Improvements in the anticorrosive properties of epoxy coatings by the addition of ZnO nanoparticles in concentrations as low as 1% have been demonstrated in laboratory studies.[128]

To improve corrosion protection and adhesion of metal substrates to applied paints and finishes, surface pretreatments are used on metal surfaces. One pretreatment is the application of chemical conversion coatings, such as phosphate. Because of the detrimental effects of concentrated phosphate on ground and surface water ecology, corrosion performance and microstructure of nanoceramic-reinforced hexafluorozirconic acid (H_2ZrF_6) conversion coatings on cold-rolled steel substrates also have been studied. These reinforced coatings were found to have better corrosion resistance than bare steel samples.[129]

4.1.2 Thermal Barriers

Metal components of aircraft engines and land-based and marine turbines are exposed to severe operating conditions, including high temperatures, thermal fatigue, wear, erosion, and hot-corrosion which, through different damaging mechanisms, reduce their service performance and life. The application of protective surface coatings makes it possible to increase the durability and reliability of these sensitive pieces of equipment. Modifying material surfaces to enhance wear and corrosion resistance is a common practice for both military and commercial applications.

Titanium has a low density, high strength, wide operating temperature range, excellent corrosion resistance, and other characteristics. The maximum operating temperature range of Ti is only about 600° C and is affected by high temperature oxidation.[130] Thermal barrier coatings (TBCs) are currently used to extend the lifetime of Ni-based and Ti-based alloy components operating in severe environments in land-based turbine and diesel engines. These coatings yield an increase in engine efficiency by allowing for higher combustion temperature and reduced cooling air flow. The selection of TBC materials is restricted by some basic requirements, such as high melting point, lack of phase transformation between room temperature and operation temperature, low thermal conductivity, chemical inertness, thermal expansion that matches the metallic substrate, good adherence to the metallic substrate, and low sintering rate of the porous microstructure.[131]

Wear-, corrosion-, and oxidation-resistant coatings are produced by high velocity combustion methods, such as detonation gun (D-Gun®, which is a trademark of Praxair, Inc.), high velocity oxy-fuel (HVOF), high velocity air fuel (HVAF), or lower velocity flame spray. Higher temperature plasma processes, such as air plasma spray (APS), are commonly used to deposit TBCs, such as yttria-stabilized zirconia (YSZ), which also is processed by electron beam physical vapor deposition (EBPVD).[132]

Nanostructured materials are a promising avenue for the development of modern TBCs to improve the efficiency of turbine engines. Nanostructured zirconia-based TBCs have received considerable attention because of some extraordinary properties not found in conventional counterparts. Researchers have shown that the development of nanostructured coatings might enhance the performance of TBCs due to the decrease of thermal conductivity, increase of bonding strength, and improvement of thermal cycling lifetime.

Zirconia-based thermal barrier coatings are an attractive option for enhancing the efficiency and durability of gas-burning engines because of their inherent capability of providing higher thermal efficiencies to fossil-fuel-fired energy conversion systems. Magnesia-stabilized zirconia (MSZ) ceramic powders have been used for more than 30 years to protect sheet metal combustors, molds and troughs, missile nose cones, and refining operations. Because the thermal conductivity of MSZ depends on the size of the particles, nanostructured zirconia-based TBCs deposited by atmospheric plasma spraying have received considerable attention. Experimental results indicate that the thermal conductivity and diffusivity of nano-MSZ are lower than that of traditional MSZ.[133]

4.1.3 Hydrophobic

Factors impacting the waterproofing of surfaces were first examined critically by Robert N. Wenzel in 1936. Wenzel recognized the importance of the preservation of the porosity of a woven material when applying a waterproofing coating. In short, Wenzel's research determined that micro and nanostructures on the surface can modify the wetting property of the solid surface.[134]

Nature has shown examples of how micro- and nanotextured surfaces can become superhydrophobic. Synthetic microstructures with surfaces that mimic lotus leaves have been designed to have high water repellency by increasing the microscopic surface roughness to support liquid droplets, with air pockets between regions of solid surface.[135]

Textiles with a superhydrophobic coating could be used as water-resistant apparel and would generally be useful for any kind of application in which textile surfaces are exposed to the environment. An advantage of superhydrophobic textiles compared to traditional waterproofing techniques is that the fibrous structure is maintained while the substrate stays breathable.[136]

In most studies, the waterproofing of textiles is considered a primary potential application of the superhydrophobic effect. While textile manufacturers tend to focus on a superhydrophobic material's ability to prevent wetting of the textile, even upon full immersion in water, by forming a thin layer of air between the textile and a liquid, such a layer could also significantly reduce frictional drag in water.[137]

In addition to their functionality in drag reduction, superhydrophobic coatings and oil-modified superhydrophobic coatings could greatly reduce or even eliminate many of the effects of ice storms and aircraft icing. Surface icing of aircraft, wind turbines, and power lines can cause serious problems, including power grid disruptions, decreased aircraft performance, loss of visibility through windshields, and component strain from buildup on exposed surfaces. Development of superhydrophobic materials also is expected to contribute to protection from ice buildup, because water that is unable to accumulate on a surface has little chance to condense and freeze.[138]

In 2013, hydrophobic and superhydrophobic coatings with different wetting behaviors were prepared using silicone rubber doped with nanopowders of TiO_2, ceria (CeO_2) and carbon black. Researchers studied the freezing behavior of small water droplets on a series of samples with different roughness and observed a correlation between rougher surfaces and longer freezing delays. The maximum freezing time for water droplets on the sample surfaces correlates with the nanostructured coatings doped with CeO_2 and TiO_2 (~780 and ~740 s, respectively). The water droplet freezing times for samples doped with carbon black particles or non-doped polyurethane were shorter, also exhibiting a good inverse correlation with surface roughness. For comparison, the water droplet freezing time on the non-coated mirror-polished aluminum surface was within a few seconds.[139]

Experiments with ZnO microhairs arranged in smooth, microstructured, and nanostructured surfaces showed that the nanostructured surfaces inhibited ice formation in a water droplet longer in a subzero environment than either the microstructured or smooth surfaces.[140] In another set of experiments, a superhydrophobic surface developed by spray coating a nanocomposite film, consisting of perfluorodecyltrichlorosilane modified silica nanoparticles dispersed in a silicon polymer, caused water droplets to slowly flow from the treated surface while the droplets spread on the untreated aluminum substrate. As predicted, the hydrophobicity allowed the treated samples to shed water before icing could occur.[141] However, investigation of a superhydrophobic SiO_2 nanocomposite film suggests that gradual mechanical damage may occur during repetitive icing/deicing cycles.[142]

4.1.4 Biofouling

Biofouling, the accumulation of biological matter, such as microorganisms, plants, algae, or animals on seagoing vessels and underwater structures, increases operational and maintenance costs. A biofilm 1mm thick can increase the ship hull friction by 80%, resulting in a 15% loss in speed. Similarly, a 5% increase in biofouling increases ship fuel consumption by 17%, leading to a 14% increase carbon dioxide (CO_2), nitrogen oxides (NO_x), and SO_2 emissions.[143]

Toxic substances, such as Cu, arsenic, lead, mercury, and tin compounds, have been used in antifouling paints for a long time to prevent the adhesion and growth of fouling organisms. These modern antifouling paints have reduced biofouling, but environmental and regulatory concerns regarding toxic leaching of chemicals from the paints make finding a better solution for use on Navy ships and underwater structures a major priority.

