



Short communication

One-Step Synthesis of MnO₂ Particles Distributed Polyaniline–Poly(styrene-sulfonic acid)

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ABSTRACT

In this paper, polyaniline–poly(styrene-sulfonic acid)–manganese dioxide (PANI–PSS–MnO₂) composite was prepared by an interfacial reaction of potassium permanganate (KMnO₄) in PSS/ANI in chloroform. This method synthesizes MnO₂ particles incorporated in PANI–PSS by reduction of Mn⁷⁺ to Mn²⁺ and oxidation of Mn²⁺ to Mn⁴⁺ (MnO₂) with the simultaneous chemical oxidation polymerization of ANI. The immiscible liquid interface offers a unique microenvironment for confining the growth of PANI to form PANI–MnO₂ in the presence of PSS. The PANI–PSS–MnO₂ composite was verified through characterization by scanning microelectronic microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and FTIR spectroscopy. Cyclic voltammetric (CV) results showed that PANI–PSS–MnO₂ effectively catalyzed the oxidation of hydrogen peroxide (H₂O₂). The simple and inexpensive route for the preparation of PANI–PSS–MnO₂ composites can be used in the production of sensor electrodes in H₂O₂ and glucose detection.

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1. Introduction

Composites of conducting polymers and inorganic nanoparticles have received much attention because of their usefulness in several applications [1–3]. Manganese dioxides (MnO₂) are a kind of attractive inorganic materials and have been thoroughly investigated because of their important application in catalysis [4] and electrodes in lithium batteries [5] and capacitors [6]. Several methods have been developed for preparing MnO₂, including chemical oxidation [7], sol–gel-derived method [8], and chemical co-precipitation [9].

Polyaniline (PANI) comes in various oxidation states ranging from reduced leucoemeraldine form to the fully oxidized pernigraniline form. The ability of PANI to exist in a range of intrinsic redox states puts them in a unique and interesting class of polymeric materials [10–12]. PANI can be prepared by electrochemical and chemical methods [13,14]. In the chemical preparation of PANI, (NH₄)₂S₂O₈ (ammonium peroxydisulfate, APS) is generally used as the oxidizing agent for the preparation from aniline (ANI). Recently, a number of research studies reported auric ions and silver ions as oxidants for the polymerization of conducting polymers [15,16]. The reduction of auric and silver ions and the oxidation of aromatic amine occur simultaneously, and this suggests that they are a redox couple.

In this study, composites of PANI–PSS decorated with MnO₂ particles were prepared using an organic/aqueous interface in which particles were highly dispersed in a polymer matrix. PANI and MnO₂ particles were simultaneously synthesized in a medium of poly(styrene-sulfonic acid) (PSS). Organic–aqueous interfacial synthesis is an alternative useful approach to conventional homogenous synthesis. A liquid/liquid interface has the potential for chemical manipulation of particles. A highly intimate contact between PANI and MnO₂ particles is expected within the PANI–PSS–MnO₂ composite. Thus, the presence of MnO₂ particles on the surface of PANI–PSS may endow them new practical applications.

2. Experimental section

2.1. Materials

Reagent-grade ANI (Aldrich) and PSS (molecular weight = 75,000; Aldrich) were used without any further treatment. Ammonium peroxydisulfate (APS; Fluka) and potassium permanganate (KMnO₄) (Aldrich) were used without further purification.

2.2. Interfacial synthesis of PANI–MnO₂ in the presence of PSS

As usual, the interfacial reaction was performed in a 20 mL glass vial. A 0.02 mmol amount of ANI was dissolved in chloroform (10 mL). KMnO₄ (0.005 mmol) was dissolved in 10 mL of 0.1 M

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PSS solution. The ANI/chloroform solution forms the lower organic layer and the Pt precursor-PSS solution forms the upper aqueous layer. The resulting two-phase system was covered with stretched parafilm to minimize solvent evaporation and left undisturbed for ~12 h. After ~12 h, the reaction mixture was suction-filtered and the dark black precipitate was washed repeatedly with double distilled water and acetone until the solution washings were colorless. For comparative purpose, PANI nanofiber was prepared by using APS as initiator.

2.3. Instruments

The surface morphology of the films was examined using Philips X1-40 FEG scanning electron microscope (SEM). XPS measurements were performed using an ESCA 210 instrument equipped with a monochromatic Mg K α X-ray source (1256.6 eV). Fourier transform infrared (FTIR) spectra were recorded with a Nicolet 550 spectrometer. Hydrogen peroxide (0.4 mM) electrooxidation on PANI-PSS-MnO₂ was examined by cyclic voltammetry at 10 mV/s range from -0.2 to 1.2 V in a phosphate buffer (pH = 7.0) supporting electrolyte medium. The working electrode, the Ag/AgCl reference electrode, and a platinum wire counter electrode were inserted into the 20 mL cell through holes in its Teflon cover. A Luggin capillary, whose tip was set at a distance of 1–2 mm from the surface of working electrode, was used to minimize errors due to *iR* drop in the electrolytes.

3. Results and discussion

The interfacial synthesis of PANI-PSS-MnO₂ composite was carried out by performing polymerization of ANI using KMnO₄ as oxidant. A solution of ANI in chloroform was mixed with solution of KMnO₄ in PSS. Free radical polymerization takes place between protonated ANI monomer and KMnO₄ and the aqueous layer becomes yellowish organic initially, then yellowish green, green and finally puce color at the interface of the two solutions. We presumed that PANI and MnO₂ particles are simultaneously formed at the interface.

