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Mesoporous Silica-Templated Assembly of Luminescent Polyester Particles

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We report the template assembly of luminescent poly-3-hydroxybutyrate (PHB) particles doped with rare-earth complexes. The hydrophobic polymer, PHB, has been infiltrated into the nanopores of mesoporous silica (MS) particles in organic solvent. Because of the van der Waals interaction of the polymer chains, PHB loaded in the nanopores yields replicated particles following removal of the MS template. To prevent aggregation of the hydrophobic PHB particles in aqueous media, the PHB-loaded mesoporous silica particles were coated with a polyelectrolyte multilayer (PEM) shell through the layer-by-layer (LbL) assembly of poly(allylamine hydrochloride) (PAH) and poly(sodium 4-styrenesulfonate) (PSS). Following removal of the silica core, the PEM-coated PHB replicas were used to effectively coordinate rare-earth complexes (europium β-diketone, EuC). The EuC-loaded PHB replicas coated with PAH/PSS emit intense luminescence over a wide pH range (3−11) and for at least several months in aqueous solution, which is due to the intramolecular energy transfer from the ligand to the luminescent center in the rare-earth complexes. The PHB replicas, with stable and intense luminescence, may find application in diagnostics and drug delivery.

Introduction

Mesoporous silica (MS) materials have attracted considerable attention in the areas of chemistry, physics, biology, and materials science since their introduction in the early 1990s.[1] Because of their high surface areas (up to ~1200 m^2 g^{-1}), unique pore structures (in the range of 2−50 nm), and tunable particle morphology, MSs have been widely used to load and encapsulate various species, and for the template synthesis of diverse nanostructured materials.[2−4] Replication of MSs with metals,[5] metal oxides,[6] carbon,[7] and polymers[8] have been achieved by filling the nanopores with small molecule precursors such as metal alkoxides, sucrose, and organic monomers, followed by hydrolysis, carbonization, or polymerization of the precursors and removal of the template.

Recently, we introduced a method to prepare nanoporous, polymer-based spheres (NPS) by templating MS spheres. This approach involves infiltration of preformed macromolecules (e.g., polymers or proteins) into the nanopores of the MS particles, followed by cross-linking of the polymer chains, and removal of the MS particle templates.[9] The general applicability of this technique facilitates the design of polymeric particles with tunable properties by varying the macromolecules used, which can include synthetic polyelectrolytes, proteins, polypeptides, and polymer-drug conjugates.[10] Furthermore, this method permits tuning of the morphology and size of the nanoporous particles. Our previous studies have focused on infiltrating water-soluble macromolecules from aqueous solution to prepare particles that are

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dispersed in water. The preparation of similar but hydrophobic polymeric particles is also fundamentally interesting, as such particles can provide significantly different physicochemical properties to their hydrophilic counterparts. This may provide new opportunities for the loading and release of hydrophobic drugs, and for the protection and stabilization of molecules and macromolecules that are sensitive to aqueous environments. However, challenges associated with preparing hydrophobic particles from hydrophobic constituents include a lack of control over the size of the particles and difficulties in dispersing them in aqueous media for water-based applications.

In this work, we report a facile method to prepare hydrophobic poly-3-hydroxybutyrate (PHB) particles through templating MS spheres. PHB is a hydrophobic polyester that has similar physical properties to those of polypropylene. Compared with previous reports, a significant difference of the current work is that no cross-linking of the infiltrated polymer chains is required to obtain intact replica particles, because of the hydrophobic PHB chains, which can strongly associate and maintain the template particle morphology after MS template removal in aqueous solution. Furthermore, PHB is biocompatible and biodegradable, and has been evaluated as a material for use in tissue engineering scaffolds and controlled drug-release carriers.[11] Recently, it was reported that PHB can also be coordinated with rare-earth complexes to construct luminescent films.[12] We demonstrate that the obtained PHB replicas can be effectively used to coordinate rare-earth complexes. The rare-earth compounds (e.g., rare-earth β-diketone complexes) have unique spectral characteristics, including sharp emission peaks with a narrow peak width at half-height, long lifetimes, high fluorescence quantum yields, and a large Stokes shift,[13] which makes them of interest in clinical diagnostic assays, genomic screening, and fluorescence immunoassays.[14] However, coordination of $-$OH groups significantly reduces the luminescence emission intensity and decay time of the rare-earth complexes because of nonradiative dissipation of energy of the high-energy $-$OH vibrations.[15] This has largely limited the application of rare-earth complexes in biology and related fields, in which aqueous media are typically required. Hence, the design of rare-earth materials with both strong luminescence and good stability in aqueous media is fundamentally important.[16] The rare-earth immobilized in the PHB replicas reported here can emit intense luminescence over a wide range of pH (3$-$11) and for at least several months in aqueous solution. The polyelectrolyte multilayer (PEM) coating (poly(allylamine hydrochloride) (PAH) and poly(sodium 4-styrenesulfonate) (PSS)) on the PHB replicas provides stable and dispersed particles in aqueous solution.

