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Facile fabrication of spherical photonic crystals microspheres with angle-independent fluorescent functionality

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ABSTRACT

In this work, we report a facile way to fabricate fluorescent spherical photonic crystals (SPCs) microspheres for the first time. The SPCs microspheres immobilizing Photonic Bandgap (PBG) structure into a hydrogel framework, which can be used to uptake nanosized CdTe NCs particles based on their reversible volume phase transition behavior. Moreover, the resultant SPCs microspheres can not only monitor surrounding humidity, but also exhibit well integration of fluorescence and PBG color in a single structure. More interestingly, the photoluminescence (PL) spectra of fluorescent SPCs microspheres are angle-independent on the curved surface which would open a novel insight into the fabrication of multifunctional optical devices based on PBG and PL functionalities.

1. Introduction

Spherical photonic crystals have attracted substantial attention in the recent decades in the terms of both PBG science and practical applications [1–3] whose features of long-range order and spherical geometries enable themselves to possess angle-independent PBG on the curved surface [4]. Photonic crystals are suitable for applications in optical sensors for pH, [5] temperature, [6] etc. [7]. As we known, optical detection via visual color-changing could offer the most widely-used way to detect a specific signal without complex data collection and subsidiary display unit. To date, much work has been done to embed colloidal crystals into hydrogels to design color-controllable photonic crystals and their optical sensors [2,6,8]. However, most literatures in this area indicate the way to applying colloidal crystals to directly coat onto the surface of the tunable hydrogels film, making the optical stopbands of them are angle-dependent on the flat surfaces [6,8,9]. So far, researches on spherical photonic crystals optical devices with the advantage of angle-independent on the curved surface are still too lacking to meet the needs in this area. Herein, we demonstrate a new facile strategy to construct versatile monodisperse gel-immobilized SPCs microspheres via microfluidic technology. The as-prepared SPCs microspheres can not only monitor the external humidity stimuli through visible color-changing, but also can be used to uptake CdTe NCs, which allow the SPCs microspheres to exhibit both PBG and photoluminescent properties. Furthermore, the PL spectra of SPCs microspheres are angle-independent on the curved surface due to their spherical geometries features. This procedure opens a way to realize the combination of electronic confinement originating from the NCs and photonic confinement from the PBG structure within a single structure.

2. Experimental

2.1. Chemicals and materials

Potassium persulfate (KPS), Acrylamide (AAM), N,N′-methy lene-bis-acrylamide (MBA) were purchased from Sigma-Aldrich used as received. Styrene (St) was purified by distillation to remove inhibitor. Ultrapure water with a resistivity of 18 MΩ/cm was used in all experiments. Monodisperse polystyrene (PS) microparticles were synthesized in our previous experiments [3].

2.2. Fabrication of SPCs microspheres

Water solutions containing 30 wt% PS spheres, 20% AAM, 0.02% MBA, and 0.2% photo-initiators 2959 were used as discontinuous phases, and methyl silicone oil was used as continuous phases. Microfluidic devices were used to prepare SPCs microspheres.

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2.3. Fabrication of CdTe-loaded SPCs microspheres

CdTe NCs were synthesized by microwave method according to the literature [10]. The SPCs microspheres were soaked in 5 wt% CdTe water solutions. The hydrogel embedded in the microspheres tended to become large and thus uptake CdTe NCs for 2 h. Collecting microspheres and drying at room temperature to original size, the CdTe on the surface of the microspheres were washed with deionized water.

2.4. Measurements

SEM images were taken using a Hitachi S-4800 field-emission scanning electron microscope. TEM images were obtained using JEOL JEM-2100 transmission electron microscope. The Varian Cary Eclipse fluorescence spectrophotometer was used to test the UV absorption spectra of the samples.

3. Results and discussion

Fig. 1a and b present typical SEM images of the top and cross-sectional views of the SPCs microspheres without filling hydrogels. The images obviously indicate that the PS particles are assembled into a long-range and ordered hexagonal close packed structure based on face-centered cubic (fcc). Furthermore, air spaces among the PS spheres are also in a fcc arrangement with long-range order structure. Thus, a typical sphere-air bicontinuous fcc superstructures are formed. In striking contrast, an obvious difference can be observed from Fig. 1c that PS particles on the surface of SPCs appear to be covered, which means that AAM have been successfully polymerzied to replace the air spaces in the PC structure. Moreover, PS spheres in Fig. 1d seem to be bonded with each other and embedded into the gel framework, which implies that the air spaces in the fcc structure have been completely infiltrated by PAAM hydrogel, and thus a new inverse bicontinuous hexagonal close packing structure were formed.

