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-dictating particle template. In this demonstration, the microshells of *Aulacoseira* diatoms were converted into Eu⁺³-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 367 nm (UV) light, the 3D microparticle replicas exhibited a bright red emission associated with the 

$$D_{4s} → ^{2}F_{2} \text{ transition of Eu}^{3+}.$$  

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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 (SiO₂) frustules into magnesia (MgO)-based replicas via a gas/solid displacement (oxidation/reduction) reaction, and (ii) application of a conformal, sol-gel-derived 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-earth activator cations (e.g., Ce, Nd, Sm, Eu, Gd, Dy, Ho, Er). 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 MgO-based 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 BaTiO₃ coating to the MgO-converted frustules. An ethanol-based precursor solution containing barium titanium ethylhexano-isopropoxide...
(Alfa Aesar Chemical Co., Ward Hill, MA), europium(III) nitrate (Alfa Aesar), ammonium hydroxide, and deionized water was prepared with a molar BaTi$_3$(OOC$_8$H$_{15}$)$_2$Et$_2$(NO$_3$)$_3$, 6H$_2$O:NH$_4$OH: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 BaTiO$_3$-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 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 BaTiO$_3$ 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 N$_2$ laser (LN1000, Laser Photonics, Orlando, FL). The specimens were excited at 45° incidence and the emission was collected at normal...
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, Hamamatsu 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. Indeed, initial attempts to generate a sol-gel derived BaTiO3 coating on SiO2-based Aulacoseira frustules were unsuccessful, owing to the formation of MgO matrix have also been synthesized by hot pressing at 1350°C for 1 h. Furthermore, prior work by Sandhage et al. has shown that SiO2-based diatom frustules can be converted into MgO-based replicas at 900°C via the following net oxidation-reduction reaction.

\[
2\text{Mg}(s) + \text{SiO}_2(s) \rightarrow 2\text{MgO}(s) + [\text{Si}]
\]

where [Si] refers to silicon present as elemental Si or dissolved within a Mg–Si phase [Mg6Si(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.

A similar Mg/g/SiO2(s) reaction process as reported by Sandhage et al. 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 replicates 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 room-temperature XRD pattern obtained over a wider range of 2θ 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. 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-4f-shell transitions from Eu3+ (5D0 → 7Fj, with j = 0, 1, 2, 3, 4, 5) were detected at 580, 593, 613, 653, 694, and 704 nm. As observed by Li and Kuwabara for Eu-doped BaTiO3, the 5D0 → 7F2 transition yielded the most intense (bright red) emission band. The width of the 5D0 → 7F2 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 sol-gel-derived Eu-doped BaTiO3. These authors reported that the intensity of the 5D0 → 7F2 transition increased as the heat-treatment temperature of Eu-doped BaTiO3 was increased up to 600°C.
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+). Therefore, the relatively bright red emission observed in the present work was a direct result of the ability to synthesize continuous coatings of Eu-doped BaTiO$_3$ 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 photoluminescence 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 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.

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