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Fabrication of composite thin films with microstructures of honeycomb, foam, and nanosphere arrays through adsorption and self-assembly of block copolymers at the liquid/liquid interface

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ABSTRACT

The adsorption and self-organization behaviors of two kinds of block copolymers, polystyrene-block-poly(4-vinylpyridine) (PS-b-P4VP) and poly(4-vinylpyridine)-block-polystyrene-block-poly(4-vinylpyridine) (P4VP-b-PS-b-P4VP), at planar liquid/liquid interfaces were investigated. A gel film decorating with honeycomb-like microstructures forms at the liquid/liquid interface between PS-b-P4VP chloroform solution and chloroauric acid aqueous solution. However, foam films were developed when the chloroauric acid aqueous solution was replaced by a chloroplatinic acid solution or a silver nitrate solution. Furthermore, a free-standing film containing the ordered arrays of nanospheres appeared at the liquid/liquid interface between P4VP-b-PS-b-P4VP chloroform solution and chloroauric acid aqueous solution. The formation of these microstructures was attributed to the adsorption of polymer molecules, combining with inorganic ions and the self-assembly of the composite species at the interface. The doped metal ions and complex ions were transformed to metal nanoparticles after further treatment. This is a facile and convenient method to prepare polymer/inorganic nanoparticle composites. These results also indicate the great influences of the polymer structures and the inorganic species in the aqueous phases on the self-assembly behaviors of the polymers at the interfaces, the final morphology, and structure of the composites. In addition, the formed thin composite films doped with well-dispersed, homogeneous small noble metal nanoparticles exhibit great and durable catalytic activities for the reduction of 4-nitrophenol (4-NP) by potassium borohydride.

1. Introduction

Polymer-based composites doped with inorganic nanoparticles have attracted much attention in recent years [1,2]. On the one hand, these composites can immobilize nanoparticles in their structure and consequently preserve the unique properties of nanoparticles. On the other hand, their desirable physical properties including good processing ability, mechanical property, and stability of polymers extend the fields of application of the nanoparticles. In addition, there are a large number of opportunities that might lead to tailor novel properties and functionalities of nanoparticles by combining and interacting between inorganic nanoparticles and the functional groups of polymers.

Various approaches have been proposed and developed to prepare polymer-based composites, which can be classified into blending [3,4], layer-by-layer assembling [5,6], emulsion polymerization [7,8] or hard template-directed polymerization/adsorption [9,10], electrospun/adsorption [11,12], and self-assembly methods [13,14]. The former two kinds of methods are most commonly used. Recently, the self-assembly of polymers, especially block copolymers, has aroused an increasing research interest [15,16] due to their abundant self-assembly behaviors. The micellization and microphase separation of block copolymers in solutions and thin films have been utilized extensively to fabricate the organized composite structures of polymer/nanoparticles [17–20].

In more recent years, the planar liquid/liquid interface system has been adapted to fabricate polymer-based composites by dissolving polymers in organic phase and dispersing inorganic species including metal ions, complex ions, and colloidal particles in aqueous phase. When the planar interface forms between the two phases, polymer molecules and inorganic species are adsorbed at the interface, interact with each other, and self-assemble into composite microstructures. For example, porous poly(4-vinylpyridine) films doped with silver nanoparticles [21], conjugated polymer nanofibers doped with CdTe quantum dots [22], and polymer composite microtubes doped with Cu^{2+} ions [23] were fabricated successfully through this approach.

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Composite foam films of a homopolymer (poly(2-vinylpyridine) (P2VP)) doped with noble metal nanoparticles and metal ions or complex ions have been fabricated by using this method in our recent work [24,25]. We found that the formation of these composite structures resulted from the adsorption, combination, and self-assembly of P2VP molecules and inorganic species at the liquid/liquid interface. It is well known that block copolymers have more abundant assembly behaviors than homopolymers, which have been studied extensively in solutions and in thin layers deposited on solid substrates [15–20] and at the air/water interface [26]. We also noticed that a diblock copolymer, polystyrene-block-poly(2-vinylpyridine) (PS-b-P2VP), could self-assemble into honeycomb structures doped with silver and gold nanoclusters at the liquid/liquid interface [27]. Apparently, this block copolymer exhibits very different interfacial self-assembly behaviors compared with those of the corresponding homopolymer, which inspires us to investigate the interfacial adsorption and self-assembly behaviors of different kinds of polymers and to fabricate various composite nanostructures.