Because of their swelling-deswelling volume phase transition nature, CdTe NCs loaded SPCs microspheres can be designed by tuning size of the hydrogels. As the water absorption increasing, the three-dimensional network structures of hydrogels between PS particles become large and thus uptake nanosized CdTe particles. The TEM image in Fig. 2a shows the initial close packed structure was retained without obvious destruction. Remarkably, the NCs distributed uniformly without obvious aggregation can be seen from Fig. 2b and c. Moreover, the HRTEM image in the inset of Fig. 2c clearly presents the well-resolved lattice fringes for a single CdTe NC, indicating an excellent crystalline structure was well-encapsulated in the hybrid SPCs microspheres. Note that a considerable amount of tellurium (Te) and cadmium (Cd) was present on the cross section of the as-prepared sample from EDS in Fig. 2d, thus further verifying the CdTe NCs successfully loaded in the hydrogel matrix between PS particles. These results show that the CdTe NCs have been successfully combined with the colloidal particles which allow the SPCs microspheres to exhibit both PBG and PL functionalities.

When they are exposed under the sunlight (Fig. 3a and d), brilliant blue color appears on the surface of the SPCs microspheres, which corresponding reflection spectra shows a peak centered at 494 nm. Meanwhile, all the microspheres in Fig. 3a also exhibit uniform size and form into hexagonal close packed structure. Moreover, Fig. 3b and c show that the SPCs microspheres emit green and red fluorescence in which embedded with corresponding color-emitting CdTe NCs, respectively. Furthermore, as shown in Fig. 3e, the PL peaks are centered at 537 nm and 627 nm for green- and red-emitting samples, respectively. These observations indicate that the as-prepared SPCs exhibit well integration of fluorescence and PBG structure in a single structure. Additionally, the PL spectra of the green-emitting SPCs microspheres of Fig. 3b with

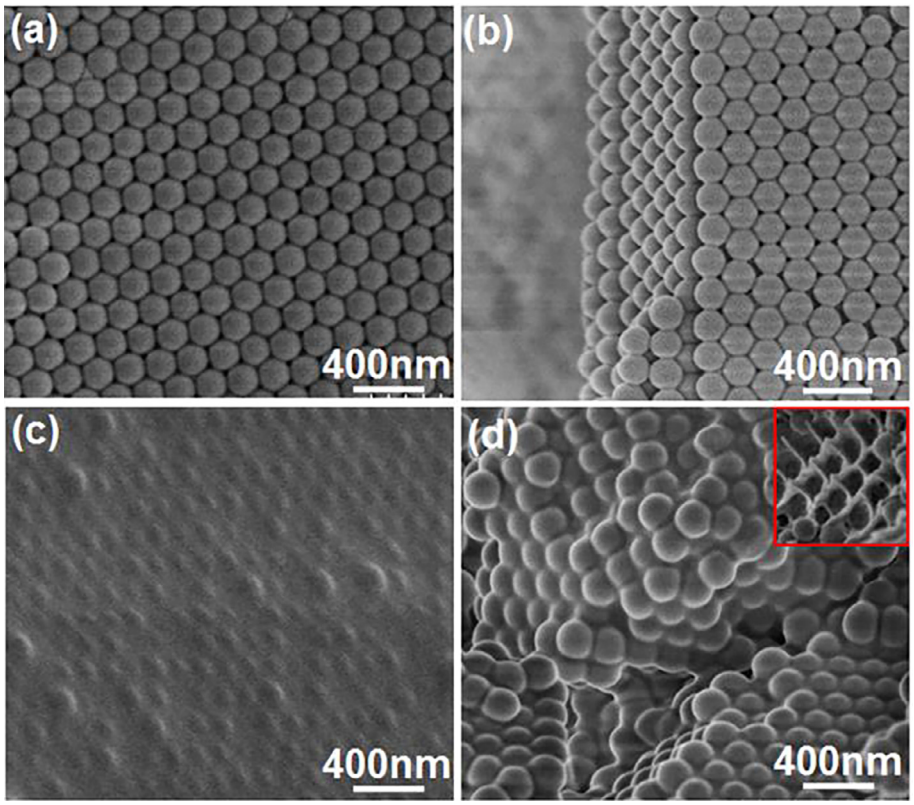

Fig. 1. Typical top-view and cross-sectional SEM images of as-prepared SPCs beads before (a, b) and after (c, d) loading PAAM hydrogel.