

Versatile Polymer-Derived Nanocrystal Microreactors towards Uniform Fluorescent Photonic Crystal Supraballs

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ABSTRACT

Versatile hydrogel-based nanocrystal (NC) microreactors were designed in this work towards the construction of uniform fluorescence colloidal photonic crystal (CPC) supraballs for the first time. As an independent NC microreactor, the carboxyl-terminated hydrogel microspheres were synthesized by seeded copolymerization of acrylic acid (AA) and 2-hydroxyethyl methacrylate (HEMA) with micrometer-sized PS seed particles. The as-obtained latices can effectively capture guest metal ion components due to the abundant carboxyl groups on their surfaces, followed by the introduction of chalcogenides, and hence the in-situ generation of higher-uptake NCs was realized. Additionally, with the aid of the microfluidic device, the as-prepared NC-latex hybrids from the hydrogel-based NC microreactors can also be directly self-assembled into bifunctional CPC supraballs bearing uniform fluorescence and brilliant structural colors.

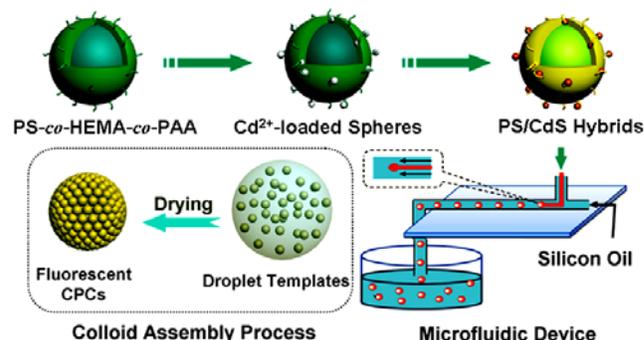
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INTRODUCTION

Colloidal photonic crystals (CPCs) with unique light manipulation and inhibition capability have been extensively investigated in areas ranging from light-emitting devices (LED), biological labels to high-density information storage.¹⁻¹² Recently, the ability to finely bind CPCs with various semiconductor nanocrystals (NCs) is of special interest, because not only high refractive index contrast towards a full photonic bandgap of CPCs is expected but also great improvement of the fluorescence properties of incorporated NCs is achieved through resonance with the periodic structures.¹³⁻¹⁹ Accordingly, tremendous methods, such as physically entrapment, layer-by-layer deposition, and heterocoagulation, have been proposed. Despite great advance in this field, much work is still highly needed. For instance, the introduction of preformed NCs onto CPCs is often accompanied with the agglomeration of the NCs, which inevitably leads to

fluorescence diminishing or the quenching of the NCs and restricts their practical applications.

In this work, a versatile hydrogel-based NC microreactor was designed for the first time towards the construction of fluorescence CPCs (Scheme 1). As an independent NC microreactor, the carboxyl-terminated hydrogel microspheres were synthesized by seeded copolymerization of acrylic acid (AA) and 2-hydroxyethyl methacrylate (HEMA) with micrometer-sized polystyrene (PS) seed particles. These as-prepared latices bearing abundant carboxyl groups can capture the guest metal ion components, followed by the introduction of chalcogenides, and hence the in-situ generation of higher-uptake NCs was realized. This process successfully produce well-dispersed NC/polymer hybrids with perfect uniformity, and overcomes the disadvantages demonstrated above, providing an alternative and effective avenue to the preparation of NC/polymer hybrids. Furthermore, the as-obtained NC-latex hybrids from the hydrogel-based NC microreactor can also be directly self-assembled into bifunctional CPC supraballs. We believe the fundamental knowledge gained from the study of these hydrogel-based NC microreactor will facilitate progress in the field of self-assembled functional colloids and photonic materials.



Scheme 1 Schematic illustration of the fabrication route to uniform fluorescent PC supraballs with the hydrogel-based nanocrystal microreactors.

EXPERIMENTAL

Materials

Styrene (St) and acrylic acid (AA) were purified by distillation under reduced vacuum to remove inhibitor. Potassium persulfate (KPS), 2-Hydroxyethyl methacrylate (HEMA), cadmium chloride ($\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$), sodium sulfide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$), sodium hydroxide (NaOH) and polyvinylpyrrolidone (PVP) were of analytical grade and used as received. Purified water with resistance greater than 18 M Ω cm was used in all experiments.

Preparation of monodispersed hydrogel microspheres

Monodispersed hydrogel microspheres used as the NC microreactor were synthesized by seeded copolymerization of AA and HEMA with PS seed particles in a four-necked round flask equipped with a condenser, a nitrogen inlet, a thermometer and a stirrer. Briefly, 130 mL of deionized water was poured into the four-necked flask. Then, 6.00 g of purified styrene, 0.24 g of PVP and 0.04 g of KPS were added with stirring under a N_2 gas atmosphere. Increase the temperature to 98 °C to initiate the reaction. After the reaction was kept at 98 °C for 1.5 h under constant stirring, an aqueous solution containing 0.3 g HEMA, 0.3 g AA, 0.002 g MBA and 0.005 g KPS was added dropwise slowly, and the reaction was terminated after about 2 h to give the final PS-*co*-PHEMA-*co*-PAA microspheres. The resulting particles were further purified with a 200-mesh nylon net to remove minor traces of agglomerates.

