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Dual-mode multicolored photonic crystal patterns enabled by ultraviolet-responsive core-shell colloidal spheres

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ABSTRACT

In this study, we developed a new kind of dual-mode multicolored photonic crystals (PCs), which could be used as a new type of dye, and achieved multicolored patterns. This kind of PCs can exhibit not only distinct structural colors due to Bragg's law of diffraction but also non-structural colors due to fluorescence. We used ultraviolet (UV)-responsive colloidal spheres synthesized by polymerization of semi-continuous emulsions to assemble the PCs. In this synthesis, the fluorescent precursors with carbamate groups were locally restricted to the shell of prepared spheres. UV irradiation can induce photo-decomposition of the carbamate groups in the fluorescent precursors, generating amino groups in the process. This process allowed the assembled PCs to exhibit fluorescence through treatment with fluorescamine. We prepared two-dimensional (2D) multicolored photonic patterns of different sizes, with both reflection and fluorescence modes. These patterns were prepared either by vertical deposition under selective UV irradiation, or by spray coating. In addition, we fabricated three-dimensional (3D) multicolored photonic patterns using 3D templates, as well as through spray coating. The results expand the concept of responsive PCs, and offer potential applications for multicolored photonic crystal patterns (PC patterns) in the field of optical storage, color displays, and anti-counterfeiting.

1. Introduction

Color plays an important role in biological visual perception. Nature has created bright structural color through microscopic surface structures, fine enough to interfere with specific wavelengths of transmitted or reflected light [1]. Photonic crystals (PCs) attracts the interest of many researchers due to their unique properties. Monodisperse colloidal spheres can be assembled in a face-centered cubic (FCC) structure to form photonic crystal via self-assembly. Similar to the electronic band structures of ordinary crystals such as semiconductors, PCs are periodic dielectric materials with photonic band-gaps (PBG). Certain wavelengths of light cannot propagate through the photonic band-gap of PCs [2–6]. They, therefore, have corresponding reflection peaks, and can exhibit structural colors due to Bragg's law of diffraction [7–10]. Based on this special property, many PCs that respond to external stimuli have wide applications in different fields—they can be used to build temperature sensors [11–17], pH sensors [10–13,18,19], stress sensors [20–23], optical devices [24–26], and displays [27]; they are also widely used in printing [28–34], metal ion detection [35–37], DNA detection [38,39], and pressure-responsive shape-memory [40,41].

Fluorescence imaging plays an important role in many fundamental and applied sciences—it has extensive application in the fields of information storage [42], color displays [43], sensors [44–46], and patterning [47–50]. There exist many different methods of fabricating fluorescent patterns, such as photo-irradiation, micro-contact printing, inkjet/screen printing, and vapor deposition. Up until now, PCs with fluorescent properties have attracted a lot of interest. For example, Song and co-workers utilized fluorescent CdS/PC nano-composites to fabricate patterns through inkjet printing, followed by a hydrogen sulfide gas treatment [51]. However, the fluorescence of CdS dispersed in the void of PCs was weak. Gallei prepared functional core-shell colloidal spheres that contain fluorescent rhodamine dye restricted in the core or shell of spheres to assemble stretch-tunable elastomeric opal films [52]. These functional core-shell colloidal spheres could

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enhance the fluorescence intensity of PCs. However, it was difficult to obtain multicolored fluorescence patterns.

In this work, we fabricated a type of PCs assembled with UV-responsive core-shell colloidal spheres that contain a fluorescent precursor (i.e. succinimido methacryloxyethyl carbamates) restricted in the shell of prepared spheres. With irradiation, the carbamate groups of succinimido methacryloxyethyl carbamates (SMC) labeled in the shell of spheres were photo-decomposed to amino groups. The subsequent reaction of fluorescamine with amino groups led to the formation of fluorescent PCs. Inspired by the photo-irradiation technique in the field of fluorescence imaging, two-dimensional (2D) photonic crystal patterns (PC patterns) that exhibit not only structural color but also fluorescence were obtained through vertical deposition followed by selective UV irradiation. As an alternative method, we fabricated multidimensional photonic patterns of different sizes also by spray coating. Notably, we use a smaller and more portable airbrush to obtain multicolored PC patterns compared to other spray coating methods reported [53]. This method is also the first one capable of fabricating three-dimensional (3D) PC patterns. These novel fabrication methods of making dual-mode PCs could broaden the applications of PCs, and in particular, be useful in the field of anti-counterfeiting.

2. Experimental

2.1. Materials

All the solvents and chemicals were of reagent quality and were used as received.

N-Hydroxysuccinimide was supplied from Heowns Biochem Technologies. 2-Isocyanatoethyl methacrylate was obtained from Tokyo Chemical Industry Co. Ltd. Styrene, methyl methacrylate (MMA), tetrahydrofuran (THF), triethanolamine (TEA) and acrylic acid (AA) were obtained from Fuchen Chemical Company in Tianjin China, allyl methacrylate (ALMA) from Alfa Aesar, sodium dodecylsulfate (SDS) from J&K Scientific and disodium 4-dodecyl-2,4′-oxydibenzenesulfonate (DBR) from Rhodia. All other chemicals were supplied from Beijing Chemical Works. All glass slides were obtained after piranha treatment, and rinsed with deionized water and anhydrous ethanol.