Experimental Section

Materials. The MS particles with a bimodal pore structure (particle diameter, 2$-$4 μm; pore diameters, 2$-$3 nm and 10$-$40 nm) were synthesized via the protocol reported by Schulz-Ekloff et al.[17] Poly(allylamine hydrochloride) (PAH, M_w 70 000), poly(sodium 4-styrenesulfonate) (PSS, M_w 70 000), europium (III) chloride hexahydrate ($EuCl_3 \cdot 6H_2O$), 2-thenoyltrifluoroacetone (TTA), chloroform, and hydrofluoric acid (HF) were obtained from Sigma-Aldrich. Poly-3-hydroxybutyrate (M_w 10 000) was purchased from Polysciences, Inc. The water used in all experiments was prepared in a three-stage Millipore Milli-Q Plus 185 purification system and had a resistivity greater than 18 MΩ cm.

Synthesis of the Rare-Earth Complex. The europium β-diketone complex, $Eu(TTA)_3 \cdot 2H_2O$ (denoted as EuC), was synthesized according to published methods.[18] Briefly, 266 mg of TTA was dissolved in a solution of 6 mL ethanol and 1.2 mL of 1 M NaOH. $EuCl_3 \cdot 6H_2O$ (146 mg) in 42 mL of water was then added to the above solution, and the mixture was heated at 60 °C for 30 min. The yellow complex of EuC precipitated during cooling the solution to room temperature. The precipitate was dried in a vacuum after removal of the solution through filtration and water washing.

PHB Replicas from MS Particles, Surface Modification, and EuC Loading. PHB was first loaded in the MS particles. Approximately 5 mg of MS particles was dispersed in 0.5 mL of the PHB solution (concentration of 35 mg mL^{-1}) in chloroform at room temperature for 16 h. After removing the supernatant with centrifugation (1500 *g* for 2 min), the PHB-loaded MS particles were dried in a vacuum desiccator to remove the chloroform. The PHB-loaded MS particles were dispersed in water with brief sonication. After centrifuging the particles (1000 *g* for 2 min) and removing the supernatant, 0.5 mL of 2.5 M HF was added to the PHB-loaded MS particles. PHB replicas were obtained following three water washing/redispersion cycles. PHB replicas coated with PAH/PSS were also prepared. Before removal of the MS templates, one PAH/PSS bilayer was coated on the PHB-loaded MS particles using the layer-by-layer (LbL) technique.[19] The PHB replicas coated with PAH/PSS multilayers were obtained after dissolving the silica particles. Details of this process are given in Figure 1. For the EuC loading, the PAH/PSS-coated PHB replicas were then dispersed in an ethanol solution of EuC for 16 h. After removal of the supernatant with centrifugation (2000 *g* for 2 min), three washings with water were carried out to remove the unadsorbed EuC.

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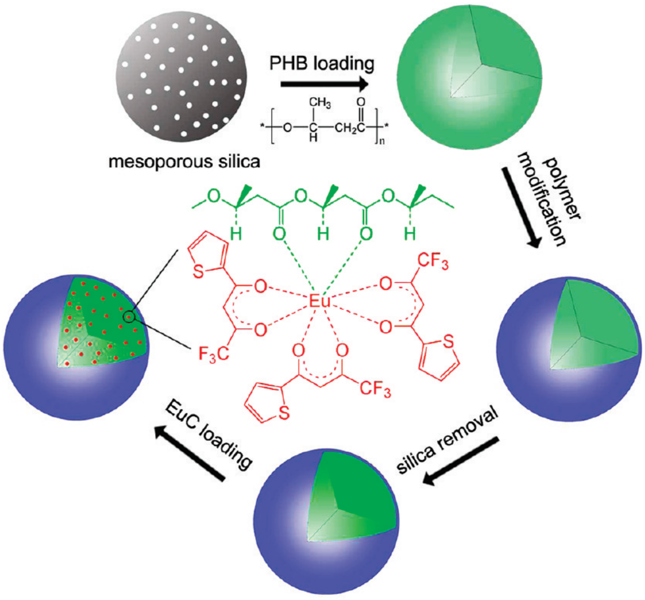

