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Preparation of conducting polyaniline/protoporphyrin composites and their application for sensing VOCs

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ABSTRACT

Polyaniline/protoporphyrin nanocomposites were prepared via a simple chemical method in the acidic suspension of protoporphyrin. The scanning electron microscope images revealed that the polyaniline/protoporphyrin composites exhibited an interesting nanosheet structure decorated with nanoparticles, which is rather different with the usual nanofiber morphology of polyaniline. The formation of the nanosheet structure is because protoporphyrin molecules may exist as a bilayer form at low pH, which is similar with the phospholipid bilayer in membranes of cells. To demonstrate the application potential of the composites, the sensing performance of the composites was tested when exposed to four volatile organic compounds, including trimethylamine, triethylamine, ethanol, and ethyl acetate. The composites exhibited highest response value (*S*) of 39.482 toward trimethylamine, and fast response time of 2–4 s toward trimethylamine and triethylamine. The outstanding sensing performance showed that the prepared composites had great application potential in electronic noses system in further work.

1. Introduction

Polyaniline (PANI) has received much attention because of its stability, flexibility and remarkable electrical and optical properties (Yuan, Ahmed, & Kim, 2011). Extensive studies have been carried out to further improve the properties of the synthesized polymers for different needs(de Barros, de Azevedo, & de Aguiar, 2003; Jaymand, 2013; Józefowicz, Epstein, & Tang, 1992; Nabid, Zamiraei, Sedghi, & Safari, 2009; Phang, Tadokoro, Watanabe, & Kuramoto, 2008; Tai, Jiang, Xie, & Yu, 2010; Zhang, Li, & Zheng, 2013; Zheng, Ma, He, Gao, & Li, 2012). Generally, the employed methods could be divided into two categories, i.e., modification of the benzene ring in the backbone chain(Bhadra, Kim, & Lee, 2010; Masdarolomoor, Innis, Ashraf, Kaner, & Wallace, 2006) and compositing of PANI and other materials (Chen & Sun, 2013; Jain, Tiwari, & Karolia, 2014; Pakapongpan, Mensing, Phokharatkul, Lomas, & Tuantranont, 2014; Tai, et al., 2008). The compositing methods show greater potential since there are considerable amount of optional materials to prepare the PANI based nanocomposites.

Among the used materials to prepare such nanocomposites, the large π-aromatic molecules, porphyrins and the derivatives, have attracted attentions in recent years (Huang et al., 2014; Li et al., 2017). Their structures with high delocalized π-bonds endow them with unique optical, electrochemical and photophysical properties(Lu et al., 2011; Valicsek & Horváth, 2013), which make porphyrin derivatives promising candidates for sensitive and selective sensing platform (Chen et al., 2016; Kawakami & Igarashi, 1996; Xiao-wei et al., 2016). The combination of PANI and porphyrins will further broaden their application range, especially in gas sensors, solid DSSC and powerful catalysts.

Unfortunately, the water-insoluble property of many porphyrin compounds is always a problem for simple and effective fabrication of PANI/porphyrin nanocomposites. To solve this problem, the introduction of hydrophilic groups such as carboxylic and sulfonic groups is an effective method to improve the solubility of porphyrins in water. However, even with two hydrophilic groups, Protoporphyrin (PpIX) would precipitate out to form suspension at acidic condition which is necessary for conducting PANI preparation. Anyway, the precipitation of the PpIX in acid solution is a dynamic process, and a dynamic interface would come into being at the surface of the suspended solids. It was found that the compositing of PANI and PpIX could be realized with a similar mechanism involved in the emulsion/microemulsion polymerization process (Alhawi, Rehan, York, & Lai, 2015; Ćirić-Marjanović, 2013; Jaymand, 2013). However, a rather different polymerization behavior was observed in the PpIX suspension since the dynamic liquid/solid interface was rather different with the stable oil/aqueous interface produced by surfactant. In this paper, the PANI/PpIX

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nanocomposites was fabricated in PpIX suspension to investigate such a polymerization process, and the sensing performance of the nanocomposites to volatile organic compounds (VOCs) was evaluated to demonstrate their application potential.

2. Experimental methods

2.1. Reagents

Protoporphyrin IX (PpIX) was obtained from Sigma-Aldrich, aniline, potassium ferricyanide ($K_3Fe(CN)_6$), trimethylamine (TMA, 30%), triethylamine (TEA), ethanol, and ethyl acetate from Sinopharm Chemical Reagent Co. Ltd (China).

Aniline was distilled under reduced pressure before use. Doubly distilled water was used to prepare all solutions.

2.2. Preparation of PANI/PpIX nanocomposites in PpIX suspension

10 mL of 5 M H_2SO_4 and 0.913 mL aniline were added to 59.09 mL of water successively under vigorous stirring. The mixture was treated with ultrasound to fully dissolve the produced aniline sulfate. Then 10 mL of 2 mM PpIX was added to the aniline solution with stirring at 400 r/min to form PpIX suspension. 20 mL of 1 M $K_3Fe(CN)_6$ was added into the suspension slowly, and the obtained mixture was stirred continuously at room temperature for 1.5 h. Finally, the precipitation was collected by centrifugation and washed several times with deionized water until the supernatant became colorless, then dried in vacuum oven at 50 °C to obtain the PANI/PpIX nanocomposites. For comparison, PANI was synthesized by a similar method.

