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CdS/C_{60} binary nanocomposite films prepared via phase transition of PS-*b*-P2VP block copolymer

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ABSTRACT

We demonstrate the well-defined control of phase transition of a polystyrene-b-poly(2-vinylpyridine) (PS-*b*-P2VP) block copolymer from spherical micelles to lamellar structures, in which CdS and C_{60} nanoparticles (NPs) are selectively positioned at the P2VP domains. The CdS NPs are *in situ* synthesized using PS-*b*-P2VP block copolymer templates that are self-assembled in PS-selective solvents. The CdS-PS-*b*-P2VP micellar structures are transformed to lamellar phase by adjusting a solvent selectivity for both blocks. In addition, a binary system of CdS/C_{60} embedded in PS-*b*-P2VP lamellar structures (CdS/C_{60}-PS-*b*-P2VP) is fabricated by embedding C_{60} molecules into P2VP domain though charge-transfer complexation between pyridine units of PS-*b*-P2VP and C_{60} molecules. The CdS/C_{60}-PS-*b*-P2VP nanostructured films are characterized by transmission electron microscopy (TEM) and UV–Vis spectrometer.

1. Introduction

Semiconducting nanoparticles (NPs) have been considered to be interesting materials since they showed the unique properties arising from high surface energy, chemical and physical stability, and the confinement effect [1–4]. Binary nanocomposites of NPs [5,6] have attracted an especially intensive attention because two different types of NPs well-distributed in matrix showed diverse properties, and had potential for advanced applications for sensors [7] and magnetic devices [8]. Simultaneously, location control of NPs in specific nanostructures is needed to obtain desired properties. Nickel et al. [9] reported that the size and the mutual distance between NPs controlled by long thiolate precursors, had an effect on the optical properties of photoluminescence.

Self-assembly of block copolymers (BCPs) is useful for their application to fabricate various structures as it provides well-ordered nanostructures with a scale of tens of nanometers [10–14]. Their domain size and structures can be controlled by varying the molecular weight, volume fraction of each block, and selection of solvent. The structures of BCP have been effectively utilized as a template to synthesize and control the location of NPs [15–19].

Recently, solvent-induced microphase separation of BCP has triggered a great deal of interests [20,21]. For example, solvent annealing is of great advantage to minimize and eliminate the defects of the microstructures and to make well-defined nanostructures. In addition, the phase of BCP was converted by reorganization of BCP microdomains, depending on the condition of solvent annealing. Knoll et al. [22] and Zhang et al. [23] confirmed the effects of solvent selectivity on morphology change and showed that various BCP nanostructures can be fabricated by optimized solvent annealing condition.

However, it is difficult to tune the structure of polymers embedding nanoparticles by using solvent annealing, because NPs interfere with rearrangement of the polymer matrix. Therefore some research groups have tried immersing [24] and floating [25] methods to make NPs embedded polymer, in which the samples were prepared by separated processes for the fabrication of matrix, synthesis of NPs, and attachment of NPs to the matrix.

We have continuously studied the polymer nanocomposites incorporated with various NPs using BCP self-assembly. In particular, various NPs were placed within specific domains of BCPs that can preferentially interact with un-paired electrons, such as pyridine [12,16,17] For example, the binary system of CdS/Au-PS-*b*-P2VP [6] was prepared by the unique property of BCPs. Nevertheless, there have been very few researches regarding *in situ* synthesis of NPs by BCP templates with various morphologies due to many obstacles such as separation of NPs from domain.

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Herein, we prepared the BCP/CdS nanocomposite using polystyrene-*b*-poly(2-vinylpyridine) (PS-*b*-P2VP) BCP scaffolds, in which CdS NPs were selectively embedded in the P2VP domains of self-assembled micelle and lamellar structures. When we added 1,2-dichlorobenzene (DCB), a neutral solvent for both blocks, to BCP colloidal dispersion, the well-defined phase transition of CdS-PS-*b*-P2VP from spherical micelles to lamellar structures took place. Moreover, by adding a C_{60} solution BCP spherical micelles were transformed to lamellar structures containing CdS/C_{60}.

2. Experimental section

2.1. Materials

A polystyrene-*b*-poly(2-vinylpyridine) (PS-*b*-P2VP) block copolymer with a molecular weight of 42 kg mol^{-1}, a polydispersity index of 1.06, and a P2VP mole fraction of 40% which was confirmed using size exclusion chromatography (SEC, Waters M 77251, M 510) with four columns and ^1H NMR spectra (JEOL JNMLA400WB) was prepared using living anionic polymerization [26–28]. Toluene (anhydrous, 98%) and 1,2-dichlorobenzene (anhydrous, 99%) were obtained from Sigma-Aldrich. For synthesizing CdS NPs, cadmium acetate dihydrate ($Cd(C_2H_3O_2)_2 \cdot 2H_2O$, reagent grade, 98%) as a precursor, sodium sulfide (Na_2S) as a reducing agent, and C_{60} (sublimed, 99.8%) were purchased from Sigma-Aldrich and used without further treatment.