Figure 1. Schematic representation of the formation of EuC-loaded PHB particles obtained by templating MS spheres. A polyelectrolyte multilayer coating is used to stabilize the PHB particles, thus avoiding aggregation in water, and to impart functional groups to the surface of the particles.

Instruments. Thermogravimetric analysis (TGA) experiments were conducted on a Mettler Toledo/TGA/SDTA851e module analyzer. The samples were heated from 25 to 120 °C with a heating rate of 5 °C per min and kept at 120 °C for 20 min under nitrogen (30 mL min^{-1}). The samples were then heated from 120 to 550 °C with a heating rate of 10 °C per min under oxygen (30 mL min^{-1}). ζ-potential measurements were performed on a Malvern 2000 Zetasizer. Fourier transform infrared (FTIR) experiments were conducted on a Varian 7000 FT-IR spectrometer. Transmission electron microscopy (TEM, Philips CM120 BioTWIN, operated at 120 kV) and scanning electron microscopy (SEM, FEI Quanta 200 FEG, operated at 5 kV) were used to examine the morphology of the PHB replicas. The TEM samples (2 μL) were placed onto Formvar-coated copper grids and allowed to air-dry. The SEM samples (2 μL) were placed onto silicon wafers and allowed to air-dry prior to gold sputter-coating. Luminescence emission spectra were recorded on a Horiba Yvon-Jacob FL3−22 fluorimeter using a quartz cuvette (excitation wavelength, 350 nm; emission wavelength range, 500−670 nm; increment size, 1 nm; excitation and emission slit widths, 5 nm). 40 μL of EuC-doped PHB replicas coated with PAH/PSS (ca. 1.5×10^9 particles mL^{-1}) was dispersed in 160 μL of 5 mM phosphate buffer solution of different pH for the luminescence measurements. Fluorescence microscopy images were taken with an Olympus IX71 inverted fluorescence microscope. The samples (1.5 μL) were placed onto glass slides and viewed using a 60× oil immersion objective.

Results and Discussion

As illustrated in Figure 1, PHB was first infiltrated into the nanopores of the MS particles in chloroform solution. After removal of the chloroform solvent, the PHB-loaded MS particles were dispersed in water by brief sonication. TEM images reveal that the PHB-loaded MS particles (Figure 2a) have the same morphology and diameter (2−4 μm) as the pristine MS template particles (data not shown). No signs of PHB clustering were observed either in the solution or on the MS particle surface. TGA was employed to estimate the PHB loading in the MS particles. Thermogravimetric analysis of the PHB-loaded particles showed a mass loss of 31.5% at 215 °C (see Figure S1 in the Supporting Information). Hence, it can be estimated that 1 g of MS particles can load ca. 0.46 g of PHB. On the basis of the TEM and TGA data, we conclude that the hydrophobic PHB can be effectively loaded in the nanopores of the MS particles from organic solvent (chloroform).