In this paper, two kinds of block copolymers, PS-b-P4VP and P4VP-b-PS-b-P4VP, are used to fabricate polymer/inorganic composite films by using the liquid/liquid interface adsorption and assembly method. The aim is to investigate the influences of molecular structures of block copolymers on their adsorption and assembly behaviors at the liquid/liquid interface, to prepare composite films with unique micro- and nanostructures and to evaluate the availability and universality of this method. It is very interesting that PS-b-P4VP exhibits very different assembling behaviors from PS-b-P2VP, although there is only a nice structural distinction between the two kinds of molecules. In addition, the triblock copolymer also shows different interfacial assembling behaviors from the diblock copolymers.

2. Experimental section

2.1. Chemicals

PS-b-P4VP (M_n: PS(3500)-P4VP(5300), $M_w/M_n = 1.15$) and P4VP-b-PS-b-P4VP (M_n: P4VP(8000)-PS(36000)-P4VP(8000), $M_w/M_n = 1.24$) were purchased from Polymer Source (Canada) and used as received. $AgNO_3$ (99+%) was purchased from Shanghai Chemical Plant, and $HAuCl_4{\cdot}3H_2O$ (99.9+%) and $H_2PtCl_6{\cdot}xH_2O$ were purchased from and Aldrich, respectively. KBH_4 ($\geqslant$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 $\geqslant$18.0 MΩ cm.

2.2. Preparation of composites

About 5 mL of chloroform solution of PS-b-P4VP (or P4VP-b-PS-b-P4VP) with a concentration of 0.20 mg mL^{-1} was poured in a small beaker. Then, 5 mL of aqueous solution of $AgNO_3$ with a concentration of 1.0×10^{-2} mol L^{-1} or $HAuCl_4$ (or H_2PtCl_6) with a concentration of 1.0×10^{-3} mol L^{-1} was added carefully and covered on the polymer solution to form a clear liquid/liquid interface in the beaker. The beaker was placed in a sealed container that was put in a dark oven. The temperature was controlled to be 25 °C. A thin film appeared at the liquid/liquid interface gradually with time. Twenty-four hours later, the water phase was removed, and the film was deposited on solid substrates, including carbon-coated copper grids, silicon, and quartz slides for further treatment and characterization. For P4VP-b-PS-b-P4VP/Au system, the formed composite film was also adhered to a framework for further treatment and catalytic application.

For PS-b-P4VP/Au system, some of the composite films formed at the interface was further immersed in pure water for 4–5 times and then deposited on solid substrates or collected for further characterization.

Some of 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 KBH_4 aqueous solution with a concentration of 2×10^{-2} mol L^{-1} for 10 min for complete reduction of the metal precursors.

For the thermogravimetric (TG) analysis and FTIR characterization, the thin films formed at the liquid/liquid interface were collected and placed in a desiccator with P_2O_5 as the drier.

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 1.0×10^{-6} Pa and a resolution of 1.00 eV. The optical properties of the films were characterized by using FTIR spectroscopy (VERTEX-70). The TG curve was obtained by using a thermal gravimetric analyzer (SDT Q600, TA Instruments) with a heating rate of 10 °C min^{-1} in air.

2.4. Catalytic reaction

0.5 mL of aqueous solution of 4-NP with a concentration of 2×10^{-4} mol L^{-1} was poured into a 1-cm quartz cuvette, and then, 1.0 mL of aqueous solution of KBH_4 with a concentration of 2×10^{-2} mol L^{-1} was added. The final concentrations of 4-NP and KBH_4 in the mixture were 6.67×10^{-5} and 1.33×10^{-2} mol L^{-1}, respectively. The thin P4VP-b-PS-b-P4VP/Au composite film treated by UV-light irradiation and KBH_4 aqueous solution was adhered to a framework and then immersed in the reaction system to catalyze the reduction of 4-NP. The progress of the 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.

In order to calculate the reaction rate constant over the weight of gold, the used thin film was rinsed thoroughly with pure water, dried in a desiccator with P_2O_5 as drier, then scraped from the framework, and weighed by using an electronic balance (BT 25 S, sartorius) with the sensitivity of 0.01 mg.

3. Results and discussion

3.1. Morphology, structure and composition

3.1.1. PS-b-P4VP/Au composite films

A smooth light yellow film appeared gradually with time at the liquid/liquid interface. After removing aqueous and organic phases, and pouring pure water into the beaker, this film floats on water surface and breaks into small pieces (Fig. 1a). This film is a gel one that contains much more water. It is hard to investigate its morphology because the film is too thick for TEM observation. Fortunately, we found somewhat thinner regions that were visualized by TEM, as shown in Fig. 2. As can be seen, a lot of rings appear which aggregate into small pieces of honeycomb-like structure.