In addition to the growth of organics, biofouling may initiate inorganic fouling, where biocorrosion causes the formation of corrosion particles. Such fouling is prevalent in boilers, cooling condensers, desalination plants, food-processing equipment, geothermal plants, and oil production equipment. Heat exchangers can develop hard deposits, called scale, or more porous deposits, such as sludge.[144] Low permeability paint, used as a water and vapor barrier, is the standard way of protecting metal surfaces from corrosion. Such paint works well until the paint develops micro-cracks. The micro-cracks hold water, and the paint, acting as a barrier, holds the water in the micro-cracks, which then promotes corrosion.[145]

Cu has been known to possess antimicrobial properties since as far back as the Phoenician era (1500 to 300 BC) when ship hulls were sheathed in bulk Cu to prevent the effects of biofouling. Research has compared the antifouling effectiveness of Cu at the macro- micro-, and nanoscale. A slime assay was used as a qualitative and quantitative assay to detect glycocalyx, a biochemical attributed to biofilm forming organisms. A linear correlation was noted between the particle size and the quantity of biomass present on the samples.[146]

Antifouling properties of both ZnO[147] and Ag[148] have been investigated extensively. The colonization of aquatic microorganisms on submerged surfaces at their early stage is similar to a bacterial colonization process; thus, the bacteriostatic properties of Ag also can be meaningful for antifouling applications. Antifouling performance of the polydopamine (PDA)-mediated silver nanoparticle (AgNP) coatings were tested on glass, polymer, and stainless steel by immersing the substrates in seawater growth. The samples were checked for their surface settlement of *Dunaliella tertiolecta* (*D. tertiolecta*), a type of motile, unicellular, green microalga which is common in marine waters. Area density of *D. tertiolecta* cells was substantially reduced in samples containing AgNPs when compared to control samples.[149] In a similar study, PVC samples coated with AgNPs were immersed in natural seawater for 45 days. Control samples showed significant algal growth, while Ag-coated samples showed no biomass coverage.[150]

Addition of biocidal components to surface coatings is not the only method employed to inhibit biofouling. Modification of the topographical structure of the surface in question, thereby limiting the ability of individual cells to attach to the surface, colonize, and form biofilms, is also an effective method for reduction of biofouling. Multiple research groups have demonstrated that micro- and nanoscale topographies significantly reduce bacterial biofouling, for both individual cells and bacterial biofilms. Xu et al. hypothesized that surface textures with dimensions less than the size of a single bacterial cell could reduce the surface area accessible to bacteria, resulting in a decreased probability of interaction with, and attachment to, the material surface.[151]

Biofouling can be reduced through underwater superhydrophobicity as a result of the development of an air film between the coated surface and the water. Superhydrophobic surfaces usually possess architectures containing micro- or nanostructures and chemical compounds with low interfacial energy. Water droplets on these surfaces are only partially in contact with the top of the architecture, allowing for the formation of a large air/liquid interface fraction, known as the Cassie-Baxter state.[152]

The reduction of the wetted area minimizes the probability that biological organisms encounter a solid surface. A variety of micro- and nanostructured surfaces, inspired by the naturally antifouling surfaces of the shells of invertebrates, shark skin, and lotus leaves, exhibit antifouling properties.[153] When the anti-biofouling properties of some superhydrophobic coatings have been subjected to scientific scrutiny, few micro-organisms attached to the superhydrophobic surfaces in the first weeks after immersion. However, after long exposure to a real marine environment, the antifouling property of the superhydrophobic coatings gradually deteriorated, indicating that the long-term stability still needs to be addressed.

De Nicola and colleagues have taken advantage of the inherent surface roughness and iron content of stainless steel to grow MWCNTs without the addition of external catalysts or pretreatment of the steel.[154] This nanotube layer exhibited long-term high contact values and high adhesive force with water.[155] A zinc-oxide nanostructure formed from woven nanorods, developed by Xia and Wu, exhibited even better drag reduction than traditional, vertically-aligned nanostructures.[156]

4.2 Concealment

There has been extensive expansion in the field of sensors and signal processing technologies that has allowed for the development of sensors that cover the entire electromagnetic spectrum, providing nearly perfect battlefield intelligence in real time. Combatants employ a variety of sensors to detect and identify soldiers, equipment, and support installations. Beginning in World War II, designers of tactical camouflage, concealment, and deception have sought solutions that could address more than just the visible portion of the spectrum. To combat new sensing and detection technologies, camouflage paint, paint additives, tarps, nets, and foams have been developed for visual camouflage and thermal and radar signature suppression. Stealth materials help to defeat sensors that detect objects by capturing the emitted or reflected electromagnetic radiation from the surface of the object.

Conceptualizing nanomaterials for camouflage and stealth applications requires consideration of some of their electromagnetic, thermal, chromogenic, and mechanical properties. This will enable researchers to create low weight, high strength structures, and coatings with a scope of altering their reflection/absorption/scattering characteristics of electromagnetic radiation in visible, infrared, and microwave regions.

4.2.1 Camouflage

Given the sensitive nature of research into camouflage techniques, it is not surprising that much of the work on the synthesis, formulation, and application of colorants remains unpublished. In the visible spectrum, the use of camouflage is an attempt to mimic natural or urban backgrounds in terms of color, patterns, gloss, and texture. Since the advent of infrared-sensitive equipment, it has been necessary to account for infrared (IR) reflectance of paints and garments in the 700–1300 nm waveband.[157] Some pigments with the potential to be used as near infrared (NIR) reflective pigments are shown below (See Table 8).

Carbon black has been used in military uniforms for several decades because of its ability to absorb radiation in the NIR spectrum. This enables soldiers to be cloaked from IR cameras as the fabrics absorb the IR radiation generated by the human body.[158] More recently, the reflectance characteristics of printed cotton/nylon fabrics with pigment printing pastes containing different loads of TiO_2 microparticles and nanoparticles has been investigated. Researchers determined that the smaller size of the TiO_2 nanoparticles produced a higher reflectance in the IR band when compared to microparticles.[159] A similar study investigated the reflectance characteristics of printed cotton/nylon fabrics with pigments containing varying concentrations of MWCNTs to simulate the dark brown, light brown, and olive green shades normally used in camouflage garments in desert regions. The study concluded that adding MWCNT-doped pigment with concentrations ranging from 0.04 – 0.12 g/kg could reduce the visible-NIR reflectance noticeably, even at lower concentrations.[160]

4.2.2 Radar

Microwave absorbing, or radar absorbing materials (RAM), have applications in stealth technology for military aircraft, reduction of television image interference due to high-rise buildings, and dark room protection from microwave radiation. Microwave absorber materials normally are characterized based on the absorption mechanism, such as dielectric absorbers, magnetic absorbers, and hybrid materials. Dielectric absorber materials typically involve polymers and their composites, such as epoxy, olefin, polyester, polyethylene terephthalate (PET), and linear low-density polyethylene (LLDPE) filled with carbon fiber and multi-walled CNTs. Magnetic absorbers, on the other hand, typically involve hard and soft ferrites that normally are used in relatively high-frequency regions.[161]

During World War II, the Germans developed a ferrite-based radar absorbing paint. Since then, scientists have expanded their investigation into the use of ferrite-based materials in their pure form and as composites. Synthesized $CoFe_2O_4$ nanoparticles possess excellent microwave absorption properties, with minimum reflection losses of -55 dB at thicknesses of 2 mm.[162] The major drawback of soft ferrites, such as $NiFe_2O_4$, is their limited absorption bandwidth and selective absorption frequencies. However, $NiFe_2O_4$ and composites, including those with large-diameter graphene oxide sheets, show high absorbance (~10 dB) of microwave radiation from 1 MHz to 3 GHz with an absorption bandwidth covering the entire L and S bands.[163]

