

## Cost-Effective Process Produces Antimicrobial Composite Nanoparticles

Titanium dioxide ( $\text{TiO}_2$ ) is an effective photocatalytic antimicrobial material when it is directly applied on an infected area of the human body or a contaminated area of the physical environment. However, it is an electrical insulator and difficult to remove from the treated surface. If  $\text{TiO}_2$  could be produced in the form of composite particles consisting of a photocatalytic shell with a magnetic core, then the application of a magnetic field would attract the magnetic core, thus facilitating the removal of the particles from a surface. Other advantages of a magnetic core would be the ability to control and target delivery of the particles. At the University of Louisiana at Lafayette, a cost-effective, near-room-temperature process to synthesize a removable, antimicrobial, magnetic photocatalytic nanomaterial has been developed. These composite nanoparticles have a wide range of applications including catalysis, degradation of organic and inorganic environmental pollutants, and photodestruction of cancer cells and microbes.

The technology developed for the synthesis of this new generation of composite nanoparticles, which consist of a photocatalytic shell of anatase titanium dioxide (a natural crystallized octahedral form) and a magnetic core of nickel ferrite ( $\text{NiFe}_2\text{O}_4$ ), involves combining the techniques of reverse micelles (in which surfactants dissolved in organic solvents form spheroidal aggregates) and chemical hydrolysis (in which water reacts with another substance to form two or more new substances). The process developed by the University of Louisiana researchers is relatively simple, environmentally friendly, and cost-effective. The composite nanoparticles produced provide an efficient and effective solution for water purification, environmental pollution control, and antimicrobial applications. Therefore, it is anticipated to have a sizable potential market including microbiologists, environmentalists, and photocatalyst developers and users.

High-magnification transmission electron micrographs of  $\text{TiO}_2$ -coated  $\text{NiFe}_2\text{O}_4$  nanoparticles are shown in Figure 1. The direct coating of crystalline titania onto the surface of the magnetic nickel ferrite particles produces a core-shell structure in which the  $\text{NiFe}_2\text{O}_4$  is predominantly concentrated in the center of the composite

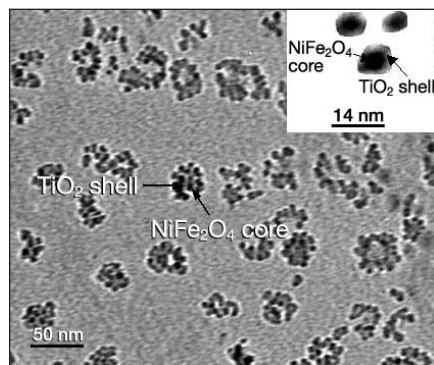


Figure 1. High-magnification transmission electron micrograph of the core-shell structure of  $\text{TiO}_2$ -coated  $\text{NiFe}_2\text{O}_4$  nanoparticles, with a closer view in the inset.

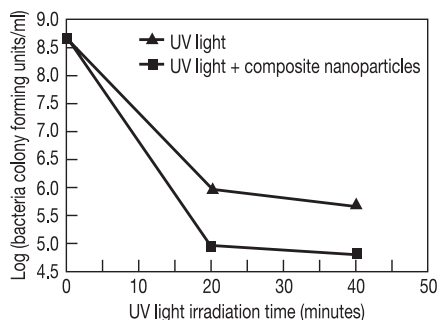


Figure 2. *E. coli* bacterial inactivation response to  $\text{TiO}_2$ -coated  $\text{NiFe}_2\text{O}_4$  nanoparticles as a function of UV irradiation time. The units of the y-axis represent the number of colonies of bacteria in 1 ml of solution. The defined circular shape of the bacteria colony enables it to be more easily counted manually, as compared with an irregular or undefined shape.

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nanoparticles. The composite nature of the particles, consisting of a dark  $\text{NiFe}_2\text{O}_4$  magnetic core and a gray  $\text{TiO}_2$  shell, can be seen in the figure. The  $\text{NiFe}_2\text{O}_4$  magnetic core is ~4–6 nm in diameter and the  $\text{TiO}_2$  shell is ~2–3 nm in diameter. The x-ray diffraction peak positions obtained for  $\text{TiO}_2$ - $\text{NiFe}_2\text{O}_4$  are consistent with standard  $\text{NiFe}_2\text{O}_4$  and the anatase phase of  $\text{TiO}_2$ . The  $\text{TiO}_2$ -coated  $\text{NiFe}_2\text{O}_4$  nanoparticles retain the magnetic characteristics of uncoated nanocrystalline nickel ferrites: superparamagnetism (the absence of hysteresis, remanence, and coercivity at 300 K) and non-saturation of magnetic moments in a high field. The retention of magnetic strength confirms their application as removable photocatalyst nanoparticles.

