

Phosphor Microparticles of Controlled Three-Dimensional Shape from Phytoplankton

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We demonstrate how the precise three-dimensional (3D) assembly characteristics of biomineralizing micro-organisms may be combined with synthetic chemical processing to generate photoluminescent microparticles with specific 3D shapes and tailored chemistries. Silica-based microshells with a rich variety of controlled shapes are assembled by a type of unicellular algal phytoplankton known as diatoms (Bacillariophyceae). Each of the tens of thousands of diatom species generates a microshell with a particular 3D morphology that can be used as a shape-dictaing particle template. In this demonstration, the microshells of *Aulacoseira* diatoms were converted into Eu³⁺-doped BaTiO₃-bearing microparticles. The silica-based microshells were first converted into magnesia-based replicas via a gas/solid displacement reaction (the silica of native diatom microshells is not chemically compatible with barium titanate). A conformal, sol-gel-derived coating of europium-doped barium titanate was then applied to the chemically compatible magnesia replicas to yield photoluminescent particles that retained the starting microshell shape. Upon stimulation with 337 nm (UV) light, the 3D microparticle replicas exhibited a bright red emission associated with the ⁵D₀ \rightarrow ⁷F₂ transition of Eu⁺³.

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Manuscript submitted May 19, 2005; revised manuscript received October 5, 2005. Available electronically January 6, 2006.

Considerable interest exists to develop advanced phosphor microparticles with uniform, controlled shapes and tailored inorganic chemistries for brighter, more efficient light-emission sources and for higher-resolution optical displays (e.g., for fluorescent lighting, high-definition televisions, flat panel displays, and portable cell phones).¹⁻⁴ The deposition, microstructure (uniformity, packing density), and properties (resolution, brightness, uniformity, efficiency, stability) of powder-based phosphor coatings are strongly dependent on the shapes and size distributions of the phosphor particles.⁵ Conventional processing methods are not capable of yielding chemically tailored phosphor microparticles with precisely controlled three-dimensional (3D) morphologies in the desired $1-8 \,\mu m$ range.^{9,11,12} The processing of micrometer-sized phosphor particles usually involves a milling step, which results in particles of nonuniform shape and a reduction in the photoluminescent brightness.^{10,12-14} Thus, novel powder synthesis routes that provide enhanced control over particle morphologies and that are chemically versatile (i.e., for a variety of luminescent compositions) could be quite attractive for phosphor coating applications.

Numerous examples exist in nature of microorganisms that assemble rigid microscale structures (microshells) with precisely controlled morphologies.¹⁵⁻¹⁷ For example, tens of thousands of uniquely shaped three-dimensional microshells are generated by aquatic micro-organisms known as diatoms.¹⁸⁻²⁰ Diatoms are planktonic, unicellular algae that are prevalent in a wide variety of marine and freshwater environments.¹⁸⁻²⁰ Each of the estimated 10^4 – 10^5 extant diatom species assembles a silica-based microshell (frustule) with a particular, intricate 3D shape that is decorated with species-specific patterns of fine features.¹⁸⁻²⁰ Maximum frustule dimensions for various species range from <1 to > $10^2 \mu$ m, with many diatom species possessing frustule sizes of a few tens of micrometers or smaller¹⁸⁻²⁰ (i.e., in the range of interest for phosphor powders¹⁻¹⁴). Continuous reproduction of a given diatom species can yield large quantities of frustules of identical shape.²¹ Indeed, large-scale diatom culturing operations, of the type used to generate phytoplankton feed stocks for aquaculture operations (e.g., algal harvests of 100,000 liters per day at 3×10^6 cells/mL^{22.23}), can generate in excess of tens of kilograms of diatom frustules per day. Such large-scale production of precisely shaped 3D microscale structures (i.e., 3D microparticles) is highly attractive for powder-based devices, and has no synthetic analogue.