Hexagonal ferrite (hexaferrite) absorbs microwave energy by loss interaction of the magnetic field of the wave with the magnetization of the individual ferrite particles. $Ba_2Co_2Cr_2Fe_{12}O_{22}$ nanoparticles have demonstrated a maximum reflection loss of -40 dB at 14 GHz at a thickness of 1.5 mm, suggesting their potential as a suitable RAM.[164]

4.3 CBRN Protection

Throughout the history of humankind, any new scientific discovery or technological advance has carried the risk of a dual use for peaceful purposes or for warfare. In the field of non-conventional chemical/biological/radiological/nuclear (CBRN) weapons, the recent exponential development of nanoscience and nanotechnology is leading to both the development of new and unpredictable threats and to the development of innovative and efficient tools for the detection, monitoring, and abatement of CBRN agents.[165]

Current physical protective measures deployed against chemical weapon agents include gas masks and chemical-resistant suits, boots, and gloves that protect the user from exposure. Chemical protective suits will prevent dermal exposure to the chemical agent, but, if the chemical threat does not spontaneously degrade over short periods of time, the personal protective equipment still requires decontamination and disposal. This could lead to accidental exposure and necessitates the development of novel materials that will combine protective measures with in situ chemical agent degradation.[166]

Many advances have been made to design methodologies and strategies to neutralize harmful chemical warfare agents. The first and longest used methods have been highly reactive chemicals, such as bleaching powder, potassium permanganate, m-chloroperoxybenzoic acid, magnesium monoperoxyphthalate, potassium persulfate, oxons, sodium hypochlorite, and hydrogen peroxide (H_2O_2).

The exposed active sites of a solid catalyst must interact efficiently with substrate molecules and promote their transformation. Because of the high surface area to volume ratio of nanoparticles, most heterogeneous catalysts are based on nanoparticles: namely, inorganic oxide nanoparticles (where metal atoms are in high-oxidation state in combination with oxygen) and/or metal nanoparticles (with metal sites in a low-oxidation state).[167]

CNTs have been used to develop sensors for the detection of organophosphates, and CNT-based materials have been designed for the degradation of blistering agents. Single-wall CNTs have been used as structural support for a Cu-containing catalytic polymer that catalyzes organophosphate nerve agents and retains its catalytic properties after repeated uses.[168]

Inorganic metal oxides, such as niobium oxide (Nb_2O_5), Al_2O_3, TiO_2, and magnesium oxide (MgO), also have been studied for their oxidation and/or degradation reactions with chemical warfare agents. In laboratory tests with a sulfur mustard simulant, the Nb_2O_5 proved to be an extremely active catalyst in the degradation of the simulant, with an acceptable degree of environmental compatibility. ZnO showed promising performances in terms of abatement activity and selectivity toward desired non-noxious catalysis products, but displayed a good deal of toxicity against environmental bacteria. TiO_2 performed less effectively than commercial M75 ammunition powder. Nanosized Al_2O_3 proved to be a moderate catalyst for the oxidative abatement of the simulant.[169] In a similar study, ZnO nanoparticles were found to have a high catalytic potential for the decontamination of a sulfur mustard simulant, especially when using n-hexane as the solvent.[170]

4.4 Nanoenergetics

Energetic materials are a major component of weapons systems used by all branches of the U.S. military. Their primary uses are in explosives and in gun and missile propulsion. Over the last century, new chemicals have been discovered or designed for rapid release of energy in either relatively simple compositions, like that used in certain warheads, or in more complex formulations like the advanced composites used as propellants. The high material density of solid propellants, in particular, leads to high energy density needed for producing the required propulsive force.[171]

Nanoenergetic materials (nEMs) have improved munitions performance compared to larger materials as they have more surface area per volume than traditional powders. They increase the speed of reaction, providing quicker ignition and creating larger energy releases in a shorter amount of time.

Aluminum (Al) is a commonly used fuel supplement in solid rocket propellants because of its ability to increase the overall system level performance of a rocket motor. The addition of Al to composite rocket propellants increases the specific impulse as well as the density of the propellant, thereby increasing the total energy density. Increases in propellant burning rate are desirable to improve the mass fraction of the propellant and, ultimately, system level performance of a solid rocket motor. The replacement of micrometer-sized Al with nanoscale Al in the propellant matrix has shown to increase propellant burning rates by as much as 100%. This, in part, is due to the lower ignition temperatures of Al nanoparticles in comparison to micrometer sized Al.[172]

Aluminum nanoparticles (Al-NPs) are the subject of considerable research in energetic materials due to their high energy density, low cost, and high reactivity. Two relevant applications are the addition of Al-NPs to high explosives to boost the energy density, and the use of Al-NPs as a fuel in binary thermite systems. Al particles form an Al_2O_3 coating in the presence of air. While micron-sized Al particles have been reported to have an ignition temperature that is very close to the melting point of the oxide shell (~2300 K), Al-NPs have been observed experimentally to ignite closer to the melting temperature of Al (~930 K).[173] A multimillion atom molecular dynamic simulation performed at the University of Southern California has revealed significant effects of the structure of oxide shells on the burning behavior of Al-NPs. Using a crystalline shell, it was discovered that radial expansion of the Al-NPs, followed by its contraction, forms pores in the shell, resulting in enhanced oxidation reactions.[174]

Comparative studies of solid propellants with and without nanoalloys (Zn–Cu, Zn–Ni, Zn–Fe), where nanoalloys are used as catalysts, show catalytic activity of metal alloys was better than the activity of alloys with ammonium perchlorate. A burning rate study shows enhancement in solid propellant burning rate with nanoalloys. The Zn-Cu nanoalloy showed the best performance, with a burning rate enhancement of 1.67 times the control rate.[175]

While Al is the most commonly used metallic fuel, other metals also are of interest. In particular, Ti and Zr have been studied for their application in pyrotechnics, fire safety, and flame synthesis. Recent interest is also based on the potential of both metals in forming special energetic alloys and formulations. When compared to aluminum, both Ti and Zr have much higher melting points, and are less reactive with oxygen. Nanosized Ti and Zr particles provide the added advantage of higher reactivity and energy release rates owing to the higher surface area to volume ratio compared to their bulk counterparts. Experimental observation of particles of both Ti and Zr concluded that burn times of both metals increase as the particle size increases, although burn times for both metals were slower than those measured for Al.[176]

Table 8: Potential Near-Infrared **Reflective Pigments**

Pigment	Overall NIR reflectance over white (700-2500 nm range)	Overall NIR reflectance over black (700-2500 nm range)
TiO_2 white	0.88	0.64
Nickel titanate yellow	0.78	0.64
Chrome titanate yellow	0.80	0.61
Iron oxide red (Fe_2O_3)	0.54	0.38
Cadmium orange	0.87	0.47
Cadmium yellow	0.83	0.34
Chromium oxide green (Cr_2O_3)	0.51	0.39
Cobalt titanate teal (Co_2TiO_4)	0.67	0.47
Strontium chromate yellow ($SrCrO_4$)	0.86	0.38
Iron titanium brown spinel (Fe_2TiO_4)	0.68	0.40
Yellow oxide (FeO(OH))	0.56	0.29
Chrome yellow ($PbCrO_4$)	0.83	0.34

Table 8: *Potential near infrared reflective pigments (http://coolcolors.lbl.gov/assets/docs/PAC-2003-03-11/Pigment-Highlights-2003-03-09.pdf).*

4.5 Lubricants

Wear and friction in systems are two of the major causes of machinery energy loss. To overcome these issues, engineers and mechanics turn to the application of a lubricant to machinery. The enhancement of lubricant oil properties is of great importance in the context of protecting machinery from damage and energy loss. Spurred by the need to replace existing oil additives and to develop environmentally benign additives, boosting the tribological performance of lubricating fluids through the addition of nanoparticles has been investigated for some time.

