



Honeycomb-like thin films of Polystyrene-block-poly(2-vinylpyridine) embedded with gold or silver nanoparticles formed at the planer liquid/liquid interface

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ABSTRACT

Composite thin films of polystyrene-block-poly(2-vinylpyridine) (PS-*b*-P2VP) decorated with Au or Ag nanoclusters and nanoparticles were fabricated at the interfaces of chloroform solution of PS-*b*-P2VP and aqueous solutions of H₂AuCl₄ or AgNO₃. Transmission electron microscopy (TEM) investigations indicated that large area of a single-layer honeycomb structure was formed, which is composed of polygons (most of them are hexagons) whose walls look like spindles with the length of several hundreds of nanometers. Large amount of Au or Ag nanoparticles are embedded in the walls and the undersides of the honeycomb structures. The formation of these novel composite structures was attributed to the adsorption of block copolymer molecules and inorganic species of AuCl₄⁻ and Ag⁺ ions at the liquid–liquid interface, the combination of the polymer molecules and the inorganic ions, and the self-assembly of the composite molecules. After UV-light irradiation and KBH₄ aqueous solution treatment, the inorganic species were reduced completely, as confirmed by UV–vis spectra and X-ray photoelectron spectra. These composite films exhibited high catalytic activities for the reduction of 4-nitrophenol (4-NP) by KBH₄ in aqueous solutions.

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1. Introduction

Noble metal nanoparticles have unique optical, electronic and catalytic properties and potential application in various areas. In order to prevent them from aggregation, these nanoparticles are usually incorporated in matrices to form composite systems. Polymers are the most popular matrices and many kinds of metal nanoparticle/polymer composites, such as thin films [1–6], microspheres [7–9] and hollow microspheres or microcapsules [10–16], nanotubes [17–19] and nanofibers [20–22], have been fabricated by using several approaches, including blending [1–4], layer-by-layer assembly [5,6,12–16], emulsion polymerization [7–9] or hard template-directed polymerization/adsorption [10,11], electrospun/adsorption [20–22], and self-assembly methods [18,19]. The former two methods have been utilized extensively to fabricate polymer-based composites. Recently, the self-assembly of polymers, especially amphiphilic block copolymers, has attracted much attention. Block copolymer molecules can self-assemble into regular and reverse micelles in solvents, or into cylindrical or lamellar structures in thin films due to the microphase separation [23–26]. Metal nanoparticles or precursors may be incorporated into micelles or cylindrical and lamellar nano-

structures during the self-assembly process with the aid of interactions between the inorganic species and the blocks [27,28].

Recently, we found that some amphiphilic polymers, such as poly(2-vinylpyridine) (P2VP) and poly(9-vinylcarbazole) (PVK) self-assembled into composite microcapsules at the planar liquid/liquid interface between chloroform solutions of the polymers and aqueous solutions of AgNO₃ or H₂AuCl₄ through adsorption and combination of polymer molecules and inorganic species [29–32]. This is a new and facile method to construct polymer-based composites and has obvious advantages over the others. For example, blending method requires similar wetting properties of metal nanoparticles or precursors and polymers; otherwise, the nanoparticles incorporated in polymer matrices would aggregate. In fact, the liquid/liquid interface has been utilized for nanoparticle synthesis [33] and nanostructure fabrication [34]. However, research on inorganic/polymer composite fabrication at the liquid/liquid interface is very rare and has just aroused interest very recently. Besides our work, there are only a few research works on this topic. For example, Chen and his co-workers obtained nanofibers of a PVK derivative doped with CdS quantum dots [35], Qian et al. fabricated nanoporous film of poly(4-vinylpyridine) (P4VP) decorated with Ag nanoparticles [36], and Li et al. fabricated nanotubes of a conjugated polymer with Cu²⁺ ions at the liquid/liquid interface [37]. In addition, polyaniline nanobelts doped with dodecatungstosilic acid [38] and asymmetric polyani-

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line/Au hybrid nanoparticles [39] were also synthesized at the liquid/liquid interface through interfacial reactions.

PS-*b*-P2VP is a typical amphiphilic block copolymer and has been used widely as matrices to fabricate metal nanoparticle/polymer composites through micellization with metal nanoparticles [40] or precursors [41–44] in appropriate solvents, through adsorption of metal nanoparticles [45] or precursors [46–48] into the deposited micellar arrays, through microphase separation in composite thin films with nanoparticles [49,50] or precursors [51] during solvent evaporation, and through adsorption of nanoparticles [52] or precursors [53,54] into the microphase separated structures. The self-assembly behavior of PS-*b*-P2VP at the air/liquid interface has also been investigated [55–57]. However, the self-assembly behavior of this block copolymer at the liquid/liquid interface has not been studied yet. In this paper, the adsorption and self-assembly behaviors of PS-*b*-P2VP at the interfaces of chloroform solution of the polymer/aqueous solutions of AgNO₃ and HAuCl₄ were investigated. It was found that the self-assembly behavior of the block copolymer was different from that in solutions, in casting or spin-coating films, and at the air/water interface. More interestingly, its self-assembly behavior was also different from that of homo-P2VP at the liquid/liquid interface [30,31]. In our previous reports, we described the formation of the composite foam films of homopolymer P2VP with different molecular weights. We found that molecular weights greatly affect the film structure and properties. Here, we describe the formation of honeycomb-like structures of a block copolymer PS-*b*-P2VP decorated with Ag or Au nanoparticles at the liquid/liquid interface. Although the fabrication method is similar, the obtained microstructures are very different from each other. This reflects the specificity of fabrication of polymer molecules with different molecular structure, which should be investigated systematically. In addition, these composite films exhibited high and durable catalytic activity.

