2010

Multifunctional Optical Coatings

by Rapid Self-Assembly

LOCKHEED MARTIN

Sandia National Laboratories

Multifunctional Optical Coatings
by Rapid Self-Assembly

2010

R&D 100 Entry

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Product Name

Multifunctional Optical Coatings by Rapid Self-Assembly

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Brief Description

This simple, safe, and economical coating process enables the development of paradigm-shifting multifunctional nanomaterials and optical coatings with architectures and properties not attainable by current processing methods.

Product First Marketed or Available for Order

October 2009

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R&D 100 Entry

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Product Price

Because this coating technology is applicable to a wide range of products, the price will vary depending on the application, materials, and performance requirements. The material costs will range from pennies per square foot for simple dielectric films to $15 per square foot for complex high-performance coatings.

Patents or Patents Pending

1. Self-Assembly of Water-Soluble Nanocrystals. Patent application #: 12/038,037.

2. Method of making monodisperse nanoparticles. Patent application #: 12/706,003.

Technical Advance

1. Self Assembled Magneto-dielectric coatings (submitted, in review).
2. Method of making nanoporous, hydrophobic coatings. (SD# 11677)

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Product's Primary Function

Optical films are widely used in the manufacture of consumer electronics, semiconductor devices, and high-performance glass and ceramic materials. Presently most of these films are manufactured using complicated and costly processes like sputter deposition and chemical vapor deposition (CVD), which require high temperature and/or high vacuum. A simpler and less expensive process is needed, and we have developed such a process—a rapid and versatile self-assembling process that employs nanotechnology as an alternative to current methods. This process is elegant and simple, with more degrees of freedom than conventional coating processes. Our technology involves the self-assembly of polymers to form nanostructured coatings with tailored properties. The process uses commercially available polymers, which are dispersed in common solvents, allowing easy and cost-effective routes to produce films through spin, dip, or spray coating in ambient conditions. During coating, evaporation of the solvents induces self-assembly, forming multifunctional films with a nanostructured surface, low surface energy, controllable porosity, and a refractive index ranging from $n = 1.2$ to 3.0. These films possess physical properties approaching those of materials that are typically fabricated using expensive processes such as CVD and sputtering. Additionally, the chemical and physical nature of the self-assembled polymer films can be further modified through a variety of near-ambient processes that allow us to tailor unique functions and properties. The ability to adjust the material parameters of the film at different stages (synthesis, deposition, or post-deposition) provides a powerful new degree of freedom over conventional

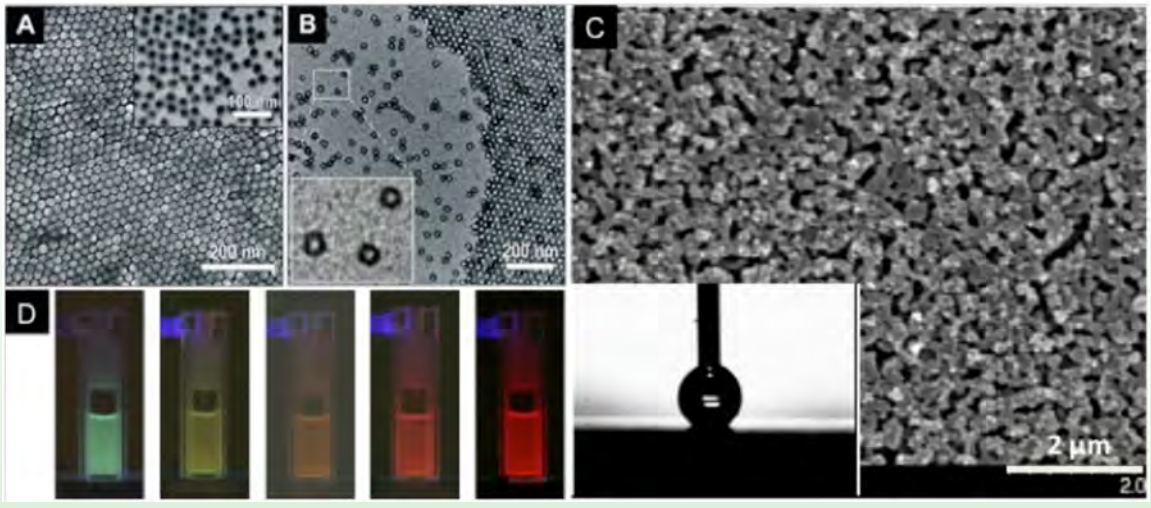

Figure 1. *Multifunctional polymer nanoparticles and coatings. (A) nanostructured film of monodisperse polystyrene nanoparticles; (B) monodisperse hollow polymer nanoparticles with controlled porosity (or refractive index); (C) nanostructured hydrophobic polymer coating; and (D) hybrid organic/inorganic fluorescent nanoparticles in aqueous solutions.*

deposition approaches (see Figure 1).

Our rapid self-assembly process has several competitive advantages over current processes:

1. The process uses evaporation-induced self-assembly of materials. By using readily available, commercial precursors or chemicals, we can fine-tune film compositions to tailor film properties. For example, by using the semiconducting polymer P3HT we can fabricate nanostructured semiconductor films for photovoltaic fabrications, and by using hydrolyzed titanium oxides we can fabricate uniform nanostructured titanium coatings for organic solar cells.
2. The intrinsic hydrophobic nature of the polymer eliminates surface tension and drying stress that can cause cracking in conventional film deposition processes. Additionally, the low surface energy and nanostructured character of the coating cause the surface to be superhydrophobic, which prevents moisture from deteriorating the optical performance. For one application, the average water contact angle is >150° (Figure 1C).
3. The solution coating process can produce nonporous films in ambient conditions without using expensive specialized equipment. Final film thicknesses ranging from a hundred nanometers to tens of micrometers (μms) can be easily controlled by modifications to the precursor concentration and coating process (e.g., coating speed).
4. The process is compatible with conventional spray processing. Hence it can be directly applied to the coating of large or complex parts and is not restricted to the typical equipment and facility limitations of conventional chemical and physical vapor deposition processes.
5. Formation of hybrid coatings through the incorporation of organic and inorganic functional elements brings new chemical and physical properties to bear that are not available in conventional coating processes.
6. Multiple-layered coatings exhibit tunable reflectivity over the visible and far infrared regions. Reflectivity of $R < 2\%$ with no absorption in the visible spectrum and incidence angles of 0° to 60° have been produced (see Figure 2).