Fullerene-like nanoparticles and nanotubes of molybdenum disulfide (MoS_2) have exhibited very good tribological behavior when used as additives for lubricating fluids, in self-lubricating coatings, and for improving the tribological and mechanical behavior of nanocomposites. When these nanoparticles are doped with rhenium, they exhibit reduced agglomeration and slower tendency to sediment from suspensions.[177] In a separate study, results indicate that the main parameter governing the lubricant efficiency for these particular nanoparticles is their crystallinity, regardless of particle size within the nanoscale range.[178]

The micro/nanostructure of low-friction coatings (i.e., their chemical- and phase composition, as well as the crystallite size) is important because it influences tribological and micro-mechanical properties of the coatings, and, as a result, the tribological and micro-mechanical properties of the system coating/substrate. Nanocomposite coatings are often used to improve tribological properties of metallic materials, decrease the coefficient of friction, and increase the wear resistance under different operating conditions, such as temperature and humidity. MoS_2 is often used as a coating material with excellent self-lubricating properties that result from a layered structure in the hexagonal elementary cell of the material. Weak bonds between individual atoms in the lattice are responsible for the low friction and good lubricating properties of the disulfide coating.[179]

MoS_2 is an important solid lubricant with excellent friction and wear properties under inert or vacuum environments. However, its short life in humid environments limits its applications due to the formation of sulfur dioxide (SO_2) and dihydrogen monosulfide (H_2S) by reacting with water, as does its poor performance at high temperatures resulting from the formation of molybdenum oxide (MoO_2) and molybdenum trioxide (MoO_3) by oxidation at high temperature. Ag is a soft metal which exhibits low shear strength. Additionally, Ag can form silver molybdate with molybdenum disulfide (Ag_2MoO_4), a good lubricant at higher temperatures. Ag–MoS_2 multi-component, nanoparticle-based lubrication systems can significantly reduce coefficient of friction, suggesting that the addition of Ag nanoparticles can prolong the life of traditional MoS_2 nanoparticles during high temperature applications.[180]

4.6 Battlefield Medicine

Nanotechnology is a diverse emerging technology that is expected to have a substantial impact on medical technology now and in the future. The potential impact of novel nanomedical applications on disease diagnosis, therapy, and prevention is foreseen to change health care in a fundamental way. An increasing number of products are currently under clinical investigation, and some products are already commercially available, such as surgical blades and suture needles, contrast-enhancing agents for magnetic resonance imaging, bone replacement materials, wound dressings, anti-microbial textiles, and microneedles. This section presents the state-of-the-art in the area of promising nanotechnology approaches for medical technology, with particular focus on those applications relevant to combat medicine.

4.6.1 Hemostasis

The majority of combat injuries (70% to 80%) in today's military operations are penetrating, mostly caused by explosive munition fragments.[181] These types of wounds offer unique challenges to medical providers both on the battlefield and during long-term care. Adequate hemostasis after trauma and during surgical operation is a big challenge in modern medicine. About 40% of traumatic injury-related fatalities and more than 90% of combat deaths take place in pre-hospital settings.[182] Approximately 50% of these deaths have been attributed to massive blood loss.[183]

Recent advances in field dressings, including the use of chitosan, Ag nanoparticles, and Cu, may offer improved outcomes following battlefield injuries. Chitosan is a biodegradable, nontoxic, complex carbohydrate derivative of chitin, which is a naturally occurring substance primarily found in the exoskeletons of insects.[184] Several products currently available on the market contain chitosan, including HemCon, Chitoseal, Celox, Tegasorb, and QuikClot.[185]

4.6.2 Wound Care

Once hemostasis has been achieved, therapeutic treatments can be focused on the remainder of the wound-healing process; namely inflammation, proliferation, and remodeling. Any alteration and complications during the wound-healing process, such as bacterial infection or re-injury of the wound site, may lead to a chronic ulcer that fails to heal.[186]

Wounds often provide a favorable environment for micro-organism growth and proliferation. Infection is a leading cause of morbidity and mortality in extensive burn injuries, traumatic injuries, and surgical procedures. The control of infection remains a major challenge in wound management. It is important to create conditions that are innocuous for the host repair mechanisms while being unfavorable to micro-organisms to promote wound healing.[187]

A wide choice of wound therapy options is provided by conventional and modern approaches to wound treatments. Generally, an effective wound dressing has the following properties: (1) a suitable water vapor transmission rate to allow maintenance of a moist environment on the wound beds, without risking dehydration or accumulation of exudates; (2) a high level of fluid absorption capable of removing excessive exudates that can be a source of nutrients for invasive bacteria; (3) sufficient gas permeability for oxygen-requiring reparative processes; (4) a good barrier against the penetration of infection causing microorganisms; (5) antibacterial activity to suppress bacteria growth beneath the dressing; and (6) the absence of any cytotoxic damage to newly forming tissues.[188]

Bacterial cellulose (BC) is a biosynthetic cellulose produced by strains of the Gram-negative bacterium Acetobacter xylinum using glucoses as the common substrate. This material is characterized by high purity, tensile strength, water-holding capacity, and biocompatibility. However, BC does not have any inherent antibacterial property, inhibiting its ability to prevent bacterial infection in treated wounds. As a solution to this shortcoming, several studies have added Ag and Ag compounds as an antibacterial adjunct to the BC, resulting in some success in burn wound healing.[189]

5. Conclusion

Nanotechnology is a diverse field with diverse practices. One of the broadest areas applies to surface applications, but they also happen to be some of the most promising technologies regarding the use of engineered nanomaterials. Specifically, the use of nanotechnology for surface applications has a myriad of practical uses to the defense industry. Nanomaterials, such as nanoceramics, can be used on hard surfaces to improve vehicle armor. New types of nanofibers can be incorporated into clothing to create smart textiles that add a new level of functionality in fabrics. Superhydrophobic coatings and flame retardant materials made from carbon nanotubes and other advanced nanomaterials provide an extra level of protection to a variety of surfaces. Even though the use of certain nanomaterials such as graphene, is currently limited, a significant amount of data on other nanomaterials exists to support their use in practical applications. Defense acquisition strategies should focus on what is reasonably achievable in the near-term and this state-of-the-art report has provided a thorough overview of nanotechnologies worth additional research and future investment.

The specialized microscopes to unlock the mysteries and potential of nanomaterials were invented only 30 years ago. For more than half that time, DoD and its eight research organizations have focused on research that has and will continue to yield products to improve the nation's warfighting capability, including keeping service members safer and healthier. This SOAR looks at promising research on nanotechnology surface applications that may meet the military's need for lighter, safer, and more efficient products. Many of the products are close to commercialization or already on the market.