2. Experimental section

2.1. Chemicals and materials

PS-*b*-P2VP ($M_{n(PS)} = 7500 \text{ g mol}^{-1}$, $M_{n(P2VP)} = 12500 \text{ g mol}^{-1}$, $M_w/M_n = 1.05$) was purchased from Polymer Source (Canada) and used as received. AgNO₃ (99%) and HAuCl₄·3H₂O (99.9%) were purchased from Shanghai Chemical Plant and Aldrich, respectively. KBH₄ (≥97.0%) was obtained from Shanghai Zhanyun Chem. Co. Ltd. 4-Nitrophenol (4-NP) (analytical reagent) was supplied by Tianjin Guangfu Fine Chemical Research Institute. Chloroform obtained from Tianjin Guangcheng Chem. Co. is an analytical reagent containing 0.3–1.0% ethanol as a stabilizer. The water used was highly purified using a UP water purification system (UPHW-IV-90T, Chengdu China) with a resistivity ≥18.0 MΩ cm.

2.2. Preparation of composites

About 5 mL of chloroform solution of PS-*b*-P2VP with a concentration of 0.20 mg mL⁻¹ was poured in a small beaker. Then, 5 mL of aqueous solution of AgNO₃ with a concentration of $1.0 \times 10^{-2} \text{ mol L}^{-1}$ or HAuCl₄ with a concentration of $1.0 \times 10^{-3} \text{ mol L}^{-1}$ was added carefully and covered on the polymer solution. So a clear liquid/liquid interface was formed. The beaker was placed in a sealed container that was put in a dark oven. The temperature was controlled to be 30 °C. A thin film appeared at the liquid/liquid interface gradually and was deposited on solid substrates, such as carbon-coated copper grids, silicon, and quartz slides for further treatment and characterization.

The deposited thin films were irradiated by UV-light with the wavelength of 254 nm for 1 h to cause the cross-linking of the

polymer molecules. The power of the lamp was 6 mW, and the distance between the lamp and the sample was tuned to be 15 cm. The UV-light irradiated samples were then immersed in a KBH₄ aqueous solution with a concentration of $2 \times 10^{-2} \text{ mol L}^{-1}$ for 10 min for complete reduction of the metal precursors.

2.3. Characterization

The morphology and structure of these samples were investigated using high-resolution transmittance electron microscopy (HRTEM, JEOL-2010) with an accelerating voltage of 200 kV. The compositions of these samples were probed by using X-ray photoelectron spectroscopy (XPS, ESCALAB MKII) with an Mg Kα exciting source at a pressure of $1.0 \times 10^{-6} \text{ Pa}$ and a resolution of 1.00 eV. The absorption spectra were obtained by using UV-vis spectroscopy (HP 8453E).

2.4. Catalytic reaction

0.5 mL of aqueous solution of 4-NP with a concentration of $2 \times 10^{-4} \text{ mol L}^{-1}$ was poured into a 1-cm quartz cuvette, and then, 1.0 mL of aqueous solution of KBH₄ with a concentration of $2 \times 10^{-2} \text{ mol L}^{-1}$ was added. The final concentrations of 4-NP and KBH₄ in the mixture were 6.67×10^{-5} and $1.33 \times 10^{-2} \text{ mol L}^{-1}$, respectively. The thin composite film deposited on a quartz slide after UV-light irradiation and KBH₄ aqueous solution treatment was immersed in the reaction system to catalyze the reduction of 4-NP. The process of reaction was monitored by using UV-vis spectroscopy (HP 8453E). The reaction temperature was controlled to be 20, 25, 30, and 35 °C through a thermostat.

3. Results and discussion

3.1. Morphology, structure, and composition

Fig. 1 shows the TEM micrographs of PS-*b*-P2VP/Ag composite films formed at the interface. Large area of honeycomb-like structure composed of hexagons together with some pentagons and other polygons formed, with the side length varying from several hundreds of nanometers to several micrometers. Most of the sides look like spindles with a bulging middle (Fig. 1b). Nanoclusters are distributed homogeneously on the spindle-like sides, and a few nanoclusters are scattered on the bottom faces of the honeycomb holes (Fig. 1c). The high-magnification image (Fig. 1d) shows the uniform size of the nanoclusters. The mean diameter was measured to be $2.07 \pm 0.60 \text{ nm}$ (Fig. 1e). Fig. 1f gives a TEM image of a piece of incubating honeycomb structure that is made up of hexagons in the center part and winnowing fan-like structure at the edge. This kind of construction may give us some hints for the film formation.

Fig. 2 shows the TEM micrographs of PS-*b*-P2VP/Au composite films formed at the interface. Similar to the composite film of PS-*b*-P2VP/Ag, honeycomb structure was formed, and the sides of the polygons present spindle shape (Fig. 2a). Numerous nanoclusters are scattered on the sides, as clearly seen from the enlarged image (Fig. 2b). Fig. 2c gives a high-magnification image of the side as well as the bottom face, from which we can see that a lot of particles are also dispersed in the bottom face. Fig. 2d and e give the high-magnification images of the bottom face and the polygon side, respectively. The size distribution of the nanoclusters in the bottom face was derived to be $1.14 \pm 0.33 \text{ nm}$ from the size distribution histogram. However, numerous nanoclusters overlap, congregate, and accumulate in the polygon side; it is difficult to make a precise size distribution. The size of the nanoclusters in the side can be estimated to be around 1 nm.

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