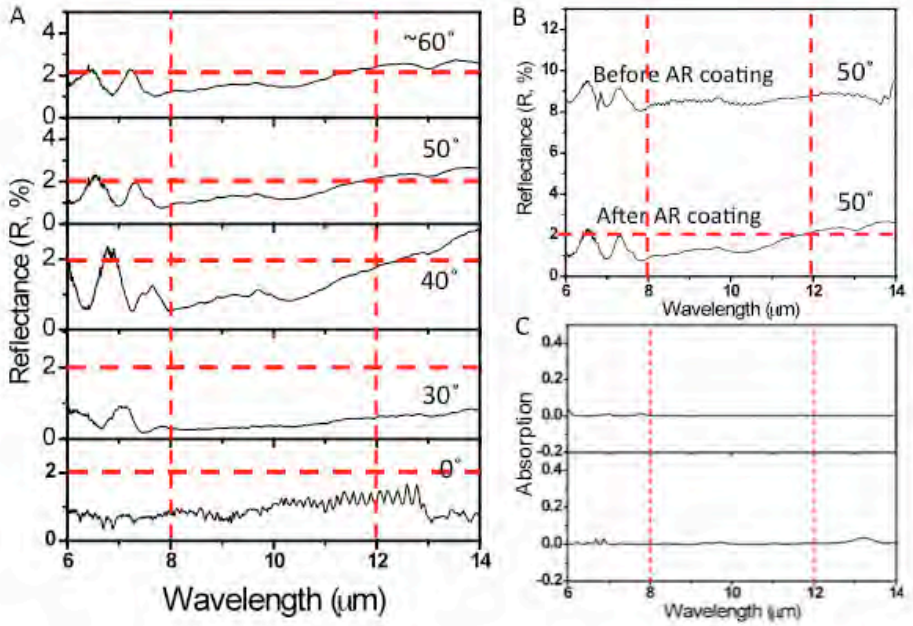

Figure 2. Measured reflectivity of multiple layered anti-reflective coatings on polyethylene at varied incident angles (A &B) and absorption (C) of the anti-reflective coatings.

Product's Competitors

The main competitors to our process are conventional CVD processes and sputtering processes, both of which require restrictive environmental conditions such as high temperature and high vacuum. Our process, in contrast, is conducted in mild, ambient conditions. The following comparison matrix highlights the most significant differences between our self-assembly approach and conventional CVD and sputtering approaches.

Comparison Matrix

Feature	Our Process	CVD	Sputtering
1) Equipment Costs	$5-50K	$3-10M	$3-7M
2) Material Toxicity	Low	High	Low
3) Tunable Material Properties	Yes	Limited	Limited
4) Substrate Heating	Room Temp.	20 – 500 °C	20–600 °C
5) High Vacuum	Ambient Pressure	Typically Required	Required
6) Large/Irregular Parts	Easy	Difficult	Difficult
7) Surface Chemistry Functionalization	Yes	No	No
8) Controlled Atmosphere	None	Yes	Inert carrier

How This Product Improves upon Competitors

Thin film deposition for semiconductor devices, consumer electronics, high-performance optical coatings and photovoltaics is dominated by methods that require nonambient processing conditions, expensive specialized processing chambers, unforgiving protocols, and highly trained operators. Although improvements in conventional physical deposition techniques, such as sputtering and CVD, have allowed thin-film deposition techniques to generally keep pace with minimum performance requirements of typical optical and semiconductor applications, this performance comes at a significant cost.

In contrast, our new self-assembled coating process can be tuned and optimized to meet the performance requirements of both current and new products while concurrently reducing costs, improving manufacturing logistics, and minimizing environmental and safety concerns. Furthermore, our new chemistry and process have enabled a new capability to incorporate multifunctional performance into coatings, a feature that is difficult or impossible to achieve with conventional deposition processes. These impacts and the other

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advantages of our process are itemized in the table on the next page.

Improvements	Our Process	CVD and Sputtering processes
1) Capital Equipment and Costs	Requires only "low-tech" equipment such as sprayers, dip-tank, rollers, and dryers.	Require "high-tech" capital equipment for high-vacuum and/or gas handling. Additionally these processes need dedicated lab space and costly facilities.
2) Material Toxicity and Costs	The precursors are comparatively inexpensive, environmentally benign, and readily available, which allows our process to be performed in an open fabrication facility requiring at most simple venting.	Require gas precursors that are typically hazardous and can be toxic and/or a fire risk. Examples of such precursors include silane, which is pyrophoric (ignites spontaneously on exposure to air) and arsine, which is both pyrophoric and rapidly fatal at exposures of 250 ppm. Materials with this level of toxicity require significant resources for handling, safeguards, and disposal.
3) Tunable Material Properties	Considerable process flexibility allows us to tailor material properties at the synthesis, surface chemistry, deposition, or post-deposition stages.	Tunability is limited to the pre-deposition stage and to tailoring of surface chemistry, ductility, or gradient optical properties of coatings.
4) Process conditions	• Ambient environment • Room temperature	• High temperature or heating • High vaccuum
5) Large/Irregular Parts	Large and irregular products can be coated, and coating logistics are simple and inexpensive. • Dip-, spin-, spray-coating • Ink-jet printing • Laminar flow coating • Roll-to-roll process	Coating requires high vacuum chambers that limit the product size. Coating logistics are complicated and time-consuming.

"Our process can be tuned and optimized to meet the performance requirements of both current and new products while concurrently reducing costs, improving manufacturing logistics, and minimizing environmental and safety concerns."

6) Surface Chemistry Functionalization	Field repairs and adaptations can be accommodated to improve supportability and logistics and permit incorporation of new technology solutions not possible with currently available technology.	Surface functionalization capabilities are limited because the properties of the thin films are necessarily bulky, controlled by either the properties of the target (sputtering) or the precursor gases (CVD).

Product's Prinicpal Applications

Sandia National Laboratories partnered with Lockheed Martin Corporation to (1) develop this coating technology; (2) identify significant applications for industry, the Department of Defense, Department of Energy, and the National Aeronautics and Space Administration; and (3) integrate this technology into product lines. Applications that demonstrate the diverse impact of this technology include optical coatings (e.g., anti-reflective coatings that cover the spectrum from visible to far infrared), three-dimensional nanoscale capacitors, sensors, and photovoltaics. The value of this new technology can be measured in four categories: cost reduction, increased producibility, improved logistics, and incorporation of new techniques not possible with currently available technologies. Coatings produced using our solution-based approach will be significantly less expensive than those produced with current processes.

Expensive, large-footprint equipment and highly trained system operators will be replaced by inexpensive equipment and versatile personnel. Furthermore, our self-assembling coatings can be applied on or near production lines, thereby reducing the manufacturing timeline. Expensive sputtering targets and toxic CVD chemicals used in current processes will be replaced by environmentally benign, OSHA-compliant chemistries. The supportability of components will be significantly enhanced by the ability to repair some coatings in the field, thereby reducing downtime and the number of spare parts required.

F35 Canopy

Aircraft Transparencies

A typical jet fighter aircraft canopy loses 8-10% of its optical transmission from the intrinsic Fresnel loss due to the refractive index of the plastic or glass material. Applying an optimized

anti-reflective coating can inexpensively add an additional 8-9% transmission through the canopy, thereby providing an additional margin of safety to the pilot. Furthermore, our optimized coating is adaptable to field repairs, unlike conventional anti-reflective coatings, which must be repaired in a manufacturing facility after disassembly and shipping. Additionally, conventional coatings are too expensive to apply routinely.

Architectural windows

The low cost of application of our optical coating technology lends itself nicely to all forms of architectural windows—both glass and plastic. Greater optical transmission reduces glare and the need for artificial light. Furthermore, the hydrophobic properties add a self-cleaning feature that reduces maintenance and time spent cleaning windows in skyscrapers, houses, greenhouses, and aquariums—to name just a few applications.