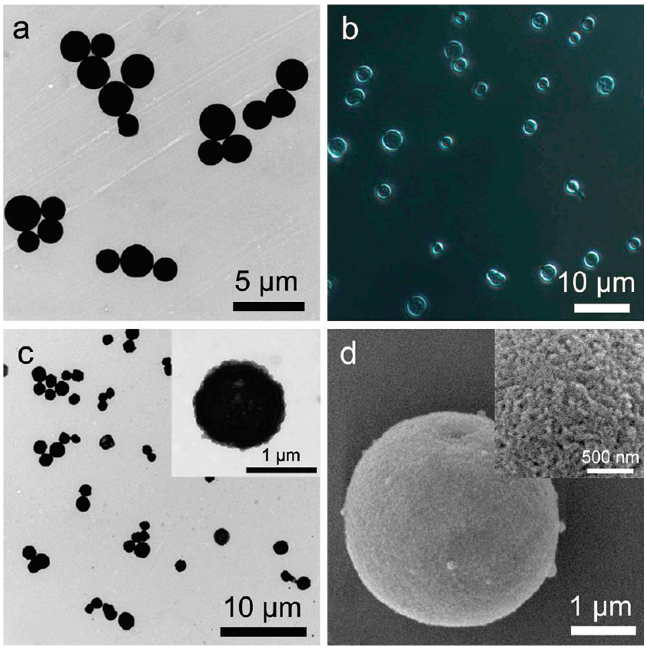

Figure 2. (a) TEM image of PHB-loaded MS particles. (b) Optical micrograph of PHB replicas coated with PAH/PSS and dispersed in water. (c) TEM images of PHB replicas coated with one PAH/PSS bilayer. The inset is a higher-magnification image. (d) SEM images of the PHB replica coated with one PAH/PSS bilayer. A higher-magnification image of the surface of the replica is shown in the inset.

PHB replicas were obtained after removal of the MS template particles, indicating that the van der Waals interaction among the hydrophobic polymer chains plays a significant role in maintaining the morphology of the particles in aqueous media. This is in contrast to our previous reports that use water-soluble macromolecules, where cross-linking of the polymer chains in the porous particles is required to obtain a stable polymer network in solution.[9,10] However, the replica PHB particles easily aggregated in water because of the hydrophobic nature of PHB, hampering their application as colloidal particles in aqueous media. To avoid such aggregation, a PEM (PAH/PSS) coating was assembled on the surface of the PHB-loaded MS particles before MS template removal. The PEM shell provides the dual role of stabilizing the PHB replicas from aggregation and functionalizing the particle surface.

The polyelectrolyte coating was assembled through alternately depositing PAH and PSS. ζ-potential measurements were used to monitor the variation in surface charge of the MS particles after PHB infiltration and polyelectrolyte coating (see Figure S2 in the Supporting Information). The PHB-loaded MS particles had a ζ-potential of -25 mV in water. After deposition of each layer of PAH and PSS, the ζ-potential of the particles alternated between ca. 30 mV (corresponding to PAH deposition) and ca. -40 mV (corresponding to PSS deposition), indicating the consecutive deposition of PAH and PSS, respectively.

After removal of the silica template, PAH/PSS-coated PHB replicas readily dispersed in water, as observed by optical microscopy (Figure 2b). The particles have a diameter of $2-4$ μm, similar to the size of the MS template spheres. Figure 2c shows a TEM image of the PHB replicas. The diameter of the PHB replicas decreased to $1-2$ μm and a rough particle surface was observed under high magnification conditions (insert in Figure 2c). Figure 2d shows the SEM images of the PHB replicas coated with PAH/PSS, which is a free-standing, noncollapsed sphere. The porosity on the surface is apparent at higher magnification (Figure 2d inset). This noncollapsed structure is in contrast to what is typically observed for polyelectrolyte capsules prepared via the sequential assembly of polymers on the surface of MS particles without PHB loading, where collapsed, hollow structures are observed.[20]

FTIR was also used to monitor the composition of the particles. For the PHB-loaded MS particles, a strong and broad absorption band at 1065 cm^{-1} was observed (see Figure S3 in the Supporting Information). The band can be assigned to the Si$-$O stretching vibration. The peak at 1723 cm^{-1} is attributed to the C=O stretching vibration of PHB.[21] No absorption band at 1065 cm^{-1} was observed for the replicas, suggesting complete removal of the silica. The spectrum of the PAH/PSS-coated PHB replicas is similar to the spectrum of pure PHB. The absorption peak at 1007 cm^{-1} originates from the SO$_3^-$ symmetric vibration of PSS.[22]

Luminescent materials are widely employed in fields as diverse as biology and information technology. Commonly sought properties for luminescent materials are brightness and stability.[23] EuC has emerged as a novel luminescent material because of its unique spectral characteristics, including sharp emission peaks, long lifetimes, high fluorescence quantum yields, and a large Stokes shift. However, the luminescence of EuC is not stable in aqueous solution because coordination of $-$OH groups extensively reduces its luminescence emission intensity and decay time. Our aim was to immobilize the EuC into the PHB replicas to construct particles with stable and intense luminescence.