2.2. Preparation of UV-responsive core-shell colloidal spheres

The reaction for the synthesis of SMC was shown in Fig. S1 of the Supporting Information. SMC was obtained after the reaction of *N*-Hydroxysuccinimide and 2-isocyanatoethyl methacrylate [54,55]. *N*-Hydroxysuccinimide (2 mmol) and TEA (0.02 mL) were dispersed THF (30 mL) and then 2-isocyanatoethyl methacrylate (2.5 mmol) in THF (5 mL) was added drop-by-drop while stirring at 25 °C for 8 h. Then THF was removed under reduced pressure at 40 °C. We obtained the product from methanol by recrystallization (with 79% yield).

General procedure for the synthesis of UV-responsive core-shell colloidal spheres was similar with the previous report [22,52]. To summarize, styrene (1 g, 9.60 mmol) and SDS (0.06 g, 0.21 mmol) were dispersed in H_2O (70.0 mL) in 250 mL flask at 75 °C with constant stirring under N_2. Sodium bisulfite (9 mg, 0.09 mmol), sodium peroxodisulfate (130 mg, 0.55 mmol SPS), and sodium bisulfite (9 mg, 0.09 mmol) were added in this sequence to initiate polymerization. After 10 min, PS seed was obtained. Then a solution of styrene (19 g, 182.43 mmol), SDS (0.06 g, 0.21 mmol), DBR (0.11 g, 0.02 mmol), KOH (0.1 g, 1.78 mmol), and H_2O (22.5 mL) were added continuously within 40 min. After 2 h, PS core was obtained. Then sodium bisulfite (6.3 mg, 0.06 mmol), SPS (25 mg, 0.10 mmol) and sodium bisulfite (6.3 mg, 0.06 mmol) were added. After 15 min, a solution of ALMA (0.75 g, 5.95 mmol), MMA (6.25 g, 62.43 mmol), SDS (0.0125 g, 0.04 mmol), DBR (0.105 g, 0.19 mmol), KOH (0.025 g, 0.45 mmol), and H_2O (8.0 mL) were added continuously over a period of 50 min. The reaction was allowed to continue for another 1 h, PS@PMMA interlayer was obtained. Then a solution of MMA (8 g, 79.90 mmol), AA (1 g, 13.88 mmol), SMC (0.05 g, 0.19 mmol), SDS (0.025 g, 0.09 mmol), DBR (0.15 g, 0.28 mmol), KOH (0.05 g, 0.89 mmol), and H_2O (10.0 mL) were added continuously over a period of 80 min. After 2 h, we got the PS@P (MMA-co-SMC).

2.3. Preparation of dual-mode multicolored PC patterns

Vertical deposition method: A glass slide was inserted into the

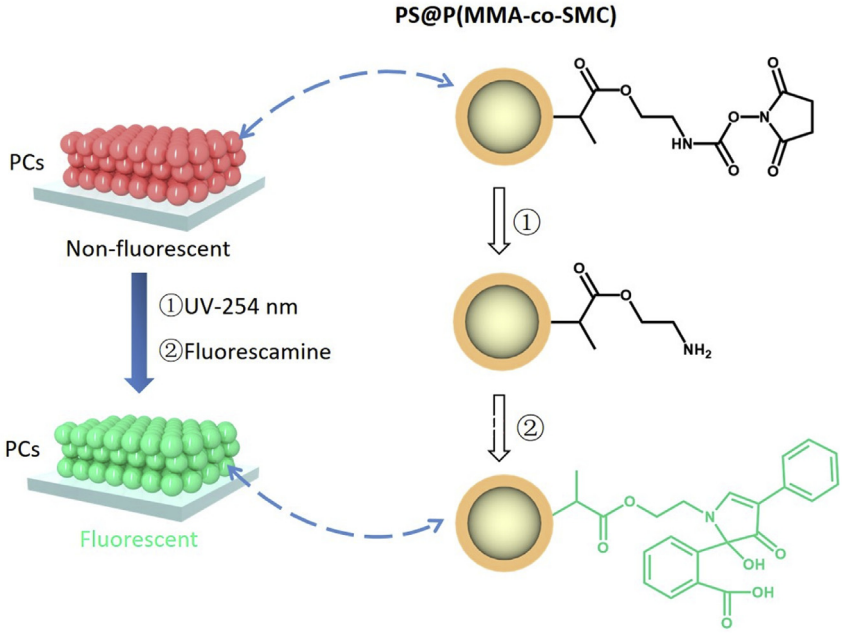

Fig. 1. Schematic illustration of reaction process for UV-responsive PCs.