Appendix A: Summary of Research at Relevant Institutions

Appendix A: Summary of Research at Relevant Institutions					
Institution Name	Naval Research Laboratory	Naval Research Laboratory	Naval Research Laboratory	Naval Research Laboratory	DOE-Center for Nanoscale Materials
Website URL	http://www.nrl.navy.mil/media/news-releases/2016/NRL-Reveals-Novel-Uniform-Coating-Process-of-pALD	http://www.nrl.navy.mil/media/news-releases/2014/nrl-researchers-develop-harder-ceramic-for-armor-windows	http://www.nrl.navy.mil/media/news-releases/2013/nrl-develops-polymer-nanofibers-for-chemical-and-biological-decontamination	http://www.nrl.navy.mil/nanoscience/sites/edit-www.nrl.navy.mil.nanoscience/files/files/nanoelectronics_poster3.pdf	http://science.energy.gov/bes/highlights/2015/bes-2015-10-h/
Lead Researcher	Dr. Kedar Manandhar	Dr. James Wollmershauser	James Wynne	Dr. Eric Snow	Anirudha Sumant/Kathleen Gregar
Article Date	4/20/2016	4/29/2014	3/27/2013		10/1/2015
Research Title	NRL Reveals Novel Uniform Coating Process of p-ALD	NRL Researchers Develop Harder Ceramic for Armor Windows	NRL Develops Polymer Nanofibers for Chemical and Biological Decontamination	Carbon Nanotube Networks: A New Nanomaterial for DOD Applications	Near Zero Friction from Nanoscale Lubricants\
Research Abstract	Scientists at the U.S. Naval Research Laboratory (NRL) have devised a clever combination of materials - when used during the thin-film growth process - to reveal that particle atomic layer deposition, or p-ALD, deposits a uniform nanometer-thick shell on core particles regardless of core size, a discovery having significant impacts for many applications since most large scale powder production techniques form powder batches that are made up of a range of particles sizes.	The Department of Defense needs materials for armor windows that provide essential protection for both personnel and equipment while still having a high degree of transparency. To meet that need, scientists at the U.S. Naval Research Laboratory (NRL) have developed a method to fabricate nanocrystalline spinel that is 50% harder than the current spinel armor materials used in military vehicles. With the highest reported hardness for spinel, NRL's nanocrystalline spinel demonstrates that the hardness of transparent ceramics can be increased simply by reducing the grain size to 28 nanometers. This harder spinel offers the potential for better armor windows in military vehicles, which would give personnel ***Continued on next page***	Chemical and biological threats pose a significant concern not only to the modern warfighter but an ever-increasing number of individuals and groups. This threat is compounded by the persistence of these agents and the possibilities of causing increased personnel exposure by the relocation of contaminated materials.	C nanotubes are 1 nm-diameter "straws" of C atoms that exhibit amazing electronic and structural properties. However, their small size poses a barrier for integrating them into an electronic manufacturing process. A recent NRL invention offers a solution to this problem in the form of a macroscopically sized C nanotube network (CNN). CNNs represent a new manufacturable nanomaterial with many Navy and DOD electronic applications. CNNs form electrically continuous thin films that can be deposited onto many different types of surfaces for electrically active coatings.	Superlubricity is the state in which the friction between two sliding surfaces is reduced to nearly zero. Friction and wear are the primary modes of mechanical energy dissipation in moving assemblies, thus it is highly desirable to minimize friction in real-world engineering-based applications. Structural defect issues, however, have stymied the realization of superlubricity. Previous studies have shown the beneficial effect of using graphene to reduce friction. A new study demonstrates that superlubricity can be achieved at the macroscale in a dry environment by the addition of nanodiamonds and graphene flakes .between two surfaces, one made of silicon and one made of diamond-like carbon. ***Continued on next page***

Appendix A: Summary of Research at Relevant Institutions					
Institution Name	Naval Research Laboratory	Naval Research Laboratory	Naval Research Laboratory	Naval Research Laboratory	DOE-Center for Nanoscale Materials
Research Abstract (Continued)		***Continued from previous page** and equipment, such as sensors, improved protection, along with other benefits. This research was reported in the January 30, 2014, issue of the journal *Acta Materialia.*			***Continued from previous page** In this system, the coefficient of friction is just 0.004, and contact areas are reduced by more than 65%. Analysis of the wear debris revealed that the graphene flakes form nanoscroll-like features wrapping the nanodiamonds. Computer simulations show that more and more graphene flakes scroll with time, gradually reducing the contact area between the nanoscrolls and the diamond-like carbon surface, which allows superlubricity to be attained.
Application of Research	Applications for this research demonstrate implications for use in materials like abrasion resistant paints, high surface area catalyst, electron tunneling barriers, ultra-violet adsorption or capture in sunscreens or solar cells and even beyond when core-shell nanoparticles are used as buildings blocks for making new artificial nanostructured solids with unprecedented properties.	"Harder nanocrystalline spinel windows can be made thinner and still meet the current military specifications. This thinness translates to weight savings on the vehicle. So the NRL-developed nanocrystalline spinel brings improvements in hardness, window thickness and weight, and cost. Beyond the use for a harder spinel in armor windows, there could be other potential DoD and civilian applications in better/stronger office windows, smartphones and tablets screens, military/civilian vehicles, space vehicles, and even extraterrestrial rovers."	"Due to the promising decontamination performance the coatings experienced against a variety of pathogens and chemical agents, we are now extending the additive-derived decontamination capacity to include materials that cannot be painted or coated, such as polymer nano- and microfibers that can be utilized for a variety of applications such as garments."	Different types of surfaces; poster depicts transparent film that can fit on curved head-up displays, avionics and navigational displays in aircraft	The new system reduces contact areas and thus reduces friction to near zero. Creating a low-friction situation has the potential for substantial cost savings because friction accounts for most of the energy lost in moving mechanical assemblies and wear accelerates mechanical failures.
Category	Hard surfaces	Hard surfaces	Soft surfaces	Hard surfaces	Nondurable
Term	Paints		Garments (clothing)		Lubricant

Appendix B: Applicable Research from ORAU University Consortium

NORTH CAROLINA AGRICULTURAL AND TECHNICAL STATE UNIVERSITY

North Carolina A&T State University

Technical POC: James Ryan, Dean, Joint School of Nanoscience and Nanoengineering, jgryan@ncat.edu.

The Joint School of Nanoscience and Nanoengineering (JSNN), a collaboration between North Carolina A&T State University and the University of North Carolina at Greensboro, has a broad array of equipment and capabilities for these applications as well as experts in their use and associated research. A partial list of the major equipment with the ability to analyze hard surfaces is provided at the end of this document.

JSNN's 105,000-square-foot facility has extensive laboratories including a 7000-square-foot combination nanoelectronic and bio cleanroom, an analytical laboratory, an NMR facility (with Agilent 400 MHz and 700 MHz systems), microscopy facilities (detailed later in this letter of interest), a nanoparticle and nanofabrication facility, a visualization facility, a nanobiophysics lab, a nanochemistry lab, a nanobiology lab, a BSL3 facility, a genomics lab, and a Cray supercomputing facility.

JSNN has three prominent programs focused on interaction with industry and therefore maintaining high availability and excellent performance with our toolset has become a way of life.