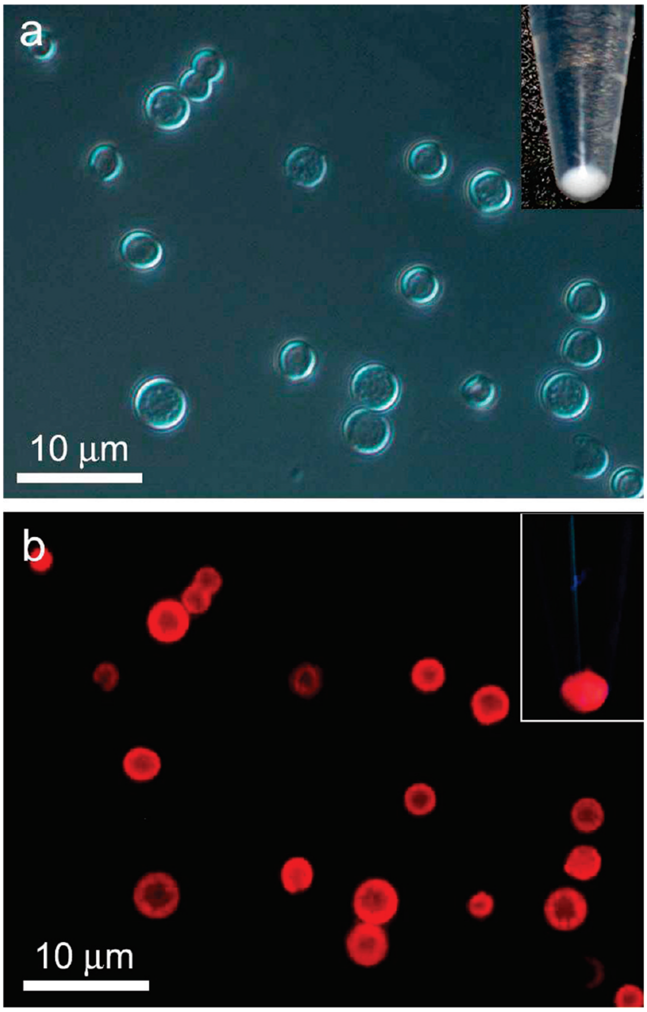

Figure 3. (a) Transmission and (b) fluorescence microscopy images of EuC-doped PHB replicas coated with one PAH/PSS bilayer. The insets in (a) and (b) are photographs of the particles after centrifugation in water and exposed to daylight and ultraviolet light, respectively. The EuC incubating concentration was 0.5 mg mL^{-1}.

The EuC-doped PHB replicas coated with PAH/PSS were visualized in situ by fluorescence microcopy (Figure 3). From the images, the replicas are observed to be spherical with a diameter of $2-4$ μm, and no aggregation was observed in both transmission and fluorescence modes. The intact replicas show no shrinkage or swelling after loading EuC in ethanol, suggesting the PHB replicas have good stability in both aqueous and alcohol solutions. The bright luminescent spheres confirm the effective loading of EuC in the replicas (Figure 3b). The insets in images a and b in Figure 3 show the images of the EuC-doped PHB replicas coated with PAH/PSS in water after centrifugation and exposed to sunlight and ultraviolet light, respectively. The intense monochromatic red luminescence of the EuC-doped replicas is easy to detect by a laboratory ultraviolet lamp at 365 nm (Figure 3b, inset).

The intense luminescence observed from the EuC-doped PHB replicas originates from the loaded EuC. Figure 4a displays an energy transfer model for the ligands, PHB, and the central rare-earth ions in the replica. First, the β-diketone ligand TTA is excited by