When  $\text{TiO}_2$  powder in aqueous suspension is irradiated with UV light, free hydroxyl radicals ( $-\text{OH}$ ) are generated that are highly toxic to microorganisms. This concept has been explored to investigate the inactivation of *E. coli* in a culture medium in the presence of UV-irradiated  $\text{TiO}_2$ -coated  $\text{NiFe}_2\text{O}_4$  nanoparticles. Figure 2 shows the effect of  $\text{TiO}_2$ -coated  $\text{NiFe}_2\text{O}_4$  nanoparticles on bacterial inactivation or germicidal action in the presence of UV light. Figure 2 demonstrates that at a constant irradiation time, both in the presence and absence of  $\text{TiO}_2$ -coated  $\text{NiFe}_2\text{O}_4$  nanoparticles, the concentration of *E. coli* bacteria was reduced, but the decrease in concentration was enhanced for the  $\text{TiO}_2$ -coated  $\text{NiFe}_2\text{O}_4$  nanoparticle system compared with UV light alone.

The titania photocatalytic shell provides the antimicrobial capability to inactivate bacteria and remove organic pollutants, while the nickel ferrite magnetic core enables controlled delivery of composite nanoparticles through the application of a small magnetic field. This supports their application as removable antimicrobial photocatalyst nanoparticles.

### Opportunities

The developers are interested in collaborating and working with companies to develop this patented process for commercial applications.

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### Nanoporous Ceramic Adsorbent Removes Mercury and Other Environmental Contaminants

Once released into the environment, mercury enters the food chain, endangering humans and other life forms. There have been no commercially viable technologies to reduce mercury concentrations in water to the 200-ppb level required by the U.S. Environmental Protection Agency. Researchers at the Department of Energy's Pacific Northwest National Laboratory (PNNL) have addressed this problem by developing a novel mercury-removing adsorbent.

Called SAMMS™ (self-assembled monolayers on mesoporous silica), the technology is a potential solution for industries such as coal-fired power plants that must manage contaminated effluents. Moreover, with their high surface area, fast kinetics, and controllable chemical selectivity, these adsorbents can be tailored to capture other materials. They also can be used as environmental and security sensors to detect a variety of contaminants.

The SAMMS technology is a hybrid of two innovative materials advances: molecular self-assembly techniques and nanoporous materials. Five grams of SAMMS powder have the surface area of a football field, and the binding molecules cover the available surface. Together, these properties produce a material that loads more than 10 times the mercury per unit mass as a resin and over 30 times the mercury per unit mass as activated carbon. Kinetically, the SAMMS material loads mercury more than 20 times faster than a resin.

SAMMS powder is produced by attaching a monolayer of contaminant-specific molecules to the nanopore surfaces of a ceramic substrate (shown schematically in Figure 1). The resulting adsorbent has a very high surface area (~600–1000 m<sup>2</sup>/g) with dense packing of contaminant binding sites. Consequently, this material exhibits high loading (up to ~600 mg mercury per gram), fast kinetics (>99% adsorption in 5 min), and high selectivity (distribution coefficient  $K_d \sim 1 \times 10^8$  ml/g).

One form, which contains monolayers of a sulfur-containing silane (the silicon and hydrogen compound mercaptopropyl-

