Colloids and Surfaces A: Physicochem. Eng. Aspects 386 (2011) 141–150

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Synthesis and assembly of catalytically active platinum-doped polymer nanocomposites at the liquid/liquid interface

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ARTICLE INFO

Article history:
Received 29 March 2011
Received in revised form 13 June 2011
Accepted 10 July 2011
Available online 20 July 2011

Keywords:
Polymer
Platinum nanoparticle
Liquid/liquid interface
Microcapsule
Solid foam
Catalysis

ABSTRACT

Platinum nanoparticle-doped polymer foam-like thin films were prepared via a synthesis and assembly process at the liquid/liquid interface of a chloroform solution of poly(2-vinylpyridine) and an aqueous solution of chloroplatinic acid hydrate and a subsequent UV-light irradiation process. Transmission electron microscopy, high-resolution transmission electron microscopy and X-ray photoelectron spectroscopy investigations indicated that the foam-like thin films formed at the interface were composed of polymer molecules, and Pt(II) and Pt(IV) ions. Platinum nanoparticles with average diameter of 2.70 ± 0.35 nm appeared after UV-light irradiation, which were embedded in and adsorbed on the walls of the foams. The formation of the composite nanostructures at the interface was attributed to self-assembly of the polymer molecules at the liquid/liquid interface, reduction of $PtCl_6^{2-}$, and interaction between $PtCl_6^{2-}$/intermediate $PtCl_4^{2-}$ ions and the protonated pyridine groups. The catalytic activity of the composite film for the reduction of methylene blue by potassium borohydride in aqueous solutions was evaluated. The apparent rate constant decreased gradually with increasing the number of runs due to the partially leaching of Pt nanoparticles and became stable after the fifth cycle, indicating that the composite film can be used as an effective, stable and reusable catalyst.

1. Introduction

Platinum nanoparticles exhibited excellent catalytic [1–12] and electrocatalytic [13–27] properties, and have important applications in chemical industry and the area of fuel cells. In addition, Pt-semiconductor hetero-nanostructures, such as Pt–CdSe [28], Pt–CdS [29] and Pt–TiO_2 [30,31] showed enhanced photocatalytic performance and have potential applications in environmental treatment. So synthesis and catalytic studies of Pt nanoparticles have attracted increasing interests. It has been established that the catalytic activity of metal nanoparticles for heterogeneous catalytic systems enhances with decreasing the size as the result of the increase of the surface-to-volume ratio, the coverage of active surface atoms, and chemical potentials [32,33].

In order to control the size, Pt nanoparticles are usually capped with polymers, such as polyvinylpyrrolidone (PVP) [3–6,15], polyethylenimide [13], polyelectrolytes [14] and polyethylenimine [16], or alkylammonium ions, such as tetradecyltrimethylammonium bromide [2] and cetyltrimethylammonium bromide [17], or oleic acid and oleylamine [18]. It has been revealed that PVP molecules adhere to Pt nanoparticles through a charge-transfer interaction between the pyrrolidone rings and the surface Pt atoms [34], and the interactions between them are very strong. So a significant number of active sites are blocked [2]. The interaction between alkylammonium ions and Pt surface are considerably weaker than that between the carbonyl group and Pt surface. It was expected that the catalytically active sites could be preserved by using alkylammonium ions as capping agents [2,17]. On the other hand, in order to avoid aggregation, Pt nanoparticles are often immobilized on matrix. The supporting materials include oxides, such as silica [8] and ceria [9], platinum and tungsten gauzes [27], carbons [10,13], carbon nanotubes [11,23,25], carbon nanospheres [26], polymer microgels [12], and polymer nanofibers [22].

In this paper, we described a new and facile approach to prepare Pt nanoparticle-doped poly(2-vinylpyridine) (P2VP) foam-like thin films. These composite nanostructures were formed at the liquid/liquid interface through self-assembly of P2VP molecules, the combination of the protonated pyridine groups with $PtCl_6^{2-}$ ions, and simultaneous reduction of $PtCl_6^{2-}$ ions at ambient temperature. Liquid/liquid interface has been utilized widely to synthesis inorganic nanoparticles [35,36] and to assemble thin membranes composed of inorganic nanoparticles [37–39] and monolayers of

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doi:10.1016/j.colsurfa.2011.07.017

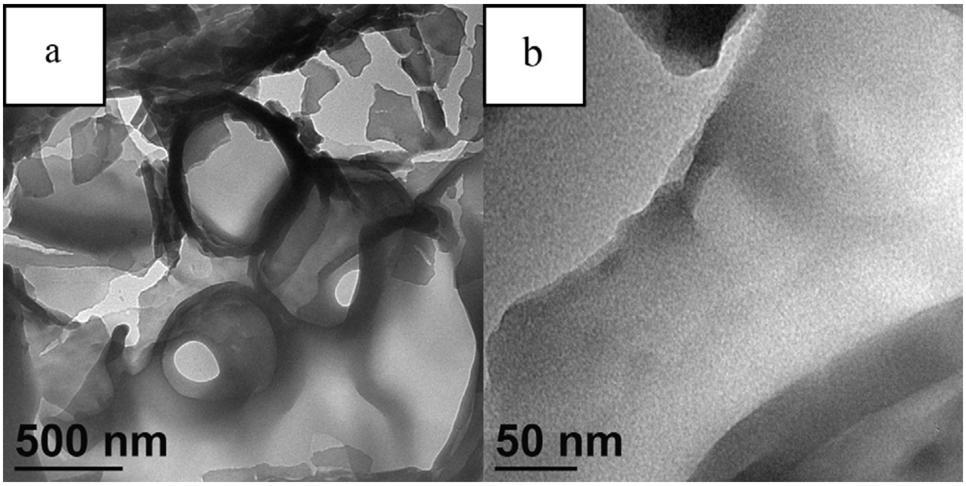

Fig. 1. TEM micrographs of the nanostructures formed at the liquid/liquid interface.