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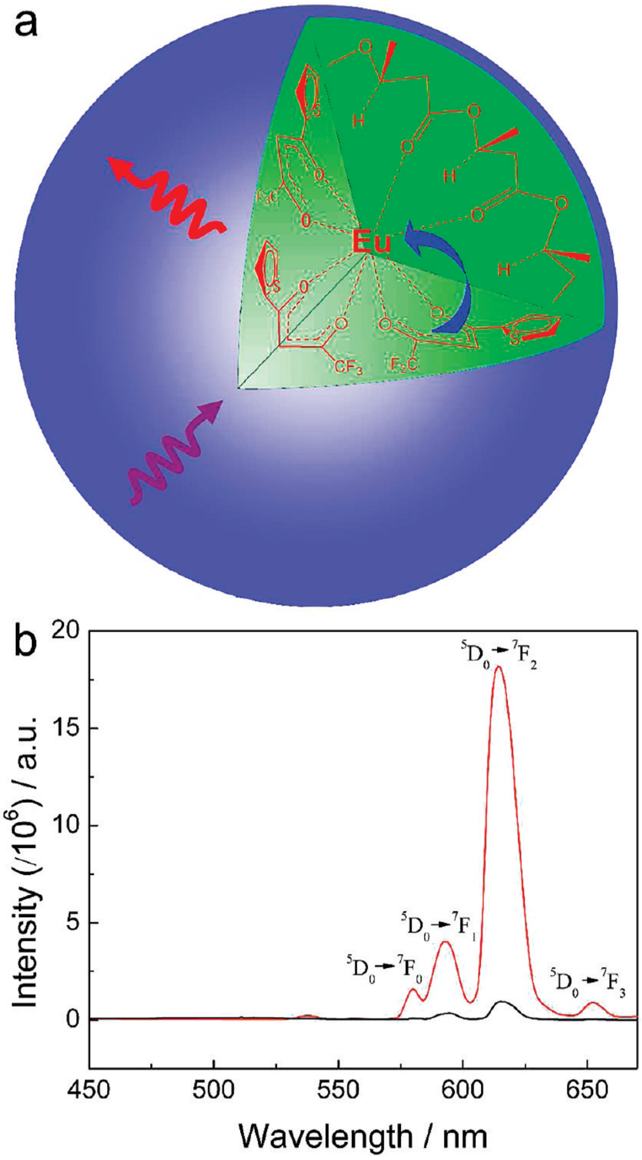

Figure 4. (a) Energy transfer model from the ligand to the Eu^{III} luminescent center in a PHB replica doped with EuC. PHB serves as an efficient cosensitizer for the Eu^{III} ion. (b) Luminescence emission spectra of EuC-doped PEM capsules composed of three bilayers of PAH/PSS (black line) and PHB replicas coated with one PAH/PSS bilayer (red line) dispersed in water ($\lambda_{\text{excitation}}$ = 350 nm). The EuC incubating concentration was 0.05 mg mL^{-1}.

ultraviolet light. Efficient intermolecular energy transfer from the ligand to the luminescent center and subsequent highly efficient emission from the excited state of Eu^{III} to the low level state endow the EuC-doped replicas with luminescent properties. This is the so-called "antenna effect".[24] A detailed energy level diagram for Eu^{III} along with the singlet and triplet levels of TTA is given in Figure S4 of the Supporting Information. Here, the PHB also serves as an efficient cosensitizer for the Eu^{III} ions.[12]

Figure 4b shows the luminescence emission spectrum of EuC-doped PHB replicas coated with PAH/PSS. There are four characteristic peaks (580, 595, 613, and 650 nm), corresponding to the electric dipole transitions of $^5D_0 \rightarrow {}^7F_J$ (J = 0, 1, 2, and 3), which is similar to that of EuC in ethanol solution. The red luminescence observed is mainly attributed to the $^5D_0 \rightarrow {}^7F_2$ transition around 613 nm.

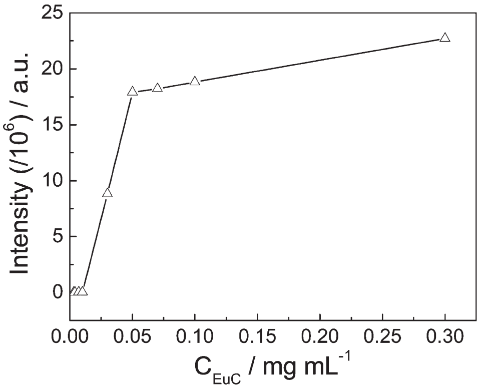

Figure 5. Luminescence intensity of EuC-doped PHB replicas coated with one PAH/PSS bilayer (dispersed in water) as a function of the EuC incubating concentration. The luminescence intensity was recorded at 613 nm ($\lambda_{\text{excitation}}$ = 350 nm).