Doped-CdS NCs synthesis within the microreactor

The in-situ synthesis of CdS NCs with the hydrogel-based NC microreactor was carried out as follows: First, under vigorous stirring, 0.2 g of hydrogel-based microspheres were dispersed into a solution containing 0.228 g of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ and 30 mL of deionized water. Then, The 1 M NaOH aqueous solution was added dropwise to adjust the solution to neutral. Subsequently, the resulting Cd^{2+} -loaded hydrogel microspheres were purified by centrifugation at 12 000 rpm and then redispersed in 30 mL of deionized water. Finally, 0.015g of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ dissolved in 5 mL of deionized water were added, and the reaction was terminated after about 2 h to give the final CdS-PS hybrids. The as-obtained products were purified by centrifugation to remove the CdS NCs weakly attached on the surface of the products.

Construction of fluorescent PC supraballs

The microfluidic device for generating fluorescence CPC supraballs was fabricated by inserting a capillary tube with a 27 G needle into a PDMS tube, which was fixed by ethyl a-cyanoacrylate instantaneous adhesive. The discontinuous (hybrid latexes) and continuous (methylsilicone oil) phases were injected into the capillary tube and the PDMS tube, respectively. The flow velocities of the two phases were independently adjusted by syringe pumps. The aqueous drops containing CdS-PS hybrids

formed at the tip of the needle, and were then heated at 45 °C for 24 h to allow water evaporation. After solidification, the uniform fluorescent CPC supraballs were finally obtained.

Characterization

Fourier-transform infrared (FT-IR) spectra were recorded on a Nicolet 6700 FT-IR spectrometer. The samples were ground with KBr crystals, and the mixture was then pressed into a disk for IR measurement. The microstructures of as-obtained CdS/PS hybrids were examined by using a transmission electron microscope (TEM) (JEOL JEM-2100). The sample was placed on a copper grid, left to dry before being transferred into the TEM sample chamber. Scanning electron microscope (SEM) observations were obtained using a HITACHI S-4800 scanning electron microscope. Photographs were taken with an optical microscope (ZEISS, Axio Scope.A1).

RESULTS AND DISCUSSION

The introduction of proper functional groups into the monodispersed hydrogel microspheres is of major importance, because these groups can serve as anchors between the metal components and the hydrogel microspheres, thus favor to the in-situ NC generation in the microreactor. In this case, core-shell hydrogel microspheres were synthesized by seeded copolymerization of AA and HEMA with PS seed particles, producing microspheres with robust PAA-*co*-PHEMA hydrogel shells bearing abundant carboxyl groups. Fig. 1 presents the FT-IR spectra of the samples containing control samples and SEM image of as-obtained hydrogel microspheres. Fig. 1a and b show FT-IR spectra of pure PS and PS-*co*-PHEMA-*co*-PAA hydrogel microspheres, respectively. Upon comparing Fig. 1b with Fig. 1a, a strong adsorption peak at 1705 cm^{-1} and a broad band peak in the range 3700–3100 cm^{-1} were noted, which is attributed to the characteristic COOH peak in PS-*co*-PHEMA-*co*-PAA microspheres. This result confirms that the PS-*co*-PHEMA-*co*-PAA microspheres already contain PAA segments. The relatively large density of incorporated AA groups on the microreactor will be helpful to anchor metal ions onto hydrogel microspheres. Fig. 1b shows a typical SEM image of as-prepared hydrogel microspheres. It reveals that the as-obtained PS-*co*-PHEMA-*co*-PAA hydrogel microspheres are highly monodispersed with regular spherical morphology.

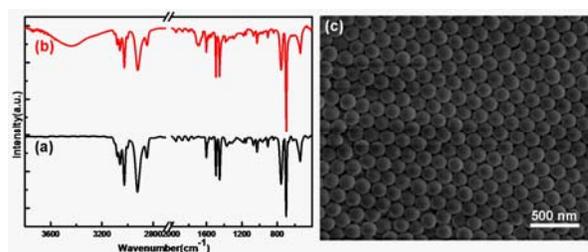


Fig. 1 FT-IR spectra of (a) PS, (b) PS-*co*-PHEMA-*co*-PAA, (c) Typical SEM image of the as-obtained hydrogel microspheres.

The in-situ synthesis of CdS NC in the 0D microreactor is shown in Scheme 1. The PS-*co*-PHEMA-*co*-PAA microspheres were first immersed into an aqueous solution containing Cd²⁺ ions. Then, the Cd²⁺ ions loading on microspheres further reacted with sulfide source (Na₂S solution) at room temperature, in-situ generating CdS NCs. The CdS/PS hybrids were finally obtained.