Photovoltaics

The same anti-reflective and hydrophobic properties that make this technology valuable for aircraft and architectural applications make it especially attractive for photovoltaic applications. When optimized for its anti-reflective properties, this coating can be used to significantly increase the efficiency of photovoltaic devices by nearly eliminating Fresnel losses. The flexible characteristics of this coating allow it to be used on both rigid devices and the newer flexible thin photovoltaic devices. Similarly, the straightforward nature of this coating technology's processing will reduce the manufacturing and facility costs when compared to conventional anti-reflective coating processes. Coatings damaged through accident can be returned to near optimum properties in the field using a simple touch-up kit. Finally, applying a super hydrophobic-optimized coating creates a self-cleaning surface that will maintain the efficiency of the

"The same anti-reflective and hydrophobic properties that make this technology valuable for aircraft and architectural applications make it especially attractive for photovoltaic applications."

Sandia National Laboratories, solar panels.

photovoltaic system.

Corrosion reduction

Although primarily developed as an anti-reflective coating, the inherent barrier properties and super hydrophobic characteristics of this material coating system should provide a level of resistance for many materials against corrosion and chemical attack.

Other Applications

Applications that demonstrate the potential diverse impacts of this

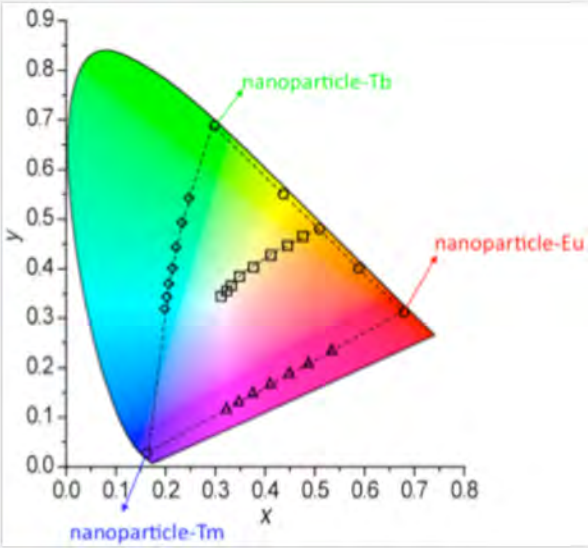

Figure 3. Hybrid rare earth nanoparticles (< 50 nm) tuning full color spectrum.

product include the following:

(1) Low-κ (dielectric constant) materials for next generation memory chips: The ability to manufacture a film with controlled high nanoporosity or low dielectric backbone architecture is critical for high-density memory where the nanoporosity isolates the microcircuits at nanoscales (10-50 nm).

(2) High-definition flat panel displays: By incorporating light emission materials such as rare earth, cadmium selenide (CdSe), monodisperse organic/inorganic nanoparticles can be formed (10-50 nm). Large areas of coatings of these nanoparticles are formed through spin-on processes that emit colors that cover the full color spectrum (see Figure 3), which provides display resolution at nanoscale (<50 nm).

(3) Sensor coatings for chemical and biological sensor platforms: Nanoparticles of noble metals such as gold and silver are key components to Surface Enhanced Raman Scattering (SERS)-based detection methods for chemical and biological sensors. The ability to place these nanoparticles in an accessible matrix with nanometer-level separation and diffusion layers increases the sensitivity of such sensors.

Summary

In order for a new technology to be quickly adopted and have a significant impact on an established industrial process, it must extend into a significant fraction of the parameter space covered by existing technologies as well as offer new advantages in functionality. Our wet solution-based self-assembly coating process is, for many thin film applications, competitive with current technologies, and it surpasses those processes by providing new manufacturing freedom with reduced equipment and personnel costs while being environmentally benign. In addition to possessing tunable physical and optical properties, the hollow particles that constitute our thin films may be functionalized to provide new capabilities or may be filled with active particles such as quantum dots, dye molecules, and conducting nanoparticles. Furthermore, the added flexibility and control over thin film properties opens the door for engineered thin films that may be repaired or adapted in the field. We think this breakthrough will certainly impact the thin film deposition industry and, as such, is worthy of consideration for a 2010 R&D 100 Award.

The cross-disciplinary relevance and economic, logistic, and environmental benefits of this new process are an indication of the impact expected from this technology. This patented technology was published in *Science* magazine and was featured on the cover and frontispiece of technical journals including *Journal of the American Chemical Society*, *Chemistry—A European Journal*, and *Chemical Communications*.

Affirmation

By uploading this form to R&D Magazine's website I affirm that all information submitted as a part of, or supplemental to, this entry is a fair and accurate representation of this product.

Hongyou Fan

Appendicies

Appendix A: Articles

- *Cooperative Self-Assembly-Assisted Formation of Monodisperse Optically Active Spherical and Anisotropic Nanoparticles*
- *Dynamic Investigation of Gold Nanocrystal Assembly Using In-Situ Grazing-Incidence Small-Angle X-ray Scattering*
- *Hydrogen-Bonding-Assisted Self-Assembly: Monodisperse Hollow Nanoparticles Made Easy*
- *Nanocrystal-micelle: synthesis, self-assembly and application*
- *Self-Assembly of Ordered, Robust, Three-Dimensional Gold Nanocrystal/Silica Arrays*
- *Synthesis and Self-assembly of Monodisperse Hybrid Polymer Nanoparticles*
- *Cooperative Self-Assembly Assisted Formation of Monodisperse Spherical and Anisotropic Polymer Nanoparticles*

Appendix B: Letters of Support

- Lockheed Martin Corporation
- Cabot Aerogel Corporation
- ARCH Venture Partners

Appendix C: Cooperative R&D Agreements

Cooperative Research and Development Agreement NO. SC99/01573. Lockheed Martin Corporation and Sandia Corporation

Appendix D: Patents

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Cooperative Self-Assembly-Assisted Formation of Monodisperse Optically Active Spherical and Anisotropic Nanoparticles

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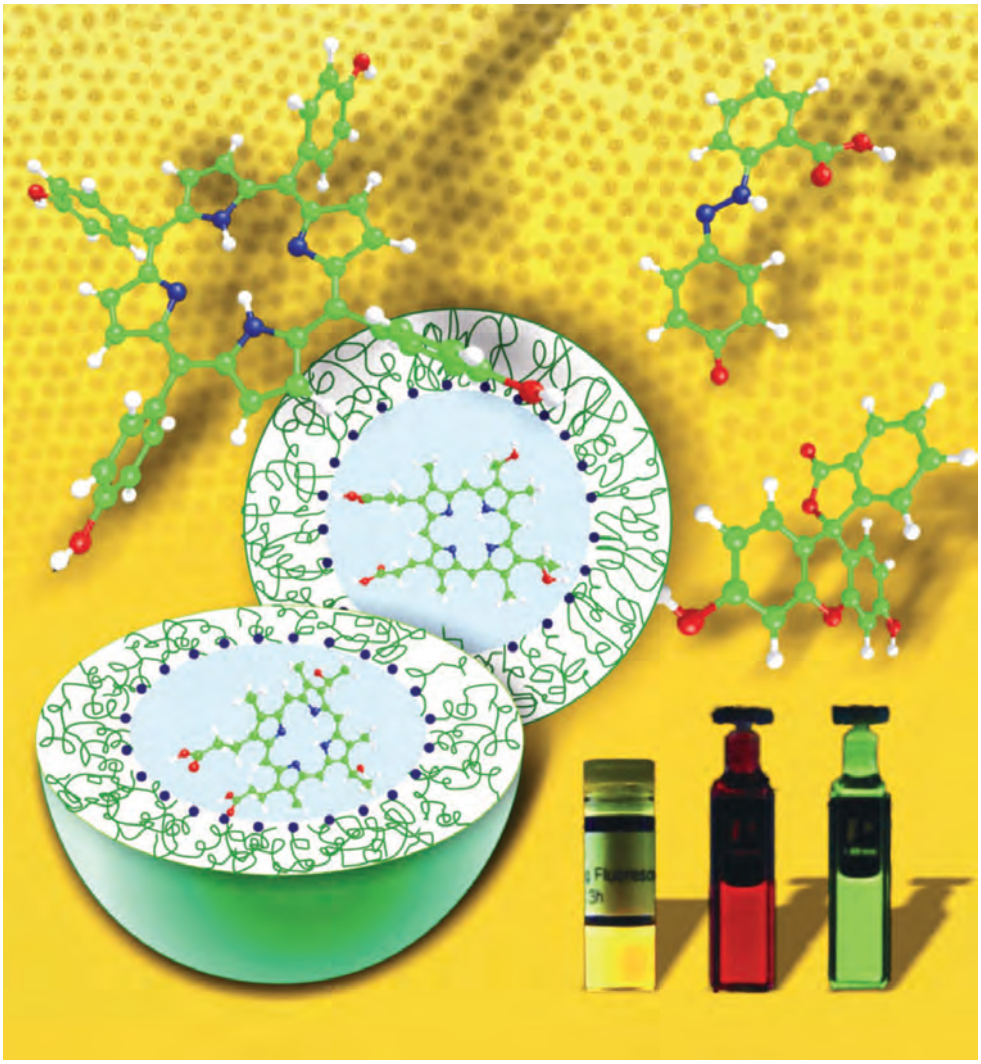