The EuC content in the PHB particles was studied at different EuC incubating concentrations. PHB replicas coated with PAH/PSS were dispersed in ethanol solutions of EuC of different concentrations for 16 h. After removal of the ethanol supernatant, and three water washing cycles, the luminescence intensity of the particles was measured in water. Figure 5 plots the relationship between the luminescence intensity and the EuC incubating concentration. The luminescence intensity linearly increases at EuC incubating concentrations in the range 0.01−0.05 mg mL^{-1}. The luminescence intensity of the PHB replicas obtained using 0.05 mg mL^{-1} EuC incubating solutions is equivalent to that of neat EuC in bulk ethanol with a concentration of 6.05×10^{-3} mg mL^{-1}. According to the TGA results, 1 g of MS can adsorb 0.46 g of PHB, and hence the EuC doping is ca. 0.5% (EuC/PHB, w/w). At this incubating concentration, the luminescence intensity of the EuC-doped PHB replicas is more than 20 times higher than that of the EuC-doped PAH/PSS multilayer capsules (3 bilayers) templated by the same MS particles (Figure 4b). With further increasing the EuC concentration, the luminescence intensity increases only marginally. This is likely caused by concentration quenching in the EuC-doped particles.

The stability of EuC in the PHB particles was also investigated. The saturated complexes can effectively preserve the rare-earth ions from being attacked by −OH groups in solution.[25] Here, PHB is used to coordinate the EuC to form saturated EuC complexes in the PHB particles. Figure 4a illustrates the EuC coordinated to the PHB backbone and the ligands. The formation of saturated complexes in the hydrophobic PHB particles protects and stabilizes the EuC in aqueous solution. Figure 6 shows the luminescence intensity of EuC-doped PHB replicas coated

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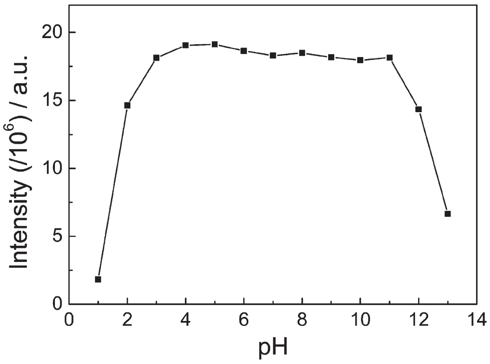

Figure 6. Luminescence intensity of EuC-doped PHB replicas coated with one PAH/PSS bilayer and dispersed in a 5 mM phosphate buffer solution of different pH. The EuC incubating concentration was 0.05 mg mL^{-1}. The luminescence intensity was recorded at 613 nm ($\lambda_{excitation}$ = 350 nm).

with PAH/PSS in phosphate buffer solution of different pH. EuC-doped PHB replicas can emit intense luminescence under ultraviolet radiation over a wide pH range of 3−11. No measurable decrease in the luminescence of the EuC-doped PHB particles was observed after several months. However, the luminescence of EuC-doped PEM (e.g., PAH/PSS) capsules dispersed in water becomes weaker and weaker, suggesting that the PHB stabilizes the EuC through coordination. As the EuC is water insoluble, uncharged, and has a low molecular weight, it has similar physical properties to some hydrophobic drugs. Therefore, the PHB replicas are interesting systems for the loading of hydrophobic (e.g., anticancer) drugs. This is an important property for the EuC-doped PHB replicas to find application.

Conclusions

We have demonstrated the preparation of PHB replicas through templating MS particles, and their subsequent surface coating with PEMs and doping with rare-earth complexes to obtain bright and stable luminescent PHB particles dispersed in aqueous media. Hydrophobic PHB was effectively assembled in MS particles, and intact PHB replicas were obtained after removal of the silica template. The broad range of MS materials available with tunable size, morphology and porosity will enable the preparation of PHB materials with tailored dimensions and morphologies. The surface properties of the PHB replicas can be easily tuned by assembly of a PEM coating. The PEM provides the dual role of preventing aggregation of the PHB replicas in aqueous solution and imparting functionality through the polymer coating. The biodegradable PHB replicas can be effectively used to coordinate rare-earth complexes. The EuC-doped PHB replicas emit intense luminescence over a wide range of pH (3−11) and for at least several months in aqueous solution, making them potentially useful for a range of bioapplications.

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Supporting Information Available: Thermogravimetric analysis of PHB-loaded MS particles; ζ-potential of the PAH/PSS-coated PHB particles as a function of the number of polyelectrolyte layers deposited; FTIR spectra of PHB-loaded MS, PHB replicas coated with PAH/PSS, and neat PHB; and energy level diagram for Eu^{III} and the singlet and triplet levels of TTA (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.