To fabricate uniform fluorescent CPC supraballs, we employed a microfluidic device with methysilicone oil as the continuous phase and CdS/PS hybrid latexes as the discontinuous phase. The hybrid latexes were cut off by the continuous flow, generating monodispersed droplets. The size of formed droplets is affected by several parameters, such as the flow velocity of each phase, surface tension and the channel geometry. In this work, the size of formed droplets was mainly controlled by the velocities of oil phase flow and hybrid latexes flow. In Fig. 2a, at 20 mL·h⁻¹ for oil phase, when the hybrid latexes velocity was increased from 0.3 to 2.0 mL·h⁻¹, the diameter of the droplets increased from 480 to 610 μm because the latexes were generated more frequently at the tip of the needle. At 1 mL·h⁻¹ for hybrid latexes (Fig. 2b), the diameter of the droplets decreased from 640 to 375 μm when the oil phase velocity was increased from 10 to 30 mL·h⁻¹ due to the faster shear stress rate imposed on the latexes.

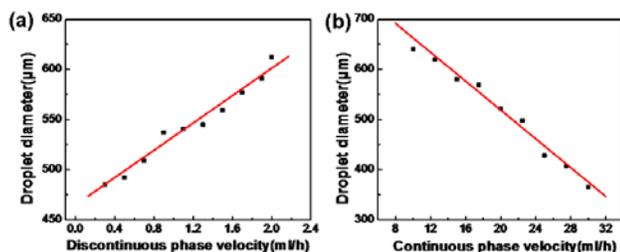


Fig. 2 (a) A plot of droplet diameter as a function of the flow velocity for hybrid latexes when the flow velocity for methysilicone oil was fixed at 20 mL·h⁻¹. (b) A plot of droplet diameter as a function of the flow velocity for methysilicone oil when the flow velocity for hybrid latexes was kept at 1 mL·h⁻¹.

Fig.3a shows the CPC supraballs after water evaporation from the spherical droplets. It can be seen that these supraballs possess excellent uniformity in size and brilliant colors on the surface. Moreover, as shown in Fig. 3b, CPC supraballs emit yellow fluorescence when the excitation wavelength was set to 395 nm indicating the successful preparation of CdS NCs. Fig. 3c shows the microstructure of the fluorescent PC supraballs mentioned above. The top-view image clearly illustrates that when crystallization is carried out in droplets, the CdS/PS hybrid microspheres organize into face-centred cubic (fcc) structures with each microsphere touching six others. Accordingly, with the aid of hydrogel-based microreactors and microfluidic devices, we successfully obtained bi-functional CPC supraballs bearing uniform fluorescence and brilliant colors.

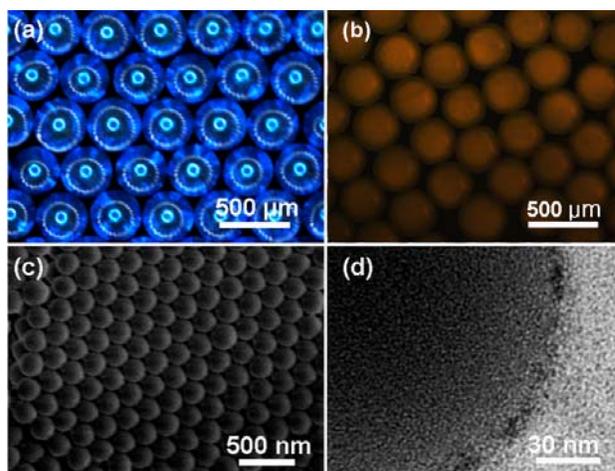


Fig. 3 Characterization of the as-obtained NC-latex hybrids from the 0D microreactor: (a) Optical micrographs of fluorescent PC supraballs; (b) Fluorescence microscope image of the PC supraballs; (c) SEM top-view images of fluorescent PC supraball assemblies; (d) TEM images of the CdS/polymer hybrids.

CONCLUSION

The utilization of PS-*co*-PHEMA-*co*-PAA microspheres as the independent 0D NC reactor is demonstrated herein to facilitate the fabrication of uniform fluorescence CPCs. The incorporation of PAA into the hydrogel microspheres endows the reactors with abundant carboxyl groups. Therefore, the microspheres can capture guest metallic components, followed by the introduction of chalcogenides, to realize in-situ generation of higher-uptake NCs. Additionally, with the aid of microfluidic devices, the as-obtained NC-latex hybrids from the 0D microreactor can also be directly self-assembled into CPC supraballs bearing uniform fluorescence and brilliant colors. We believe the fundamental knowledge gained from the study will facilitate progress in the field of self-assembled functional colloids and photonic materials.

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