Langmuir **2008,** *24,* 10575−10578

Dynamic Investigation of Gold Nanocrystal Assembly Using In Situ Grazing-Incidence Small-Angle X-ray Scattering

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Here we investigate the dynamic self-assembly pathway of ordered gold nanocrystal arrays during the self-assembly of gold nanocrystal micelles, with and without the presence of colloidal silica precursors, using grazing-incidence X-ray scattering performed at a synchrotron source. With silica precursors present, a lattice with rhombohedral symmetry is formed from the partial collapse of a face-centered cubic structure. In the absence of silica, a transient body-centered orthorhombic phase appears, which rapidly collapses into a glassy nanocrystal film. The appearance of face-centered and body-centered structures is consistent with a phase diagram for charged colloidal particles with assembly modulated via Coulomb screening.

Nanocrystals (NCs) have become a highly significant class of nanomaterials, at least in part from the possibility of unique collective behavior obtained through interactions of neighboring NCs within ordered two- (2D) and three-dimensional (3D) arrays readily obtained via a low-cost, rapid self-assembly process.[1−3] While extensive research has been directed toward the synthesis of novel NC shapes, compositions, and surface functionalization,[4−6] less effort has been given to examining the self-assembly process used to form well-ordered NC lattices with specified functional properties. Practical integration of these materials into durable coatings and devices will require a fundamental understanding of many technical issues regarding the self-assembly of extended NC structures, including optimization of long-range order,[7] or the development of pathways to non-close-packed morphologies.[8,9] To this end, several reports have appeared recently that address the development of thin film structure for highly ordered 2D lattices[1,7,10] as well as more glassy NC aggregates[11,12] and NC monolayers formed on a Langmuir trough.[13] Although various experimental techniques were employed for these investigations of NC film formation (for example, ex-situ electron microscopy,[7,10,13,14] or in situ optical measurement of NC island growth at the surface of an evaporating film[14]), grazing incidence small-angle X-ray scattering (GISAXS) studies using synchrotron radiation have proven to be a particularly useful method of obtaining direct, real-time structural information during NC self-assembly[10−13] under ambient conditions. In GISAXS, an X-ray beam is incident upon a sample at an angle greater than the critical angle of the film but less than that of the substrate, thus maximizing the scattering volume inside the film and, coupled with the high photon flux obtained at a synchrotron source, enabling the investigation of fast (on the time scale of seconds) self-assembly phenomena of films as thin as one monolayer.[10] GISAXS has been used to investigate the self-assembly mechanism of Au NC ordering in evaporating drops,[10,11] as well as to probe the structure of one-dimensional (1D) NC gradient films.[12] However, these studies have all focused on thiol-modified Au NCs that organize into close-packed hexagonal arrays through short-range "hard-sphere" forces. Recently, we developed a new self-assembly method to form ordered NC arrays assembled within a metal oxide matrix.[1,2] In this method, alkane thiol-capped Au NCs are encapsulated within micelles of ionic surfactants, producing water-soluble NC micelles compatible with the synthesis of metal or semimetal oxides (here we limit our discussion to only the case of silica) from molecular precursors using low-temperature sol−gel chemistry.[15] Solution precipitation from or spin-coating of a NC-micelle/silica precursor solution yields powders or thin films of ordered NC-micelle/silica superlattices with (based upon transmission electron microscopy (TEM) and standard 1D X-ray diffraction (XRD) characterization) a face-centered cubic (fcc) arrangement of NCs.

Here we present the results of a GISAXS study on the structure and self-assembly pathway for ordered Au NC-micelle/silica films deposited using solution casting onto Si substrates. We

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Hydrogen-Bonding-Assisted Self-Assembly: Monodisperse Hollow Nanoparticles Made Easy

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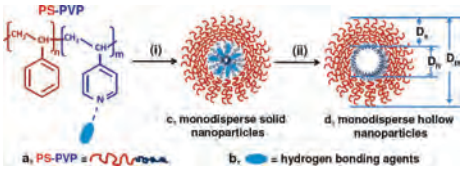
Because hollow nanoparticles play important roles in many applications, including catalysis and nanoreactors, optics, sensing, and controlled release, there have been numerous synthesis efforts.[1−6] Hollow particles or nanostructures have been synthesized primarily through the "template method". Through the use of colloid particles with reactive surfaces as templates, both inorganic and polymer hollow particles have been prepared.[1,2,5,7−9] Block copolymer self-assembly has been developed to form hollow vesicles or capsules and hybrid organic−inorganic hollow nanoparticles.[10−14] A freeze-dry process was developed to prepare hollow polymer particles.[15] Recently, through a spontaneous dissolution−regrowth process, uniform hollow silica colloids were synthesized with an average particle size of 300 nm.[16] The development of more facile and efficient methods for synthesis of monodisperse hollow nanoparticles is critically important for the continued advancement of this area. Here we report a new facile self-assembly technique for synthesizing monodisperse hollow spherical nanoparticles that are less than 50 nm in diameter. Preferential hydrogen bonding between an amphiphilic block copolymer and a hydrogen-bonding agent (HA) enables formation of monodisperse spherical solid polymer nanoparticles with the HA residing in the particle core surrounded by the polymer. Removal of the HA results in monodisperse hollow nanoparticles with tunable hollow cavity size and surface reactivity.