2.2. Synthesis of CdS NPs in PS-b-P2VP block copolymer (CdS-PS-b-P2VP)

In order to prepare BCP spherical micelles, PS-*b*-P2VP was dispersed in toluene, a selective solvent for PS blocks, at concentration of 5 mg mL^{-1}. This colloidal dispersion was stirred for 24 h at room temperature. $Cd(C_2H_3O_2)_2 \cdot 2H_2O$ (dispersed in H_2O, 30 wt%) with 0.5 mol/L was added into 1 mL of the polymer colloidal dispersion to synthesize CdS NPs and was stirred for 48 h. The Cd^{2+} in BCP micelles was reduced by mixing with a Na_2S solution, which also was dissolved in H_2O (30 wt%) for 6 h, resulting in the formation of CdS-PS-*b*-P2VP micelles. Phase transition of CdS-PS-*b*-P2VP micelles to lamellar structures was experimented on by introducing 1,2-dichlorobenzene (DCB) into the polymer colloidal dispersion (1:1 v/v).

2.3. Preparation of CdS/C_{60} binary system (CdS/C_{60}-PS-b-P2VP)

Before adding C_{60} to CdS-PS-*b*-P2VP colloidal dispersion for the CdS/C_{60} binary system, C_{60} molecules were dissolved in DCB. And then, the CdS/C_{60}-PS-*b*-P2VP was obtained by adding 1 mL of C_{60} solution with 0.5 mol/L of P2VP into the CdS-PS-*b*-P2VP colloidal dispersion and mixing with them for 24 h.

2.4. Characterizations

A high resolution-transmission electron microscopy (HR-TEM, JEOL JEM-2100) was used for the morphological study. For TEM measurements, specimens were drop-coated on carbon-coated copper grids. To increase contrast, P2VP blocks were selectively stained by I_2 vapor for 12 h. TEM results were obtained at an acceleration voltage of 120 kV. An energy dispersive X-ray microanalyzer (EDX, OXFORD, INCA X-sight) attached to the HR-TEM was utilized for the element analysis of the NPs. A UV–Vis spectrometer (Varian, Win CARY 1E) was used to measure the absorbance.

3. Results and discussion

Fig. 1 shows the schematic illustration of the preparation of the CdS/C_{60} binary system by phase transition of BCPs from spherical micelles to lamellar structures. The direct approach is not suitable for the preparation of the binary nanocomposites because it is difficult that BCPs form an effective template for the synthetic process of CdS and C_{60}. Whereas, stepwise approach provides the enough time to organize BCP templates for decorating them. Therefore, the preparation of binary nanocomposites was carried out by following our approach to control the shape, size, and location of CdS NPs in the confined architecture than by the direct method. In detail, the solvation of PS-*b*-P2VP BCPs in a PS-selective solvent (toluene) led to the formation of spherical micellar structure with an insoluble P2VP core and soluble PS shell (Fig. 1b), as previously reported [6,10,18]. The BCP micelles were utilized as a template for the synthesis of CdS NPs. When the precursor of CdS NPs was added into BCP colloidal dispersion, Cd^{2+} ion clusters were selectively located in the P2VP cores of micelles due to the interaction with pyridine units (Fig. 1c). CdS NPs were synthesized *in situ* and established in the P2VP cores of micelles after reduction by Na_2S, as shown in Fig. 1d. Next, the combined system of

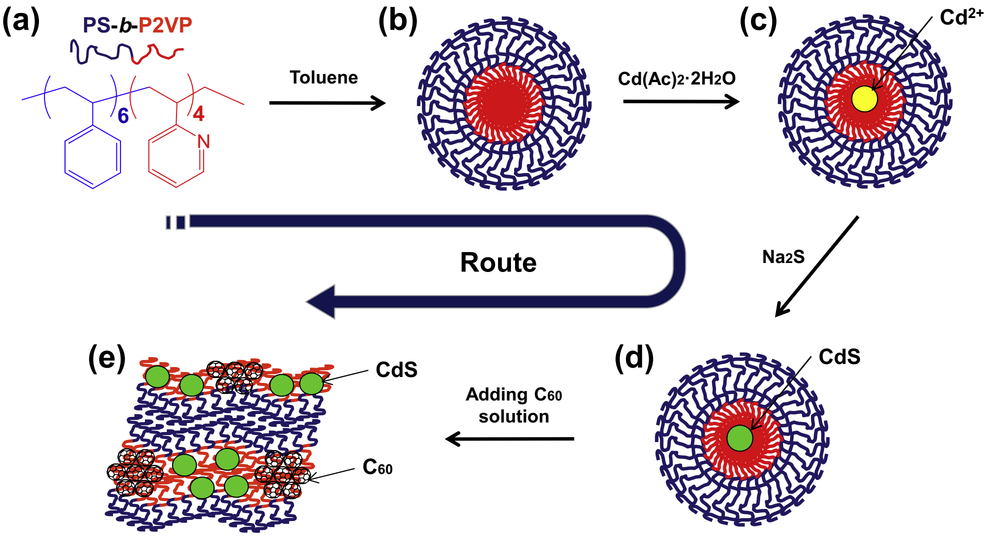

Fig. 1. The scheme of the CdS/C_{60} binary system prepared in block copolymer templates via phase transition: (a) formula of PS-*b*-P2VP, (b) PS-*b*-P2VP micelles, (c) Cd^{2+}-PS-*b*-P2VP micelles, (d) CdS-PS-*b*-P2VP micelles, and (e) CdS/C_{60}-PS-*b*-P2VP lamellar structures.