- JSNN is a site for NSF's National Nanotechnology Coordinated Infrastructure through its collaboration with NC A&T State University and Georgia Tech in the Southeastern Nanotechnology Infrastructure Corridor (SENIC) team. This designation has increased the research profile of the school and has brought in additional academic and industrial partners as well as financial support for five years.
- JSNN's Nanomanufacturing Innovation Consortium (NIC) offers leverage to the high tech business community and has helped JSNN to increase its economic impact. Employees of its 32 partner companies routinely use JSNN instrumentation (and in particular its microscopy assets). The revenue from corporate use supports the maintenance of the school's equipment.
- JSNN has an extensive mechanical testing and chemical analysis toolset for our nanomaterials and nanochemistry research. These capabilities have enabled the formation of the Gateway Materials Testing Center (GMTC) which provides testing services for aerospace, automotive a textile companies. The testing lab is ISO 17025 certified.

The microscopy assets of the Joint School of Nanoscience and Nanoengineering are summarized below (as a way of addressing the ability to analyze hard surfaces).

Helium Ion Microscopy Facility

The Joint School of Nanoscience and Nanoengineering Helium Ion Microscopy (HIM) Facility houses a Zeiss Orion Helium Ion microscope, one of only twenty dedicated HIM microscope facilities in the world, and the only HIM facility in the southeastern USA. HIM is a relatively new scanning particle beam microscopy technique that offers several advantages over standard scanning particle beam imaging techniques that include increased absolute resolution (~0.3nm resolution), extremely high depth of field, and enhanced imaging of uncoated soft materials such as polymers and biological materials. HIM data collection and imaging formation is performed through two separate detectors, a secondary electron detector that is similar to standard Scanning Electron Microscopy, and a Helium ion backscatter detector, which provides semi-qualitative elemental analysis of a sample. In addition to imaging, the HIM is also capable of nanoscale He ion beam milling, used in our facility to generate nanopores and other nanoscale features < 5nm.

Scanning/Transmission Electron Microscopes (SEM and TEM) Facilities

JSNN houses three scanning electron microscopes: A Zeiss Auriga Dual Beam (Focused Ion beam milling/SEM), a Zeiss Evo Environmental SEM, and a Hitachi 4800 SEM. Each SEM is equipped with Energy-dispersive X-ray spectroscopy detectors to facilitate simultaneous elemental analysis during image capture. The Dual Beam Auriga SEM enables standard SEM imaging and focused ion beam milling via a gallium ion source in a broad range of materials including biological, polymers, metallic, and semiconductor materials. The dual beam nature of the Auriga allows for sequential FIB milling and SEM imaging, enabling the virtual 3D nanoscale reconstruction of a sample. The Auriga SEM is equipped with two secondary electron detectors, a backscatter electron detector, and allows for scanning transmission electron microscopy (STEM) functionality as well. JSNN's Zeiss Evo LS ESEM allows imaging of 'wet' hydrated samples and samples in different gaseous environments. In addition to imaging, the EVO LS ESEM is also equipped with a beam patterning system permitting e-beam lithography. The JSNN Hitachi 4800 is a fully function SEM with detectors for secondary electron, backscatter electrons, and elemental analysis via EDX. The JSNN Transmission Electron Microscope facility is equipped with a Carl Zeiss Libra 120 Plus TEM Microscope with full electron energy loss spectroscopy (EELS) capability for elemental analysis.

JSNN Confocal and Optical Microscope Facility
The JSNN optical microscope facilities houses three optical microscopes: a Zeiss Axio Observer Spinning Disc Confocal microscope, a Zeiss Axio Observer A1 Fluorescent and Polarized light microscope, and a Horiba XploRA One Raman Confocal Microscope System. The Spinning Disc system is fully outfitted with objectives ranging from 10X-100X and four channel laser excitation from the near UV into the near infrared range. Additional features include a stage mounted temperature controlled CO2 chamber for long term live cell imaging. The Zeiss Axio Observer A1 is an upright compound microscope that is fully equipped four channel wide-field fluorescence, bright-field, dark-field and polarized light microscopy. The Horiba XploRA One Raman Confocal Microscope System allows for simultaneous chemical analysis via RAMAN spectroscopy during the imaging of materials including live cells.

JSNN AFM Facility
The JSNN AFM facility houses an Agilent Technologies 5600 LS Series Atomic Force Microscope. This instrument is equipped for various scanning probe techniques, including standard topography mapping of various materials including soft polymeric materials and biological samples, force spectroscopy and the determination of mechanical properties of a variety of materials including living cells, the mapping of surface functionalities, and the physicochemistry of surfaces and nanostructured materials.

JSNN Sample Prep Room
In addition to the microscopes, the JSNN sample prep room is equipped to serve all electron, atomic force, and optical sample preparation needs. The room includes a fully functional vented hood, refrigerators, full stock of stains and chemical fixatives, a South Bay Technologies PC2000 Plasma Cleaner, critical point dryer and critical CO2 preparation tool, and a Leica EM ACE600 High Vacuum Coater.

Also attached is a brief summary of our Gateway Materials Testing Center for aerospace, automotive and textile testing.

For soft surfaces, we have an environmental SEM, a nanoindentor and we will soon receive an Imprio Nanoimprinter. We also have several types of patterning techniques for nanomaterials including both direct write capability and optical lithography. We also have extensive biotechnology capability including a BSL3 lab, a genomics lab and nanobiology and nanochemistry labs.

For non-durable goods, we have all manner of coating capability including an e-beam evaporator, sputtering system (to be delivered in September), Plasma Enhanced Chemical Vapor Deposition (PECVD), Chemical Vapor Deposition (CVD), spin-apply, 3D printing and many heat treatment methods including an autoclave for composite materials, a vacuum furnace capable of 1500C processing and various high temperature air box furnaces.

For a complete tool listing, please visit http://jsnn.ncat.uncg.edu.

JSNN Equipment List

- Agilent Technologies 400 NMR 400 Mhz NMR Spectrometer
- Agilent Technologies 700 NMR 700 Mhz NMR Spectrometer w/ Liquid Solid & Cryo Probe Capability
- Agilent Technologies Oxford Gemini X-Ray Diffractometer
- Horiba XploRA One Raman Confocal Microscope System

- Horiba FluoroMax-4 Spectrofluorometer
- Varian 240 MS/GC Ion Trap Mass Spectrometer
- Varian 320 MS GC/LC Triple Quad Mass Spectrometer
- Varian 500 MS LC/MS Ion Trap Mass Spectrometer
- Varian Cary 6000i UV-Vis Spectrophotometer
- Varian 670 FTIR Spectrometer
- Varian 670 FTIR/610 Spectrometer w/Single Point Detector
- Varian 710 ES ICP Axial Spectrometer
- Cascade REL – 4800 Probe Station
- Kiethley Instruments 2400 Digital Source Meter
- Kiethley Instruments 2602A Dual Channel Source Meter
- CEM Corp 908005 Microwave Reactor Discovery System
- Horiba SPRi-LAB+ Surface Plasma Resonance System
- Microtrac Inc. NPA152-31A Zetatrac
- Instron 3384 Materials Testing System w/Environmental Chamber
- Instron 8802 Dynamic Testing System
- Instron 9250G Impact Test System
- LR Technologies ST867TUL240V90KW Walk in Oven
- PerkinElmer DMA 8000 Dynamic Mechanical Analyzer
- PerkinElmer DSC 6000 Differential Scanning Calorimeter
- Rame Hart 260-F4 Goniometer/Tensiometer
- Tenney C-Evo Environmental Test Chamber 10cu. ft.
- ThermTest Inc. TPS2500S Thermal Property System w/Anisotropy & Slab Modules
- Flow International M2-1313b Water Jet Cutting Table
- TSI 3785 Water-based Condensation Particle Counter
- Material Testing Tech ASTM.CO097.11.N Flatwise Tension Fixture w/5 sets of 2 in. sq. Bonding Blocks
- Material Testing Tech ASTM.C0393.17 Sandwich Long Beam Flexure Fixture
- Material Testing Tech ASTM.D0790.22 Three & Four Point Flexure Fixture
- Material Testing Tech ASTM.D3410.20.S IITRI Compression Loading Test Fixture
- Material Testing Tech ASTM.D5379.16 V-Notched Beam Test Fixture
- Material Testing Tech ASTM.D6484.10 Open Hole Compression Test Fixture
- Material Testing Tech ASTM.D6641.10 Loading Compression Test Fixture
- Material Testing Tech ASTM.D7137.10 Compression After Impact Test Fixture
- Wyoming Test Fixtures ASTM.D3344 Short Beam Shear Three/Four Point Fixture
- Wyoming Test Fixtures ASTM.D5379 Iosipescu Shear Test Fixture
- Wyoming Test Fixtures ASTM.D6641 Combined Loading Compression Test Fixture
- Malvern Instruments ZEN3600 Zetasizer Nano-ZX
- Nanosight LM10-HSBF Nanoparticle Characterization
- TA Instr. Q200 DSC w/ Cooling System
- TA Inst. TGA Q500 Thermogravimetric Analyzer