Scheme 1. (i) Hydrogen-Bonding-Assisted Self-Assembly and (ii) Formation of Hollow Nanoparticles



Scheme 1 describes the hydrogen-bonding-assisted self-assembly process and the formation of hollow nanoparticles. The amphiphilic block copolymer was polystyrene-*b*-polyvinylpyridine (PS-PVP). 2-(4′-Hydroxybenzeneazo)benzoic acid (HBBA) was used as the HA. For a typical synthesis, we added a 2 wt % solution of HBBA in dioxane to a 2−4 wt % solution of PS-PVP in dioxane. After the mixture was stirred and heated (70 °C) for up to 10 h, the nanoparticles were collected through centrifugation. Formation of hydrogen bonds between the −COOH groups of HBBA and the hydrophilic PVP chains[17] facilitates phase separation, producing solid nanoparticles with HBBA in the particle core (process i). This was confirmed by dynamic light scattering results (Figure S1 in the Supporting Information). Before addition of HBBA, PS-PVP disperses in solvents without phase separation. Addition of HBBA induces PS-PVP phase separation and nanoparticle formation in the solution. Removal of HBBA was conducted using an alcohol (methanol or ethanol) wash. Alcohols are good solvents for PVP chains and nonsolvents for PS chains. During the alcohol wash, the preferential solvation of the PVP chains with alcohol breaks the hydrogen bonds between the PVP chains and HBBA; the alcohol then dissolves and selectively removes the HBBA to form hollow nanoparticles (process ii). The scanning electron microscopy (SEM) image in Figure 1A shows as-prepared polymer nanoparticles obtained using 2 wt % PS-PVP and 2 wt % HBBA before removal of HBBA. The nanoparticles were monodisperse with an average diameter (D_p) of 35 nm and a narrow size distribution [standard deviation (σ) of <7%]. The Figure 1A inset shows a transmission electron microscopy (TEM) image of these nanoparticles. The uniform electron contrast across each nanoparticle suggests that the nanoparticles are solid particles. The TEM image recorded after removal of HBBA by the alcohol wash (Figure 1B) shows evident electron contrast between the cores and shells of the particles, confirming the formation of hollow particles. The TEM image also reveals that the hollow nanoparticles remain spherical in shape after removal of HBBA, demonstrating their stability. The formation of hollow nanoparticles further confirms that HBBA associates with PVP chains and resides at the nanoparticle core surrounded by PS. Because of the monodispersity, the hollow nanoparticles form large areas of ordered arrays (Figure 1B and Figure S6). By careful control of the molar ratio of HBBA to PVP, we determined a HBBA/PVP molar ratio threshold of ∼1.5 above which the hollow diameter (D_h) does not increase. Any extra HBBA crystallizes in solution. Below the threshold, we can control D_h from several nanometers up to tens of nanometers by gradually increasing the chain length of polymer and/or amount of HBBA (see Figures S2 and S3).

The hollow nature and the accessibility of the cavity were further verified by nitrogen sorption measurements using a surface acoustic wave technique.[18] Figure 1C compares nitrogen sorption isotherms of solid and hollow nanoparticle films at 77 K. Both films followed type-IV sorption isotherms. The solid nanoparticle films showed a dramatic nitrogen uptake starting at $P/P_0 \approx 0.8$ with a small hysteresis, suggesting the existence of large mesopores.[19] This is due to the gaps between neighboring nanoparticles. After removal of HBBA, the hollow nanoparticle film exhibited an H1-type hysteresis loop, with almost vertical steps on the ascending and descending curves starting at P/P_0∼0.8, which is characteristic of a mesoporous material with a narrow pore size distribution. The

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FEATURE ARTICLE
Hongyou Fan
Nanocrystal-micelle: synthesis, self-assembly and application
COMMUNICATION
Fabienne Burlina et al.
Modifications in the chemical structure of Trojan carriers: impact on cargo delivery
1359-7345(2008)12;1-7

RKKY interaction is not a settled matter (*26*).

Both single-dot and coupled-dot configurations (27) show roughly linear peak splitting as a function of in-plane magnetic field in the range $B_{\parallel} \sim 2$ to 4 T, with slopes of ~70 μeV/T. This slope is larger by a factor of ~1.5 than expected for the GaAs g factor of 0.44, but is consistent with g-factor measurements in other devices made from the same wafer. Both the single-dot and coupled-dot cases show an unexpected strengthening of the zero-bias peaks with $B_{\parallel}$ before splitting is observed (for $B_{\parallel} < 2$ T). This is not understood at present and will be investigated in more favorable device geometries in future work.

We have demonstrated coherent control of quantum dot spins by a nonlocal RKKY-like interaction. The present results suggest an approach to nonlocal control of spin and entanglement (*28*–*30*), which may be relevant to scaling of solid-state quantum information processing beyond the constraint of nearest-neighbor exchange.

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25. The device was patterned using surface gates (Cr/Au) fabricated by electron-beam lithography. Peripheral dots have a lithographic area of 0.25 μm^2; the central dot has a lithographic area of 0.35 μm^2. The device was fabricated on a delta-doped GaAs/AlGaAs heterostructure with electron gas 100 nm below the surface. Mobility 2×10^5 cm^2/Vs and two-dimensional electron density 2×10^{11} cm^{-2} give a transport mean free path of ~2.0 μm in the unpatterned material.
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Self-Assembly of Ordered, Robust, Three-Dimensional Gold Nanocrystal/Silica Arrays

Hongyou Fan,[1,2]* Kai Yang,[3] Daniel M. Boye,[4] Thomas Sigmon,[3] Kevin J. Malloy,[3] Huifang Xu,[2] Gabriel P. López,[2] C. Jeffrey Brinker[1,2]*

We report the synthesis of a new nanocrystal (NC) mesophase through self-assembly of water-soluble NC micelles with soluble silica. The mesophase comprises gold nanocrystals arranged within a silica matrix in a face-centered cubic lattice with cell dimensions that are adjustable through control of the nanocrystal diameter and/or the alkane chain lengths of the primary alkanethiol stabilizing ligands or the surrounding secondary surfactants. Under kinetically controlled silica polymerization conditions, evaporation drives self-assembly of NC micelles into ordered NC/silica thin-film mesophases during spin coating. The intermediate NC micelles are water soluble and of interest for biolabeling. Initial experiments on a metal-insulator-metal capacitor fabricated with an ordered three-dimensional gold nanocrystal/silica array as the "insulator" demonstrated collective Coulomb blockade behavior below 100 kelvin and established the current-voltage scaling relationship for a well-defined three-dimensional array of Coulomb islands.

Despite recent advances in the synthesis and characterization of nanocrystals and NC arrays (*1*, *2*), there remain numerous challenges that limit their practical use. First, for example, synthesis procedures generally used for metallic and semiconducting NCs use organic passivating ligands that make the NCs water insoluble. This is problematic for biological imaging and more generally for uniform incorporation of nanocrystals in hydrophilic matrices like silica or titania needed for the fabrication of robust, functional lasers (*3*, *4*). Second, while steric stabilization of nanocrystals with organic passivating layers suppresses attractive particle-particle interactions, thereby facilitating self-assembly of NC arrays, it necessarily causes the arrays to be mechanically weak and often thermally and chemically unstable. Third, although evaporation of NC dispersions has been used to prepare quasi-3D NC arrays (*5*) and films containing isolated 3D NC islands (*6*), there exist no procedures to reliably fabricate 3D NC arrays as uniform thin films. These combined factors ultimately limit routine integration of nanocrystals into 3D artificial solid devices, in which electronic, magnetic, and optical properties could be tuned through electron charging and quantum confinement of individual NCs mediated by coupling interactions with neighboring NCs (*7*, *8*).