Fig. 1 shows the scanning electron microscopy (SEM) images of PANI-PSS and PANI-PSS-MnO₂. PANI-PSS (Fig. 1a) showed good cohesion with compact layer structure. In comparison with the PANI nanofiber structure by interfacial synthesis route in the literature [17,18], the cohesion and compact layer structure of PANI-PSS is attributed to the influence of PSS molecules on the orientation of PANI. PSS acts as not only the dopant but also the bridge to connect the interchain of PANI to form the spatial network structure. In contrast to APS as oxidant for polymerization of ANI, the dramatic change in morphology (Fig. 1b) was observed by employing KMnO₄ as oxidant. The SEM images revealed that the PANI-PSS spatial network structure was completely covered by small spherical MnO₂ particles. The structure of PANI-PSS-MnO₂ was porous, having lots of nano-dimension pores and agglomerates of fine oxide particle. This improved homogeneity was due to the spatially network structure of PANI-PSS, which improved the connectivity of the MnO₂ particles.

The XPS spectrum of PANI-PSS and PANI-PSS-MnO₂ is shown in Fig. 2. From the observation of the survey scan of PANI-PSS-MnO₂, the existence of Mn 3p and Mn 2p signals supplied clear evidence that MnO₂ particles had been successfully embedded in PANI-PSS matrix. The Mn 2p region consisted of a spin-orbit doublet with Mn 2p_{1/2} having a binding energy of 653.5 eV and Mn 2p_{3/2} with a binding energy of 641.5 eV, which is characteristic of a mixed-valence manganese system (Mn⁴⁺ and Mn³⁺) [19].

Fig. 3 gives the FTIR spectra of the PANI-PSS and PANI-PSS-MnO₂ composite. In the FTIR spectra, the bands at

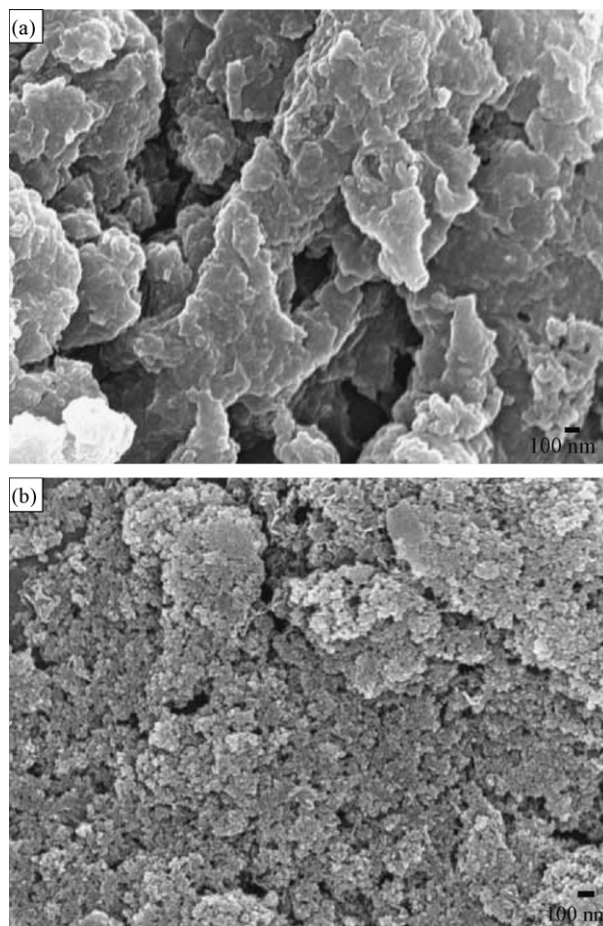


Fig. 1. SEM images of (a) PANI-PSS and (b) PANI-PSS-MnO₂.

the higher wavenumber region correspond to the N-H stretching (3250–3450 cm⁻¹). The group N=Q=N, where Q represents a quinoid ring, absorbed at ≈1580–1600 cm⁻¹ and N-B-B (B represents a benzenoid ring) absorbs at ≈1480–1500 cm⁻¹ [20]. The band at 1310 cm⁻¹ was assigned to the C-N stretching of the secondary aromatic amine whereas the band at 1250 cm⁻¹ was related to the protonated C-N group. The absorption band at 1150 was due to the aromatic C-H in-plane bending modes. PANI-PSS-MnO₂ exhibited characteristic bands similar to those of PANI-PSS, which confirmed the presence of PANI-PSS in the composite. However, a significant shift of the adsorption bands was observed for PANI-PSS-MnO₂ (1570, 1510, 1140, 1020, and 881 cm⁻¹). The shift of the adsorption bands was due to the physicochemical interaction between PANI-PSS and MnO₂ particles [21].

Xia et al. [22] reported the preparation of MnO₂ at a liquid/liquid interface. The aqueous phase contains a mixture of KMnO₄ and sodium dodecylsulfate (SDS) which serves surfactant in water. At the present of SDS, the micelles were formed and acted as colloid nanoreactors. The micelles containing permanganate salt arranges at the aqueous/organic interface, ferrocene molecule contacted the permanganate at the core of the micelles, redox took place at the interface and the MnO₂ particles were in the micelles. In the present case, it was hypothesized that the ANI moieties were electrostatically aligned at the interface by interacting with the anionic polymeric electrolyte (PSS). The sulfonate groups were expected to be preferentially oriented in the upper layer of the aqueous phase. Thus, the ANI moieties were aligned over the backbone of anionic polymer electrolyte (PSS) to form a protonated ANI. The

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