We show here how the precise assembly characteristics of diatoms may be combined with synthetic, shape-preserving chemical processing to generate photoluminescent microparticles with specific (diatom-derived) 3D shapes and tailored (non-natural) chemistries. The tens of thousands of extant diatom species provide a wide range of frustule shapes from which to select for specific microparticle morphologies. By utilizing the frustules of a single diatom species as microtemplates for shape-preserving chemical conversion, phosphor microparticles with identical morphologies would be generated. To demonstrate this hybrid biological/synthetic chemical approach, silica-based Aulacoseira diatom frustules were converted into photoluminescent microparticles through a two-step process: (i) conversion of the silica (SiO_2) frustules into magnesia (MgO)-based replicas via a gas/solid displacement (oxidation/ reduction) reaction, and (ii) application of a conformal, sol-gelderived coating of europium-doped barium titanate (Eu-doped BaTiO₃) to the chemically compatible magnesia replicas. BaTiO₃ has been found to be an attractive host material for luminescent dopants in that it is a wide bandgap (3.2 eV) electro-optical material that possesses relatively high solid solubilities for a variety of rare- $2^{2/2}$ earth activator cations (e.g., Ce, Nd, Sm, Eu, Gd, Dy, Ho, Er).² Europium was selected as a luminescent activator, owing to the significant level of doping (up to 8 mol %) reported for Eu cations in BaTiO₃ prior to the onset of concentration quenching of photoluminescence.

Experimental

The conversion of SiO₂ *Aulacoseira* diatom frustules into MgObased replicas was conducted within steel ampoules. Diatom frustules and magnesium granules were placed inside and at opposite ends of mild steel tubes (2.5 cm internal diameter, 20 cm internal length). An excess of magnesium granules relative to silica frustules (Mg:SiO₂ molar ratio = 2.5:1) was placed inside the steel tubes in order to ensure that the source of magnesium vapor was not depleted during the course of reaction. The tubes were then crimped and welded shut. The sealed steel ampoules were then thrust into a horizontal tube furnace preheated to 900°C and held for 1.5 h. After such heat-treatment, the reacted frustules were immersed in an aqueous 0.49 M NaOH solution for 3 h at 60°C with ultrasonication in order to selectively dissolve Si-bearing reaction products of the oxidation-reduction reaction.

A sol-gel process was used to apply a Eu-doped $BaTiO_3$ coating to the MgO-converted frustules. An ethanol-based precursor solution containing barium titanium ethylhexano-isopropoxide

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Figure 1. Secondary electron (SE) images at various stages of chemical conversion: (a) a starting *Aulacoseira* diatom frustule, (b) a MgO frustule replica, (c) a MgO replica coated with a Eu-doped BaTiO₃ layer (after heat-treatment for 1 h at 600°C), and (d) Eu-doped BaTiO₃ grains on the surface of the specimen in (c).

(Alfa Aesar Chemical Co., Ward Hill, MA), europium(III) nitrate (Alfa Aesar), ammonium hydroxide, and deionized water was prepared with а molar $BaTi(OOC_8H_{15})$ \times (OC₃H₇)₅:Eu(NO₃)₃·6H₂O:NH₄OH:H₂O:EtOH ratio of 1.0:0.010:1.5:1.4:110. A 0.4 g batch of the magnesia-converted frustules was immersed in 20 mL of this precursor solution. The mixture was stirred and refluxed at 100°C for 3 h, after which 8 mL of the solution was allowed to slowly evaporate at 56°C. The refluxing treatment was repeated for another 1.5 h at 100°C, after which 5 mL more of the solution was allowed to evaporate. After a final 1.5 h refluxing step, the remaining volatile solution was allowed to evaporate at 56°C. After drying for 1 h at 100°C, the coated frustules were heated at 3°C/min in air to 600°C for 1 h.

The morphologies of the starting Aulacoseira diatom frustules, the MgO frustule replicas, and the Eu-doped BaTiO₃-coated frustule replicas were evaluated with a field emission scanning electron microscope (1530 SEM, LEO Electron Microscopy, Gmbh, Thornwood, NY) equipped with energy-dispersive X-ray analysis capability. The phase content was determined at room temperature using X-ray diffraction (XRD) analyses (PW1800 diffractometer, Philips Analytical, Almelo, The Netherlands). High temperature X-ray diffraction (HTXRD) analyses (X-pert Pro MPD diffractometer, PANalytical Corp., Almelo, the Netherlands) were conducted with the use of a platinum strip heater (HTK2000 furnace, Anton-Paar, GmbH, Graz, Austria). The diffractometer used a vertical theta-theta goniometer, 0.5° divergence slits, and a solid-state detector (Xcelerator, PANalytical). The temperature of the heating strip was calibrated using standard reference materials (SRM 759, NIST, Gaithersburg, MD). HTXRD analyses were conducted in air either with a constant heating rate of 3°C/min up to 750°C, or at a fixed temperature of



Figure 2. X-ray diffraction (XRD) analyses at various stages of chemical conversion: (a) starting SiO_2 *Aulacoseira* diatom frustules, (b) MgO frustule replicas, and (c) MgO frustule replicas coated with Eu-doped BaTiO₃ layer (after heat-treatment for 1 h at 600°C).