Here, we describe the direct synthesis of water-soluble NC gold micelles and their further self-assembly with silica into robust, ordered 3D NC arrays in bulk or thin-film forms. The synthetic approach is general and avoids the complicated multistep procedures reported previously (*9*). Our concept is to consider monosized, organically passivated NCs as large hydrophobic molecules that, if incorporated individually into the hydrophobic interiors of surfactant micelles, would result in the formation of monosized NC micelles composed of a metallic (or other) NC core and a hybrid bilayer shell with precisely defined primary and secondary layer thicknesses (Fig. 1H). The hydrophilic NC

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Synthesis and Self-assembly of Monodisperse Hybrid Polymer Nanoparticles

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INTRODUCTION

Monodispersed polymer nanoparticles exhibit important applications in coatings, chemical and biological sensors, microelectronics, nanolithography, and drug release devices, which stimulates widespread synthetic efforts. Despite of previous extensive work, ability to accurately control over particle shape, size (<50nm), dispersion, and functionality still presents technical challenges[1-3]. Here, we present a simple approach where cooperative interactions such as hydrogen bonding, π-π stacking, ligand coordination between block copolymer (polystyrene-b-poly(4-vinylpyridine), PS-PVP) and functional molecules enables formation of both spherical and anisotropic hybrid functional nanoparticles.

EXPERIMENTAL

Materials. The following BCPs were purchased from Polymer Source Inc. and used as received. 2-(4´-hydroxybenzeneazo)benzoic acid (HBBA), titanium (IV) tert-butoxide, tetraethyl orthosilicate (TEOS), Na_2PdCl_4, $HAuCl_4$, and all solvent was purchased from Aldrich Chemicals.

Synthesis of Polymer Nanoparticles. In general, 2 ml of 4wt% block copolymers into dioxane was added to 2 ml solutions containing varied amount of structure directing agents (SDAs) in same solvent. After stirring or heating to 180˚C for up to 10 hours in an autoclave, the nanoparticles were collected by centrifuging. The resulting nanoparticles were re-dispersed into common solvents like toluene, chloroform, dioxane, THF, etc. For preparing hybrid polymer particles containing metal or metal oxide nanocrystals, varied amount of precursors were added into the dioxane solution containing block copolymers and SDAs. For TEM and SEM characterization, samples were prepared by drop-casting of a small amount of solutions on TEM grids or Si wafer. SEM images were taken using an Hitachi 5200 FEG microscope. TEM was performed on a JEOL 2010 with 200KV acceleration voltage, equipped with a Gatan slow scan CCD camera.

RESULTS AND DISCUSSION

Figure 1 shows the TEM images of hybrid polymer nanoparticles containing CdSe/ZnS nanocrystals. The hybrid nanoparticles' diameter is about 35nm with a narrow distribution and containg 5nm CsSe/ZnS nanocrystals inside the particle shown in Figure 1 inset. The hybrid polymer nanoparticles were prepared by self-assembly of PS-PVP ($PS_{19.9K}$-$P4VP_{29.4K}$) and hydroxyl group-functionalized CdSe/ZnS through hydrogen bonding between hydroxyl groups and PVP. CdSe/ZnS nanocrystals were prepared according to Yang et al[4]The nanocrystals were then functionalized with hydroxyl (-OH) groups[5] that are capable of forming hydrogen bonds with nitrogen (-N=) of PVP chains. The hybrid nanoparticles exhibit optical properties with an optical absorption over 550-600nm and an emission between 500-600nm coming from nanocrystals enclosed in the particles (not show here). We can easily tune the optical properties of these hybrid nanoparticles without requiring complicated chemistry.

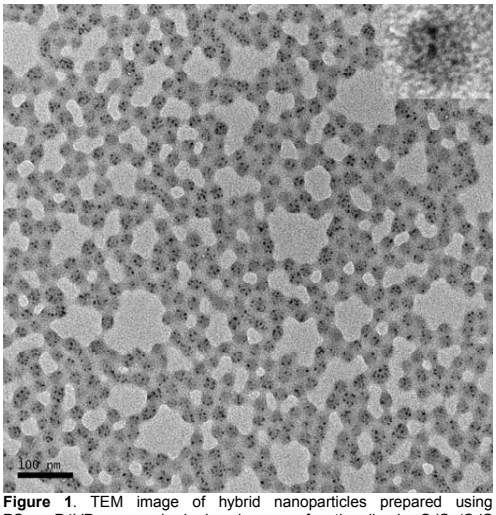

Figure 1. TEM image of hybrid nanoparticles prepared using $PS_{19.9K}$-$P4VP_{29.4K}$ and hydroxyl group-functionalized CdSe/CdS semiconducting nanocrystals.

We synthesized hybrid spherical nanoparticles and cylindrical rods containing uniform Pd, Au nanocrystals by adding different metal precursors (e.g., $H2PdCl_4$, $HAuCl_4$, etc) during the self-assembly process. Figure 2A shows the corresponding TEM image of monodiperse hybrid nanoparticles (~20nm) containing Pd nanocrystals (1-2nm) prepared using ($PS_{19.9K}$-$P4VP_{29.4K}$) and H2PdCl4. Figure 2B shows the corresponding TEM image of monodiperse hybrid nanoparticles (~30nm) containing Au nanocrystals (2-3nm) prepared using ($PS_{19.9K}$-$P4VP_{29.4K}$) and $HAuCl_4$. But when we changed the block polymer to $PS_{5.3K}$-$P4VP_{58K}$-$PS_{5.3K}$ and kept same amount of $HAuCl_4$ as precursors, we got cylindrical hybrid nanowires (diameter about 45nm, length 3-10 μm) containing individual 2-3nm gold nanocrystals.

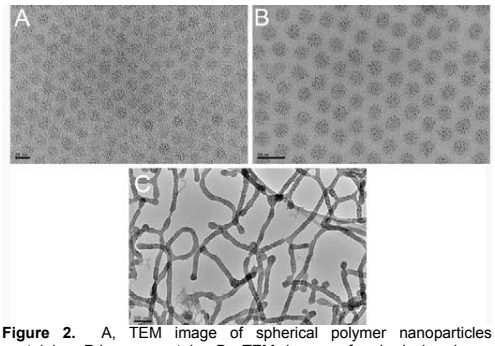

Figure 2. A, TEM image of spherical polymer nanoparticles containing Pd nanocrystals; B. TEM image of spherical polymer nanoparticles containing Au nanocrystals; C. TEM image of cylindrical hybrid polymer wires containing Au nanocrystals.

Removal of SDAs (such as) HBBA results in nanocavity and available nitrogen (-N=) of PVP chains, which provide surface reactive sites and act as nanoreactor for further introduction of functional

Cooperative Self-Assembly Assisted Formation of Monodisperse Spherical and Anisotropic Polymer Nanoparticles

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INTRODUCTION

Widespread use of polymer particles in precision coatings and pigment, photonic, electronic, and controlled release devices has promoted extensive research efforts[1-3]. Block copolymer (BCP) self-assembly is a general method for fabrication of monodispers polymer nanoparticles or micelles that are formed through phase separation in the selective solution. However, these micellar nanoparticles are sensitive to environmental solvent and temperature. They subject to size and shape changes upon subtle environmental solvent and temperature changes. Here, we reported a facile method to produce polymer nanoparticles with enhanced solvent and thermal stability using Poly(styrene-b-4-vinyl pyridine) (PS-P4VP) and structure directing agent (SDA). The SDAs such as 8,13-Bis(1-hydroxyethyl)-3,7,12,17-tetramethyl-21H,23H-porphine-2,18-dipropionic acid (HPDC) and 2-(4´-hydroxybenzeneazo)benzoic acid (HBBA) are molecules that have both aromatic rings and hydrophilic groups such as -OH, -COOH, etc. On one end, SDAs form hydrogen bonds with hydrophilic chain PVP to facilitate the phase separation. On the other end, they form intermolecular non-covalent bonds, such as hydrogen bond and/or aromatic π-π stacking that stabilize the final nanoparticles. These nanoparticles are very stable and can be well redispersed into common solvents such as tetrahydrofuran, dioxane, chloroform, and toluene etc. HBBA is alcohol soluble, can be selectively removed by wash with alcohol to form hollow nanoparticles.