graphene nanosheets [40] or graphite nanoplatelets [41], and even coordination polymers [42,43] recently, however, to the best of our knowledge, study on the assembly of polymer thin films, especially composed thin film consisting of polymer and inorganic species at the liquid/liquid interface is very rare. We found that numerous Pt nanoparticles embedded in and adsorbed on the walls of the foams and capped with the protonated pyridine groups in the composites after UV-light irradiation. It should be noted that the interaction between Pt and P2VP is weaker than that between Pt and PVP due to the different molecular structures. It was also demonstrated that for some catalytic reactions, the catalytic efficiency of the nanoparticles depends mainly on two parameters. One is the available active surface area for adsorption and other is the number of nanoparticles present in per volume [44,45]. The formed composites fulfil the requirements, and exhibited high catalytic activity for the reduction of methylene blue by KBH_4.

2. Materials and methods

2.1. Chemicals

Poly(2-vinylpyridine) (P2VP. M_w: 5300, M_n: 5000), chloroplatinic acid hydrate ($H_2PtCl_6 \cdot xH_2O$, 99.9+%) and platinum standard solution (981 μg mL^{-1} (20 °C)) were purchased from Aldrich. KBH_4 ($\geq$97.0%) was purchased from Shanghai Zhanyun Chem. Co. Ltd. Methylene blue (MB, $\geq$98.5%) and chloroform ($\geq$99.0%) were obtained from Tianjin Guangcheng Chem. Co. The chloroform contains 0.3–1.0% of ethanol served as stabilizer. Concentrated hydrochloric acid (35%) and concentrated nitric acid (35%) were supplied by Matsunoen Chem. Ltd. Japan, and extra pure NaCl was obtained from Junsei Chem. Co., Ltd., Korea. The water used is highly purified with the resistivity $\geq$18.0 MΩ cm.

2.2. Preparation

10 mL P2VP chloroform solution with the concentration of 0.2028 mg mL^{-1} was poured in a clean beaker, then 10 mL aqueous solution of H_2PtCl_6 with the concentration of 1×10^{-3} mol L^{-1} was added carefully to form a clear liquid/liquid interface. The beaker was put in a sealed container that was placed in a dark oven. The temperature was controlled to be 25 °C. 24 h later, thin films appeared at the liquid/liquid interface and air/aqueous solution interface, respectively. The films were transferred on carbon-coated copper grids, silicon slides and quartz slides for further characterization. The deposited films were further irradiated by UV-light with the wavelength of 254 nm using a UV-lamp with the power of 6 W for a certain time. The distance between the deposited film and the lamp was 15 cm.

2.3. General characterization

The morphology, structure and compositions of the deposited and the UV-light irradiated films were investigated by using high-resolution transmission electron microscopy (HRTEM, JEOL–2010) with the accelerating voltage of 200 kV and X-ray photoelectron spectroscopy (XPS, ESCALAB MKII) with Mg Kα ($h\nu$ = 1253.6 eV) as the exciting source at a pressure of 1.0×10^{-6} Pa and a resolution of 1.00 eV. The optical properties of these films were characterized by using UV–vis spectroscopy (HP 8453E).

2.4. Measurement of platinum content

Platinum content was analyzed by using microwave digestion inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Varian Inc. – Liberty Series II). A certain amount of the sample was dissolved in aqua regia for 15 min predigesting, then digested in a CEM MARS5 microwave accelerated reaction system for 30 min. Then the reaction system was evaporated to dryness by using rotary evaporator, cooled down to room temperature, washed with a small amount of concentrated HCl, and diluted with water. The prepared sample was analyzed by using ICP-AES with monitoring the emission wavelength of Pt at 214.423 nm. The standard curve was obtained by using the platinum standard solution. The content of platinum in the composite sample was calculated.

2.5. Catalytic experiments

0.5 mL MB aqueous solution with the concentration of 2×10^{-4} mol L^{-1} was poured in a quartz cuvette with the side length of 1 cm; then 1.0 mL aqueous solution of KBH_4 with the concentration of 2×10^{-2} mol L^{-1} was added. The total volume of the reaction solution is 1.5 mL, and the concentrations of MB and KBH_4 are 6.67×10^{-5} and 1.33×10^{-2} mol L^{-1}, respectively. A deposited thin film on a quartz slide after UV-light irradiation was immersed in the reaction system to catalyze the reduction of MB. The reaction was monitored by using UV–vis spectroscopy (HP-8453E) at room temperature (~15 °C).