600°C. In the latter case, diffraction patterns were taken at 600°C after every 68 s up to 6.8 min, and then every 340 s thereafter. Transmission electron microscopy (4000 EX, Japan Electron Optics Laboratory, Tachikawa, Tokyo) and electron diffraction analyses were used to evaluate the structure of the Eu-doped BaTiO₃ coatings. Photoluminescence measurements were conducted at room temperature using 337 nm (UV) excitation from an externally triggered (Chopper Sync II, Spiricon, Inc., Logan, UT), pulsed N₂ laser (LN1000, Laser Photonics, Orlando, FL). The specimens were excited at 45° incidence and the emission was collected at normal



Figure 3. High-temperature X-ray diffraction (HTXRD) analyses of sol-gel coated MgO replicas: (a) during heating to 750°C and (b) for various times at 600°C.



Figure 4. Transmission electron (TE) microscopy of Eu-doped $BaTiO_3$ -coated, MgO frustule replicas (after heat-treatment for 1 h at 600°C): (a) low magnification and (b) higher magnification TE micrographs of ion-milled cross sections, and (c) ED pattern obtained from the coating (consistent with tetragonal $BaTiO_3$).

incidence using a collimating lens (74-UV, Ocean Optics, Inc., Dunedin, FL) and a fiber probe (LG-455-020-3, Acton Research Corp., Acton, MA). The fiber probe was coupled to an emission monochromator (Spectra Pro 500i, Acton Research Corp.) affixed with a thermoelectrically cooled photo sensor module (H7422-50, Hammamatsu Co., Bridgewater, NJ).

Results and Discussion

The formation of a thin, BaTiO₃-based coating directly on a SiO₂-based diatom frustule was complicated by the chemical incompatibility of these oxides; that is, barium titanate can react with silica to form other ternary oxide compounds.²⁸ Indeed, initial attempts to generate a sol-gel derived BaTiO₃ coating on SiO₂-based *Aulacoseira* frustules were unsuccessful, owing to the formation of BaTiSiO₅. BaTiO₃ is, however, chemically compatible with MgO.²⁹ Indeed, stable BaTiO₃ thin films (0.2–0.5 µm thick) have been generated on MgO substrates after annealing at up to 850°C for 3 h.^{27,30} Composites of BaTiO₃ nanoparticles (0.3 µm diam) dispersed in a MgO matrix have also been synthesized by hot pressing at 1350°C for 1 h.³¹ Furthermore, prior work by Sandhage et al.³² has shown that SiO₂-based diatom frustules can be converted into MgO-based replicas at 900°C via the following net oxidation-reduction (displacement) reaction

$$2Mg(g) + SiO_2(s) \rightarrow 2MgO(s) + {Si}$$
[1]

{Si} refers to silicon present as elemental Si or dissolved within a Mg–Si phase [Mg₂Si(s) or Mg–Si(l); such phases can be generated by the continued reaction of elemental silicon with excess magnesium vapor]. Because the Mg–Si liquid poured out of the reacted frustules and spread over the underlying steel substrate, the reacted frustules were depleted of Si and enriched in MgO.³²

A similar $Mg(g)/SiO_2(s)$ reaction process as reported by Sandhage et al.³² was used in the present work to convert Aulacoseira frustule templates into MgO-based replicas. After this 900°C reaction treatment, the reacted frustules were exposed to a 0.49 M sodium hydroxide solution to selectively dissolve residual Si-bearing phases. Secondary-electron (SE) images of the frustules before and after such treatment are shown in Fig. 1a and b, respectively. The starting Aulacoseira frustules were cylindrical in shape. One end of each cylinder was open and possessed a protruding rim, whereas the other end was closed and exhibited fingerlike extensions. This 3D frustule morphology was preserved after conversion into MgO. X-ray diffraction (XRD) analyses revealed that the reaction and dissolution treatments were successful in converting the SiO₂ frustules into MgO (Fig. 2a and b). Diffraction peaks for residual Si-bearing phases (cristobalite SiO₂, Mg₂Si, or Si) were not detected in the MgO replicas.