EXPERIMENTAL

Materials. The following BCPs were purchased from Polymer Source Inc. and used as received: Poly(styrene-b-4-vinyl pyridine) (PS_{12k}-$P4VP_{11.5k}$), PS_{20k}-$P4VP_{19k}$, PS_{20k}-$P4VP_{29k}$. HPDC was purchased from Frontier Scientific Inc. HBBA and all solvents were purchased from Aldrich Chemicals.

Synthesis of Polymer Nanoparticles. In general, 2 ml of 4wt% block copolymers into dioxane was added to 2 ml solutions containing varied amount of SDAs in same solvent. After stirring and heating to 180˚C for up to 10 hours in an autoclave, the nanoparticles were collected by centrifuging. The resulting nanoparticles were re-dispersed into common solvents such as toluene, chloroform, dioxane, THF, etc. For TEM and SEM characterizations, samples were prepared by drop-casting of a small amount of solutions on TEM grids or Si wafer. For films, specimens were prepared by dip- or spin-coating on substrates such as Si wafer, microscope glass, and carbon films, etc. In the case of synthesis of hollow polymer nanoparticles, HBBA was used as the SDA. Removal of HBBA was conducted using an alcohol (methanol or ethanol) wash.

RESULTS AND DISCUSSION

Figure 1 shows the SEM images of polymer nanoparticles film dip-coated from dioxane solution. The diameter of the nanoparticles is about 40nm with a narrow distribution (standard deviation less than 7%) Through solvent evaporation, these polymer nanoparticles self-assemble into thin films of ordered nanoparticle arrays. FTIR spectroscopy results provide evidence for the formation of hydrogen bonds between HPDC and P4VP segments. FTIR spectra show clear red-shift of key PVP peaks caused by hydrogen bonding at 1415 cm^{-1} and 1597 cm^{-1}, which is consistent with previous report[4]. UV-vis spectracopy results confirm the formationof π-π stacking between SDAs. Both B-band (401nm) and Q-band (500-650nm) in UV-vis spectra for polymer nanoparticle specimen shift to higher wavelength in comparison with pure HPDC. The red-shifting is caused by J-aggregation of HPDC through aromatic π-π stacking. The slight blue-shifting after addition of 5mg HDPC may be due to H-aggregation between SDAs.

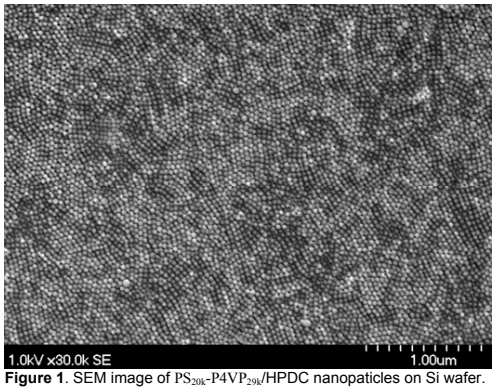

Figure 1. SEM image of PS_{20k}-$P4VP_{29k}$/HPDC nanopaticles on Si wafer.

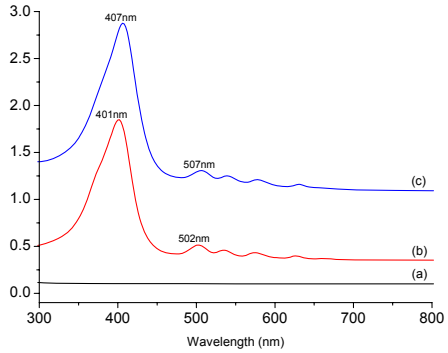

Figure 2. UV-Vis spectra of (a) PS-P4VP, (b) HDPC, and (c) PS-4VP/HPDC nanoparticles.

By using alcohol soluble SDA such as HBBA, we can synthesize hollow nanoparticles. Figure 3 shows the TEM image of PS-4VP/HBBA nanoparticles after methanol wash. TEM image confirms that the diameter of the hollow cavity is 13 nm and the shell is 15 nm. The films of the hollow nanoparticle exhibit low porosity resulted form the hollow cavity and low refractive index. We have shown these films are potential candidate materials for antireflective coatings. Figure 4 shows UV-Vis spectra of these coatings on glass slides. The transmittance of such a sample with a 250nm thickness is ~98% within 1000nm to 1500nm window .

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Corporate Engineering & Technology
6801 Rockledge Drive, Bethesda, MD 20817

LOCKHEED MARTIN

March 16, 2010

From:
Thomas E. Herald, Jr., Ph.D.
Lockheed Martin Fellow and Shared Vision Research Manager
(407) 242-1470

To:
R&D Magazine, Judging Committee
2000 Clearwater Drive
Oakbrook, IL 60523

RE: Letter of support for *Multifunctional Optical Coatings by Rapid Self Assembly* research at Sandia National Laboratories

Lockheed Martin's Dr. Earl Stromberg has been collaborating with Sandia National Laboratories and Dr. Hongyou Fan's talented team for several years. The initial research focused on the development of affordable, self-assembled, nanocomposite coatings and associated fabrication processes with properties tailored to specific performance requirements, such as antireflective (AR) optics. This included conquering both the materials composition and the challenges of process development to uniformly coat surfaces (i.e. lenses) and to do so at room temperature. The business benefits for this are quite diverse and include: improved affordability of the coating materials, improved supportability wherein field repairs are now possible (no longer requiring a return to the factory for conventional high temperature particle vapor deposition techniques), and scalability from a small dimension process to large scale spray and tank dip coating processes.

Since these original achievements, the collaborative team has developed a new chemical process that enables a radical shift toward improving the optical design and material fabrication in two distinct ways. First is to significantly improve anti-reflective performance over a broader angle of incidence and the second is regarding the understanding of "layer tuning" so that various materials and deposition thicknesses can tailor a material to specific applications. A side benefit that has been observed and is just now being explored is the hydrophobic characteristics of the material applications.

At Lockheed Martin, we are excited about the possibilities that this ground-breaking research has opened up for our company and our military forces. We are also proud to have been a part of advancing this scientific research for our country. I am recommending this innovative research in consideration for the prestigious 2010 R&D 100 Award.

Sincerely,

Thomas E. Herald, Jr.

CABOT

March 1, 2010

To,
The Judging Committee,
R&D Magazine.

Dear Committee Members,

It is my pleasure to recommend the exciting new technology, "Multifunctional Optical Coatings by Rapid Self-Assembly" developed by Dr. Fan and his co-workers for the R&D 100 award. My current role as Global Applications Development Leader with Cabot Aerogel and prior experience in the R&D function at Cabot Corporation, a global performance materials company, gives me perspective to comment on the value of this technology.