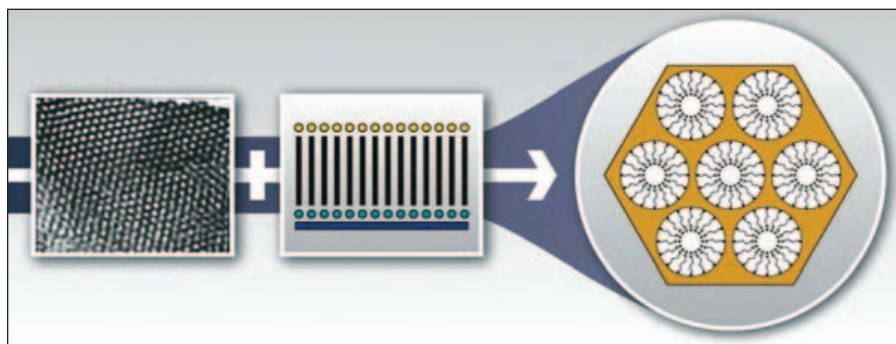


Figure 1. SAMMS™ (self-assembled monolayers on mesoporous silica) is a combination of two novel technologies: (left) a nanoporous ceramic substrate, shown in a transmission electron micrograph, that displays a regular hexagonal array of nanopores ~6.0 nm in diameter, and (center) a contaminant-selective self-assembled monolayer with a cross-linked silane end attached to the pore surface and a functional moiety constituting the top surface of the monolayer. In the resulting SAMMS material (right), the functional monolayer lines all the pore surfaces.

trimethoxy silane), has shown exceptional adsorptive properties for mercury and other metals such as silver, cadmium, and lead. Tests conducted on 160 l of an alkaline waste stream (pH = 9) containing ~11 ppm mercury in a matrix of sodium, borate, fluoride, chloride, iodide, sulfate, and nitrite showed that after treatment with ~0.5 kg of a sulfur-containing SAMMS, 99.4% of mercury had been removed from the waste solution. The total cost of treatment was estimated to be \$200, significantly less than the estimated \$3,500 required for conventional disposal methods.

Several functional self-assembled monolayers have been developed specifically to adsorb groups of contaminants with similar chemical characteristics. For example, PNNL has developed a functional monolayer that adsorbs tetrahedral oxyanions such as arsenate, selenate, molybdate, chromate, and pertechnetate, even in the presence of high concentrations of sulfate. The results demonstrate that the functionality of this compound, an ethylenediamine-Cu(II) complex, is stereospecific (i.e., it has a definite order of arrangement in space) and can adsorb up to about 130 mg/g of chromate, 170 mg/g of molybdate, and 400 mg/g of arsenate, respectively.

Materials have also been developed

that have been shown to specifically adsorb radiocesium (~180 mg/g,  $K_d = 1 \times 10^5$  ml/g) and radioiodine ( $3.5 \times 10^8$  Bq/g,  $K_d = 1 \times 10^5$  ml/g), respectively. In addition, SAMMS material has been synthesized that can separate the actinides (i.e., heavy radioactive elements starting with actinium). Experimental data demonstrate that these moieties can effectively adsorb the actinides <sup>241</sup>Am, <sup>237</sup>Np, <sup>239</sup>Pu, and <sup>238</sup>U with high specificity ( $K_d$  as high as  $4 \times 10^5$  ml/g).

#### Opportunities

PNNL is seeking potential collaboration for developing engineered forms of SAMMS, including research, manufacture, and licensing.

Source: Research and collaboration: Richard Skaggs, Program Manager, Pacific Northwest National Laboratory, Environmental Technology Directorate, PO Box 999, Battelle Blvd. Richland, WA 99352 USA; tel. 509-375-5900, fax 509-375-6966, and e-mail Richard.Skaggs@pnl.gov. Licensing: Eric Lund, Commercialization Manager, Pacific Northwest National Laboratory, Environmental Technology Directorate, PO Box 999, Battelle Blvd. Richland, WA 99352, USA; tel. 509-375-3764, fax 509-375-2323, and e-mail Eric.Lund@pnl.gov.

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**Nano-Sized Rubber Balls Toughen Plastics and Enhance Their Environmental Stability**

Rubber-toughening is a common industrial procedure for improving the mechanical properties of many plastics. Manufacturers blend rubbery compounds with plastics or polymer/inorganic composites to increase their resistance to cracking and fatigue. However, problems associated with poor mixability between the components frequently result in uncontrolled blend morphology and weak interfacial adhesion. Often, the resulting materials have unsatisfactory mechanical properties and performance. To minimize these mixing problems, diene-based rubbers (compounds with straight- or branched-chain carbon atoms containing double bonds) and acrylic-based rubbers with some chemical reactivity and desirable surface energies are commonly used, despite concerns about their long-term environmental stability. Researchers at the Pennsylvania State University have invented a novel rubber-toughening technology that addresses both mixability and stability problems.