2.3. Characterization techniques

The scanning electron microscopy (SEM) images were taken on JSM-7001F (JEOL, Japan), and the energy dispersive spectra (EDS) were obtained from an X-max EDS spectrometer (OXFORD, UK). The Raman spectra were obtained on a DXR Laser Raman Spectrometer (ThermoFisher, America). The FT-IR spectra were collected on a Thermo Scientific Nicolet iS50 FT-IR Spectrometer (ThermoFisher, USA). The cyclic voltammograms (CVs) and electrochemical impedance spectra (EIS) were performed on a CHI660D electrochemical workstation (Chen Hua Instruments, Shanghai, China) with a three-electrode system, which employed a modified glass carbon electrode (GCE) as working electrode, a platinum wire as counter electrode, an Ag/AgCl (KCl (sat'd)) electrode as reference electrode. The modified GCE was prepared by dropping 6 μL of PANI/PpIX nanocomposites suspension (0.5 mg/mL) onto GCE and drying under nitrogen flow.

2.4. Evaluation of sensing performance of the PANI/PpIX nanocomposites to VOCs

To demonstrate the application potential of the PANI/PpIX nanocomposites, the sensing performance of the composites was tested when exposed to several kinds of VOCs, including TMA, TEA, ethanol, and ethyl acetate.

2.4.1. PANI/PpIX nanocomposites sensor

2.4.1.1. Interdigitated Au electrode (IAE) preparation. Fig. 1(a) shows the schematic and photo of the IAE made up of interdigitated Au ‘fingers’ and silicon dioxide (SiO_2) substrate. The dimension of the IAE is 4 mm × 4.3 mm with electrode area of 2.4 mm × 2.25 mm and a gap of 3 μm, the thickness of the Au interdigitated ‘fingers’ is 100 ± 10 nm. The IAEs were rinsed with alcohol and water successively before use.

2.4.1.2. Sensor preparation by drop coating method. Briefly, 3 μL of 0.5 mg/mL PANI/PpIX nanocomposites suspension was dropped onto the surface of the IAE to form a thin film of the composites, and the modified IAE was then dried under nitrogen.

2.4.2. Measurement system

The resistance response of the modified IAEs to VOCs was analyzed using a home-made setup as shown in Fig. 1(b). The system was consisted of a gas chamber (20 L in volume), a test chamber (150 mL in volume), a multi-meter (Agilent 34410A), a computer, five needle values and the attachment configuration.

(1) Experiments were performed in a temperature-controlled room at 25 °C. The whole system was purged with air for 20 min at a flow rate of 5 L/min before starting the tests.
(2) VOC liquid of needed volume was injected into the gas chamber with a micro-injector to obtain VOC gas of certain concentration.
(3) The sensor in the test chamber was exposed to VOC gas or air by adjust the on/off status of the five needle values (NVs). The flow rate of the gas through the test chamber was controlled at 1 L/min.

3. Results and discussion

3.1. Characterization: SEM images, EDS, Raman spectra and FT-IR spectra of PANI, PpIX and PANI/PpIX nanocomposites

The SEM images of PANI and PANI/PpIX composites are shown in Fig. 2 to reveal the effects of PpIX on the polymerization of PANI. For pure PANI polymerized in the absence of PpIX, a typical porous network structure similar with previous reports was observed (Chen, Yang, Yan, & Xue, 2010; Zheng et al., 2012). The network mainly consisted of nanofibers with a diameter of about 100 nm. However, the PANI/PpIX composites exhibited a rather different surface morphology as shown in Fig. 2(b) and (c). Some stacked nanosheets decorated with nanoparticles at the edges or on the surface of the nanosheets were observed obviously. Furthermore, it was interesting to find that the percentage of the nanoparticles in the composites decreased significantly (see Fig. 2(d)) when increased the employed concentration of PpIX from 2 mM to 4 mM. This phenomenon may be explained by the proposed mechanism as illustrated in Scheme 1. The PpIX molecules at low pH may exist in a bilayer form similar with the phospholipid bilayer in membranes of cells. As shown in Scheme 1, the hydrophilic propionyloxy heads pointed “out” to the water on either side of the bilayer and the hydrophobic porphyrin ring bodies pointed “in” to the core of the bilayer. The alkaline aniline molecules would capture the proton of PpIX to form a thin film of aniline-PpIX salts on the surface of the bilayers. For the polymerization of these anchored aniline, the first step involves the oxidation of the aniline monomers to radical cations, which leads to formation of the dimeric species, i.e., *p*-aminodiphenylamine, N,N′-diphenylhydrazine, and benzidine (Wei, Hariharan, & Patel, 1990). Soon after formation, the two dimers will be oxidized to their diimine forms, which could be deprotonated to afford nitrenium ions (Wei et al., 1990). An electrophilic attack of aniline monomer by the diimines or the nitrenium ions would accomplish a growth step and lead eventually to the final polymer (Wei, Tang, Sun, & Focke, 1989). Since the whole process was realized on the surface of the PpIX bilayers, PANI/PpIX nanosheeets as shown in Fig. 2 were finally obtained. However, some PANI nanoparticles would come into being due to the exhausted propionyloxy anchors at the edge of the nanosheets, and the independently formed particles would also intersperse in the composites during the drying steps, resulting in the final morphology of the composites.

EDS as shown in Fig. 3(a) was obtained to confirm the presence of PpIX in the PANI/PpIX composites preliminarily. The emergence of the oxygen in the EDS spectrum indicated the existence of propionyloxy in the PANI/PpIX composites.

Raman spectroscopy as shown in Fig. 3(b) was used to confirm the chemical composition of the PANI/PpIX composites. In the spectrum of PANI/PpIX, the relative intensity of the band at 1586 cm^{-1}, assigned to