Duke University

POC: William Joines, william.joines@duke.edu

Duke University has extended some work that was started in WWII; namely, the Jaumann shield and the Salisbury screen. These involve placing thin conductive films at quarter wavelength intervals from a highly conductive surface to prevent or minimize reflections. We have developed the design theory to achieve a maximally-flat response for any number of layers, where the bandwidth for negligible reflections increases with the number of layers. But beyond that, by just adjusting conductivities and spacing, we can achieve better than 10 dB return loss (10% reflected) over the entire frequency range from 1 to 100 GHz (or 300 nm to 3 nm wavelength). We believe these results could be extended to even higher frequencies. Materials can be found or developed that would allow us to create a uniform of layered material that makes soldiers on the battlefield and military vehicles undetectable by radar. Zero reflection would not be required, but just enough reflection to blend into the background. Our future plans are to optimize the bandwidth versus return loss at the levels of 10 dB, 15 dB and 20 dB of return loss.

Min Zou, Mechanical Engineering:

Dr. Min Zou is the statewide lead on a $24M EPSCOR Track 1 grant that focuses on Advanced Surface Engineering (CASE). Briefly, CASE is a center that combines the expertise of faculty to create nextgeneration surfaces for a wide range of applications in manufacturing, aerospace, defense, healthcare, etc. Our work focuses on creating new surfaces that have low friction, high durability, tunable optical properties, and multifunctional nanocellulose-based materials.

- Soft Surfaces – includes surfaces consistent with the coverings of textiles, to include clothing, fabrics, nettings, and flexible gear (backpacks, footwear, and body armor). We developed soft coatings that can potentially be used to cover textiles including clothing, fabrics, nettings, and flexible gear (backpacks, footwear, and body armor).
- Nondurable Goods – includes other materials that can be applied to a surface and may affect the properties of surfaces, such as lubricants and sprays that have applications to military vehicles and operations. We developed solid lubricant coatings that can potentially be applied to a surface to reduce friction and improve corrosion resistance of components in military vehicles and operations.

Lauren Greenlee, Chemical Engineering:

My group has expertise in two areas related to defense applications.

- Hard Surfaces: we design and synthesize non-precious metal and metal oxide nanoparticle catalysts that are reactive towards contaminants. Our nanoparticles also have antimicrobial activity and can be used in wet environments as reactive nanomaterials. We also synthesize graphene/graphene oxidenanoparticle composites.
- Soft Surfaces: We can make nanoparticle-polymer composite films that have antimicrobial and reactive contaminant degradation functionality. These films can be used as coatings on textiles or other surfaces to impart reactive/catalytic functionality. We currently work with a multi-block copolymer that has charged and neutral blocks and can form different structures, such as micelles, in solution. We can imbed catalytic nanoparticles into or outside the micelles and use polymer and nanoparticle processing techniques to control composite film properties.

Steve Tung, Mechanical Engineering:

I'm interested in participating in the Call for Expertise regarding Uses of Nanotechnology on Surfaces for

Military Applications. I believe I can contribute to the area of Soft Surfaces. My research group is currently developing flexible biomimetic coatings to change the surface properties of streamlined bodies. One example is the use of 3D printing of a soft, flexible polymer to emulate the skin texture of sharks. Similar techniques can be applied to change the heat transfer properties of clothing and footwear, for example.

Joseph Herzog, Physics:
My group has expertise in the following defense-related applications:

- Hard Surfaces: Nano-fabrication of nanostructures with nanogap spacing. One use of these structures is that the nanogap spacing exponentially increases plasmonic enhancement in metal nanostructures. This\ fabrication technique has the potential for mass production. Potential applications include: sensors, NIR photodetectors, photovoltaics, etc.

Expertise which could be applied to all of the listed categories: Nanoscale fabrication; Optical characterization of nanostructures and materials: Raman spectroscopy, photoluminescence, dark field spectroscopy, and nanoscale resolution spectroscopy with near-field scanning optical microscope; computational modeling of optical and electrical properties of materials.

Jingyi Chen, Chemistry and Biochemistry:
My group specializes in the synthesis of nanoscale metals and nanocomposites for surface engineering. We have the expertise to synthesize different shapes of metal nanoparticles and some polymers tailored to enhance durability while maintaining low friction. We can contribute to hard surfaces and nondurable goods area.

UNIVERSITY OF GEORGIA

University of Georgia

POC: Jason Locklin, Associate Professor, Department of Chemistry; and Director, Integrated Bioscience and Nanotechnology Cleanroom, jlocklin@uga.edu

- Expertise in surface patterning and nanoparticle derivatization a variety of click chemistries.
- Material and surface composition analysis using grazing angle X-ray diffraction and powder X-ray diffraction
- Micro-analysis using confocal Raman spectroscopy
- Surface wetting property analysis using contact angle analysis
- Electric property analysis using four-point probe measurement
- Organic device fabrication: Active layer of the device includes conducting polymers and semiconducting and ferroelectric materials. We also perform optoelectronic and magnetic characterization of the devices. The fabrication requires to use lithography techniques, and thin film fabrication and characterizations.
- Optical characterizations includes birefringence measurements (Optical Rotation Polarimetry, Linear and Circular Dichroism in UV-Vis and IR, Magnetic Circular Dichroism, Fluorescence Polarization...), photoluminescence and photo-induced absorption. The characterized materials include organic materials, magnetic nanoparticles, semiconducting quantum dots.
- Fabrication and characterization of plasmonic devices that show surface plasmon polariton and localized surface plasmon resonance.
- Nanostructured metal borides, especially compositions that are ultra-high temperature ceramics and electrically conductive ceramics. Currently this research is funded by ONR for hypersonic applications (coatings, EM shielding, lightning strike protection functionalities).
- Nanomaterials that luminesce in the near infrared region. The defense application is specialty paints

that can be detected at non-visible wavelengths. Another area is near infrared imaging through tissue.