The Penn State team has developed a new family of preformed, ethylene-based, spherical rubber particles—tiny rubber balls—with a controlled particle size from 30 nm to 5 μm and a cross-linked matrix with a low glass-transition temperature ( $T_g < -45^\circ\text{C}$ ). The material is always in a pliable state at ambient temperature. This new family of rubber particles is suitable for outdoor applications, unlike the more commonly used polymer acrylonitrile-butadiene-styrene (ABS). Functional groups on the exterior of the particles (e.g., OH, COOH, NH<sub>2</sub>, epoxide, anhydride, styrene, borane, and silane) can be tailored to adhere to most plastic or ceramic materials. The cross-linked ethylene-based particles provide strong mechanical strength and environmental stability. The surface-functional groups offer strong interface interactions (in many cases, specific chemical bonds) with various plastics and composites.

A broad range of rubber-toughened materials can be fabricated, including

- PP/EP (polypropylene/ethylene propylene);
- PMMA/EP [poly(methyl methacrylate)/EP];

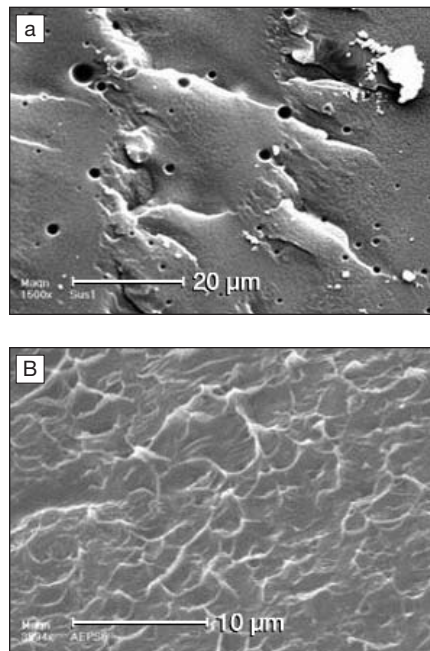


Figure 1. Scanning electron micrographs of the surfaces after fracture at liquid N<sub>2</sub> temperature of two AES materials prepared by (a) a simple polymer blend of S/AN and EP rubber particles and by (b) the Penn State reactive process using functional EP rubber particles. Both AES materials contain about 15 wt% EP rubber particles and 85 wt% S/AN copolymer (with S/AN = 70/30 wt%).

- Nylon/EP;
- Polyester/EP;
- Epoxy/EP; and
- AES (acrylonitrile-EP-styrene).

The materials are produced by pre-selecting the appropriate surface-functional groups, particle size, cross-linking density, and glass-transition temperature ( $T_g$ ) of the pre-formed ethylene-based rubber particles. Despite the cross-linked particle matrix, the reactive ethylene-based rubber particles are completely dispersible and processable in both solution and melt. They are also suitable for standard toughening procedures including reactive extrusion and emulsion/suspension grafting. All the resulting materials have core-shell structures with a cross-linked rubber core

and a grafted polymer shell connecting the rubber particle with the rigid matrix, which produces the toughening effect.

One example is a new AES material. In addition to replacing PB domains with environmentally stable EP rubber particles, the combination of well-defined rubber particles and strong interfacial interactions provides superior toughening and stability for outdoor applications. A comparison between the cryofractured surfaces of two AES materials prepared by the Penn State method and a simple polymer blend of styrene/acrylonitrile (S/AN) copolymer and EP rubber particles, respectively, is shown in the scanning electron micrographs in Figure 1. Both materials contain about 15 wt% EP rubber particles and 85 wt% S/AN copolymer (S/AN = 70/30 wt%). Many convex particles and concave holes exist on the fractured surfaces of the simple blend. The formation of these particles or holes is related to the separation or pullout of the rubber particles from the continuous S/AN polymer matrix during the fracturing of the simple blend sample (Figure 1a). By comparison, no convex particles or concave holes can be found on the fractured surfaces of the Penn State AES material (Figure 1b). The cryofracture occurs in the continuous S/AN domain due to a cohesive failure, not an adhesive one. This demonstrates the presence of strong interfacial adhesion between the cross-linked EP rubber particles and the S/AN matrix, which is essential for the rubber-toughening mechanism.

**Opportunities**

Penn State is seeking collaboration with resin processors and end users for the cooperative development of new products. The university is also interested in licensing its production technology to resin producers.

Source: For research and development projects: T.C. Mike Chung, Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA; tel. 814-863-1394, fax 814-865-2917, and e-mail chung@ems.psu.edu. For licensing: Matthew D. Smith, Intellectual Property Office, The Pennsylvania State University, 113 Technology Center, University Park, PA 16802, USA; tel. 814-863-1122 and e-mail mds126@psu.edu.

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