A sol-gel process was used to apply a thin, continuous layer of Eu-doped BaTiO₃ on the MgO frustule replicas. The temperature at which BaTiO₃ formation commenced on the coated MgO replicas during heating was evaluated with high-temperature X-ray diffraction (HTXRD) analyses. A series of diffraction patterns obtained during heating from 400°C up to 750°C at a rate of 3°C/min are shown in Fig. 3a. These patterns revealed that the formation of

BaTiO₃ commenced between 500 and 550°C. HTXRD analyses were then conducted for various times at a constant temperature of 600°C, as shown in Fig. 3b. Little change in the relative intensities of the BaTiO₃ diffraction peaks was detected between 30 and 60 min at 600°C, which indicated that BaTiO₃ formation was completed well within the 1 h treatment at this temperature. A roomtemperature XRD pattern obtained over a wider range of 20 values after the 600°C/1 h treatment is shown in Fig. 2c. Only diffraction peaks associated with MgO and BaTiO3 were detected. Scherrer analysis of BaTiO₃ diffraction yielded an average crystallite size of 23 nm.³³ SE images of such coated frustule replicas are shown in Fig. 1c and d. The coatings appeared to be continuous and were comprised of 10-40 nm diameter particles (consistent with Scherrer analysis). Transmission electron (TE) images of cross sections of the coated MgO frustule replicas are shown in Fig. 4a and b. The lower magnification TE image in Fig. 4a of a frustule cross section revealed that the coating was continuous and submicrometer in thickness. A higher-resolution TE image in Fig. 4b shows that the coating was comprised of 10-50 nm diameter crystallites (consistent with Scherrer analysis). Electron-diffraction analysis (Fig. 4c) confirmed that these fine crystallites possessed the tetragonal barium titanate structure.

The room-temperature photoluminescence (PL) spectrum obtained from the Eu-doped BaTiO₃-coated MgO frustule replicas after stimulation with 337 nm (ultraviolet) light is shown in Fig. 5. Six emission bands characteristic of intra-4*f*-shell transitions from Eu³⁺ (${}^{5}D_{0} \rightarrow {}^{7}F_{j}$ with j = 0, 1, 2, 3, 4, 5) were detected at 580, 593, 613, 653, 694, and 704 nm. 27,34,35 As observed by Li and Kuwabara for Eu-doped BaTiO₃, the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition yielded the most intense (bright red) emission band.²⁷ The width of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ emission peak at half of the maximum intensity (18 nm, Fig. 5) was also similar to that observed by Li and Kuwabara (16 nm) for solgel-derived Eu-doped BaTiO₃. These authors reported that the intensity of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition increased as the heat-treatment temperature of Eu-doped BaTiO₃ was increased up to 600°C.²⁷



Figure 5. Room-temperature PL emission spectra ($\lambda_{ex} = 337$ nm) of the Eu-doped BaTiO₃-coated frustule replicas.

However, a further increase in temperature up to 700°C resulted in a significant reduction in the intensity of this emission, which was attributed to partial reduction of the Eu valence state (from 3+ to 2+).²⁷ Hence, the relatively bright red emission observed in the present work was a direct result of the ability to synthesize continuous coatings of Eu-doped BaTiO3 on compatible MgO frustule replicas with a modest 600°C/1 h heat-treatment.

While the present conformal coating process may be further optimized for enhanced optical performance (e.g., thicker coatings may yield higher photoluminescent intensities), this work demonstrates the feasibility of synthesizing photoluminescent microparticles of controlled shape and size through the use of biologically derived microshell templates. This conformal coating approach is not limited to europium-doped barium titanate phosphors; that is, photoluminescent or electroluminescent microparticles containing other activator ions or host lattice materials may also be synthesized.

Conclusions

This work demonstrates that biogenic microstructures with specific 3D morphologies can be converted via synthetic processing into chemically tailored photoluminescent inorganic microparticles of similar 3D shape. Given the extensive diversity of microshell shapes generated by the tens of thousands of species of diatoms (as well as by other biomineralizing microorganisms), and the broad range of chemistries that can be accessed by the approach of the present work (i.e., combined gas/solid reaction and sol-gel processing), this merger of biological assembly with synthetic chemistry enables the syntheses of phosphor microparticles with a wide variety of well-controlled 3D shapes, sizes, and compositions for a host of lighting or display applications.

Acknowledgment

This work was supported by the Air Force Office of Scientific Research (Dr. Joan Fuller, Dr. Hugh De Long, Program Managers).

Georgia Institute of Technology assisted in meeting the publication costs of this article.

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