- Design and synthesize near-infrared (NIR, 700-950 nm) and short-wave infrared (SWIR, 950-1700 nm) persistent luminescent nanoparticles that emit very-long (>10 h) NIR or SWIR afterglow after excitation by sunlight or UV light. The NIR and SWIR nanoparticles can be incorporate into paints that can be conveniently applied to any surfaces (hard, soft or nondurable surfaces) by painting or spraying for tagging, tracking and locating applications. The NIR afterglow can be seen by regular night vision goggles, the SWIR afterglow can be seen by SWIR imaging devices.
- AFM based single molecular recognition of chemical components on soft/solid surfaces in addition to the atomic scale resolution surface morphology; and AFM based nano-indentation to measure the rigidity (Young's Modulus) of surfaces.
- Quantitative nano mechanical mapping of hard and soft surfaces.

West Virginia University
Ahmed E. Ismail, Department of Chemical and Biomolecular Engineering

CAPABILITIES OVERVIEW

Our research group uses high-fidelity atomistic molecular simulations to study the interfacial properties of both soft and hard materials, and in interaction with nondurable materials. Particular focuses have included:

- Developing improved models for contact phenomena and tribology between bare and functionalized surfaces. These improved stress-strain and constitutive models can then be applied in finite-element simulations to greatly improve the accuracy and efficiency of macroscopic modeling of contact phenomena. These modeling approaches also yield macroscopic constitutive models with significantly fewer parameters than so-called "state of the art" models, which fail to achieve the same accuracy as the combined MD-FEM approach modeling.
- Measuring the wetting properties of "pure" and surfactant-laden water droplets on polymer surfaces (e.g., fibers and adhesives). These studies show the effect of different functionalizations of the polymers as well as the surfactant on the wetting behavior and dynamics of the droplet on the surface.
- Studying the effect of functionalization on the flow and transport properties of functionalized nanoparticles for processing applications. The primary advantage of these capabilities is the ability to act in a "predictive" manner: proposed new materials can be tested via molecular simulations without the need to develop a synthesis mechanism for the new material and achieving sufficient yields to enable non-destructive and destructive testing of the materials at the laboratory scale.

WEB SITE

http://molecularsimulations.wvu.edu (Under "Research," see "Contact" and "Interfaces" pages)

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University of Kentucky, John Balk

POC: John Balk, Professor of Materials Science & Engineering, john.balk@uky.edu

Prof. Balk's research focuses on the mechanical behavior of metals and alloys, especially with respect to deformation mechanisms in thin films and coatings. Ongoing projects include the effects of geometric size (film thickness) effects on strength of coatings, and the development of new high entropy alloys (thin film coatings as well as bulk alloys) for high strength at ambient and elevated temperatures. Prof. Balk is director of the Electron Microscopy Center at the University of Kentucky, and has 20+ years' experience in the characterization of materials using electron microscopy and x-ray diffraction. His group also applies a range of mechanical test techniques in the study of new materials, including bulk tension and compression testing, millimeter-scale specimen testing using a home-built test system, and nanoindentation for probing the surface mechanical properties of bulk specimens and thin films (hardness and modulus can be measured reliably at depths as low as 50 nm).

University of Kentucky, Kozo Saito

POC: Kozo Saito, Director, Institute of Research for Technology Development, ksaito@uky.edu

Hard Surface and Nondurable Goods

- UKY has developed quick curing paint which can be cured much quicker than traditional paint. When a small amount of carbon nanotubes (CNT) are added to polymer-based paint and exposed under RF light (13.56 MHz), it was cured in a matter of one minute compared to 15 to 20 minutes curing time required for traditional paint at 350F (see attached).
- UKY has developed a patented unique flame synthesis method to produce carbon nanotubes, to be added to the above quick curing paint (see my resume).
- UKY has worked on fluorescence-added paint which only can be seen under the illumination of black light. This technique was applied to detect defects and missed spots in the painted surface

of ships' ballast tanks.

Soft surfaces

- UKY has developed a non-destructive Infrared Thermography-based technique to inspect the structural integrity of body armor. This inspection technique was able to inspect body armor's surface structure which was covered by thick fabric and to characterize the type of fabric. Currently those armors are inspected using an X-Ray system at the manufacturers. However, there is a strong need for field inspection to protect the lives of soldiers and civilians. Our new technique can serve this purpose.

Quick Curing

Project Description: Paint quality and durability is affected by the curing process which in addition requires high energy consumption over a prolonged time; some of this energy is wasted due to the spectral optical material properties of the paint and the substrate. Other waste sources are the heating of the oven and the air in it, the heating of the vehicle metallic body, and heating of the carrier, all those will result in heating efficiency of less than 5% to be used in curing process.

To prevent that selective heating of the paint by nano-particles might direct ~100% of the energy to curig. We propose introducing nanoparticles such as carbon nanotubes and metallic oxides to enhance the electrical properties of the material, especially the dielectric constant. Selective heating of the paint (i.e., without heating the substrate) will reduce oven energy consumption and energy waste. Selective heating of the paint will be done by induction heating, since metals have a skin effect whereby all the energy applied heats the surface of the metal. More energy will thus be absorbed by the paint, resulting in higher energy efficiency.

Preliminary studies show that the aspect ratio of the length to diameter plays a major role in selective heating of the paint. Epoxy resin is mixed with various nano-sized materials:

- Carbon nano-spheres with 50 nm Diameter (Carbon Black)
- Single wall carbon nanotubes with tube diameter of 1-2 nm and tube length 5-20 μm (SWCNT).
- Double wall carbon nanotubes with diameter of 2-4 nm and tube length 50 μm (DWCNT).
- Multi-wall carbon nanotubes with diameter of 8 nm and tube length 10-30 μm (MWCNT 8 nm).
- Multi-wall carbon nanotubes with diameter of 20-30 nm and tube length 10-30 μm (MWCNT 25 nm).
- Multi-wall carbon nanotubes with diameter of 50-80 nm and tube length 10-30 μm (MWCNT 75 nm).

As shown in Figure 1 the radio frequency did not heat the glass substrate, the resin, or samples with 5% Carbon nano-spheres. While the highest heating efficiency was for samples containing Double wall carbon nanotubes followed by the largest Multi-wall carbon nanotubes.

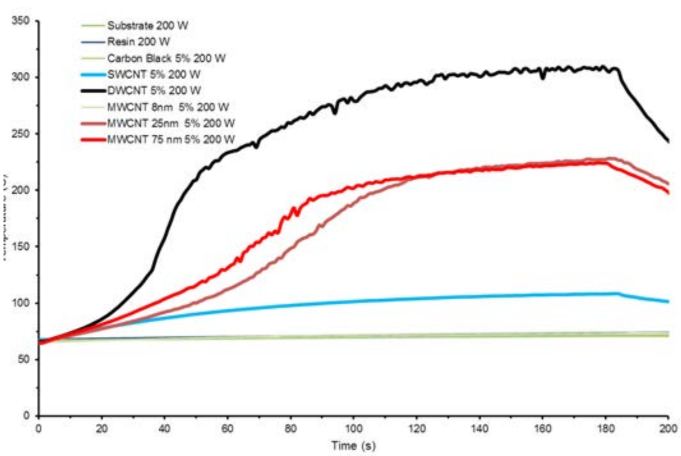

Figure 1: *Temperature history of samples heated in 13.56 MHz Radio-frequency heater at 200 W intensity*

How the project may be transformative and/or benefit society and Military: Understanding of electromagnetic wave absorption mechanisms of nanoparticles in polymers and paint might result in stealth systems. Paint that will absorb and reflect various electromagnetic waves including, Radar, Infrared, UV, and Microwave might be desirable for hard to detect airplanes, ships, and vehicles.

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