There is a constant stream of problems, which the world faces today, that require new and novel material solutions. While material cost is always a barrier to adoption for an otherwise technically successful solution, ease of use and compatibility with existing infrastructure are two additional criteria that play a key role in determining whether an invention or solution will see light of day. It is this combination of factors that the "rapid self-assembly" process addresses that excites me about the prospective broad impact of this work.

The use of organic and inorganic particles of various shapes and morphologies (hollow versus solid) with commonly available polymers to be able to create anti-reflective coatings that are also superhyrophobic is ingenious. The process is simple, flexible and practical. It holds promise to solve problems in both light harvesting and transmitting elements used in the energy sector. Improving the light capture ability of solar cells by 8-9% is a significant improvement. The additive nature of anti-reflective coating solution makes it versatile and relevant for a board range of solar cell technologies in use today and in the future. Flexibility of the innovation is further seen in its ability to manipulate the anti-reflective nature of the coatings from the visible spectrum to the infra-red spectrum.

The ability to create multifunctional optical coatings using a simple, flexible and low cost process has far reaching benefits to society in terms of national security, energy security, and controlling global warming. With this, I sincerely urge the committee to consider the application by Dr. Fan and co-workers a worthy recipient of the prestigious R&D 100 award.

Regards,

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Global Applications Development Leader
Cabot Aerogel
Email: dhaval_doshi@cabot-corp.com
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ARCH Venture Partners 8725 W. Higgins Road, Suite 290 Chicago, IL 60631

April 4, 2010

Dear Judging Committee, R&D Magazine,

ARCH Venture Partners would like to offer this Letter of Support (LOS) for the exciting innovative technology, "Multifunctional Optical Coatings by Rapid Self-Assembly" developed by Dr. Hongyou Fan *et al.* at Sandia National Laboratories (SNL) for the 2010 R&D 100 award application.

We have been involved with the Enterpreneur in Residence Program at Sandia National Laboratories since April 2008 which was a pilot program funded by the Department of Energy's Energy Efficiency and Renewable Energy Office (DOE - EERE). ***During the course of this effort, we have reviewed over 500 technologies at SNL with this technology standing out as one we feel has true potential via commercial impact and one that we intend to spend much more due diligence on to attempt to form a new company around***.

This innovative technology provides simple and inexpensive self-assembly processes for fabrications of ordered multifunctional nanocomposite coatings with more degrees of freedom than conventional coating processes (e.g., CVD, Sputtering, etc) for target applications. This technology can be implemented to make tailored microstructures, it could have some interesting applications in energy efficient windows (an area in which we also reviewed far more complex offerings). For example, the broadband AR coating could be very interesting for canopy and windshield applications to increase clarity and for solar cells to increase light transmission to enhance solar cell efficiency. Thinking about how one could use small structures to waveguide visible daylight into a room where you want it, and couple it to an IR filter to keep out the heat. Just a few ideas…. Window & glass manufacturers are aggressively looking at solutions. Seems there's a ready market for a good solution such as proposed here.

In addition to our excitement about the technology and its platform application base, we have enjoyed working with Dr. Fan and his team as they demonstrate deep innovative insight into new methods that circumvent long standing traditions in the use of vacuum technology and high temperatures to produce functional materials in ambient conditions. Our interest also extends to Dr. Fan himself as he demonstrates a refreshing perspective of what is required of a technology to extract maximum commercial benefit.

For all these reasons and more, we would like to strongly recommend this piece of work for a 2010 R&D 100 award.

Sincerely,

Tom B

Tom Brennan
ARCH Venture Partners

505.350.9091 – tbrennan@archventure.com – www.archventure.com

STEVENSON-WYDLER (15 USC 3710)
COOPERATIVE RESEARCH AND DEVELOPMENT AGREEMENT
(hereinafter "CRADA") NO. SC99/01573

Lockheed Martin Umbrella

BETWEEN
Sandia Corporation
(a wholly owned subsidiary of Lockheed Martin Corporation)
As Operator of Sandia National Laboratories
under its U.S. Department of Energy Contract
No. DE-AC04-94AL85000
(hereinafter "Sandia")

AND
Lockheed Martin Corporation and Its Affiliates
(hereinafter "Participant")

Lockheed Martin being a corporation of the State of Maryland
having a principal office in Bethesda, Maryland

Sandia and Participant being hereinafter jointly referred to as the "Parties."

Amendment No. 4
November 1, 2007

ARTICLE I. DEFINITIONS

A. "Government" means the United States of America and agencies thereof.

B. "DOE" means the Department of Energy, an agency of the United States of America.

C. "Contracting Officer" means the DOE employee administering Sandia's DOE Contract.

D. "Generated Information" means information produced in the performance of this CRADA.

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APPLICATION NUMBER	FILING or 371(c) DATE	GRP ART UNIT	FIL FEE REC'D	ATTY.DOCKET.NO	TOT CLAIMS	IND CLAIMS
12/706,003	02/16/2010	1795	1090	SD11306/S116206	20	3

CONFIRMATION NO. 9824

20567
SANDIA CORPORATION
P O BOX 5800
MS-0161
ALBUQUERQUE, NM 87185-0161

FILING RECEIPT

OC000000040461067

Date Mailed: 03/08/2010

Receipt is acknowledged of this non-provisional patent application. The application will be taken up for examination in due course. Applicant will be notified as to the results of the examination. Any correspondence concerning the application must include the following identification information: the U.S. APPLICATION NUMBER, FILING DATE, NAME OF APPLICANT, and TITLE OF INVENTION. Fees transmitted by check or draft are subject to collection. Please verify the accuracy of the data presented on this receipt. **If an error is noted on this Filing Receipt, please submit a written request for a Filing Receipt Correction. Please provide a copy of this Filing Receipt with the changes noted thereon. If you received a "Notice to File Missing Parts" for this application, please submit any corrections to this Filing Receipt with your reply to the Notice. When the USPTO processes the reply to the Notice, the USPTO will generate another Filing Receipt incorporating the requested corrections**

Applicant(s)

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Zaicheng Sun, Albuquerque, NM;

Power of Attorney: The patent practitioners associated with Customer Number 020567

Domestic Priority data as claimed by applicant

Foreign Applications

If Required, Foreign Filing License Granted: 03/05/2010

The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is **US 12/706,003**

Projected Publication Date: Request for Non-Publication Acknowledged

Non-Publication Request: Yes

Early Publication Request: No

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APPLICATION NUMBER	FILING or 371(c) DATE	GRP ART UNIT	FIL FEE RECD	ATTY.DOCKET.NO	TOT CLAIMS	IND CLAIMS
12/038,037	02/27/2008	1794	1030		20	2

CONFIRMATION NO. 4894

20567
SANDIA CORPORATION
P O BOX 5800
MS-0161
ALBUQUERQUE, NM 87185-0161

FILING RECEIPT

OC000000028861623

Date Mailed: 03/17/2008

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This application is a CIP of 10/683,810 10/10/2003

Foreign Applications

Projected Publication Date: Request for Non-Publication Acknowledged
Non-Publication Request: Yes
Early Publication Request: No
Title

Self-Assembly of Water-Soluble Nanocrystals

Preliminary Class

428

PROTECTING YOUR INVENTION OUTSIDE THE UNITED STATES

Since the rights granted by a U.S. patent extend only throughout the territory of the United States and have no effect in a foreign country, an inventor who wishes patent protection in another country must apply for a patent

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