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Short communication

"One-pot" synthesis, characterization, and NH_3 sensing of Pd/PEDOT:PSS nanocomposite

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ABSTRACT

In this letter, we report a novel route to prepare stable Pd/poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (Pd/PEDOT:PSS) colloid. With addition of PSS, the Pd/PEDOT:PSS aqueous dispersion was formed by simultaneous oxidation–reduction reaction between $Pd(NO_3)_2$ and ethylenedioxythiophene (EDOT) at room temperature. The morphologies of the Pd/PEDOT and Pd/PEDOT:PSS nanocomposites were characterized by transmission electron microscope. The Pd nanoparticles in the composites were identified with X-ray powder diffraction and UV/vis/NIR spectrum. The chemical structures of PEDOT were studied using FTIR spectra and UV/vis/NIR spectra. The results confirmed the formation of oxidized PEDOT polymer. The sensing property of the Pd/PEDOT:PSS thin film to the NH_3 vapor was investigated.

1. Introduction

Organic semiconductors including small molecules and polymers are promising candidates for large-area, low-cost, and rugged flexible electronics [1]. Poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS), one of the commercial available conducting polymers, has been used in applications such as antistatic coating, hole-transport layer in organic light-emitting diode, and conductive ink [2,3]. In particular, PEDOT:PSS and other conducting polymers have been investigated as potential chemical and biological sensors, due to their high biocompatibility, the fine tuning of their chemical–physical properties by precise synthesis, and low-temperature fabrication on flexible substrates [4–6].

Incorporation of inorganic nanoparticle into the organic semiconductor brings unique properties in the hybrid inorganic/organic system and potential applications in electronics, energy conversion, and sensors. Specifically, the metal nanoparticle can interact with conducting polymer synergically and result in remarkable optical, electronic, and/or catalytic properties [7–12]. One example is the dispersion of gold nanoparticles into a conducting polymer-based electrochromic device [12–14]. The surface plasmon absorption of the gold nanoparticle, which depends on the size and shape of the nanoparticle, may modulate the electrochromic response of the nanocomposite film. However, few studies on the chemical sensors based on the unique properties of nanoparticle/conducting polymer have been published [11,15].

One key issue on nanoparticle/conducting polymer nanocomposite is to achieve the uniform and stable colloid that can be used to process into devices via low-cost printing and spincoating techniques. To prepare the nanocomposite of nanoparticle/conducting polymer, the most common method is to disperse the nanoparticles in a conducting polymer solution. Other methods include micro-emulsion, polymerization after dispersion of nanoparticle in a monomer solution, etc [16,17]. Recently, a simple "one-pot" synthesis using simultaneous oxidation–reduction reaction in the presents of surfactant has been demonstrated to prepare nanoparticle/conducting polymer composites including Au/PEDOT and Pd/polypyrrole. This method leads to a well-dispersed nanoparticle/conducting polymer colloid [18–20], which is readily used to prepare thin film device. To the best of our knowledge, there has been no report on the Pd/PEDOT colloid synthesized via the "one-pot" method. In this letter, we report the synthesis of stable Pd/PEDOT colloid with PSS as surfactant via simultaneous oxidation–reduction reaction and demonstrate the NH_3 sensing property of the thin film device based on the Pd/PEDOT:PSS nanocomposite.

2. Experimental

All chemical reagents were purchased from Aldrich and used without further purification. We synthesized Pd/PEDOT composite with or without PSS. In a typical reaction, 40 mg $Pd(NO_3)_2{\cdot}2H_2O$

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were dissolved in 1 mL of 1 M HCl, and then the $Pd(NO_3)_2$ solution was added dropwise to a 15 mL ethylenedioxythiophene (EDOT) solution (0.01 M) in deionized water under vigorous stirring. The reaction solution became black in less than 30 s, and was kept stirring overnight at room temperature. The product Pd/PEDOT was washed with deionized water twice and then dried under vacuum. For Pd/PEDOT:PSS dispersion, the $Pd(NO_3)_2$ solution was added to a 15 mL EDOT solution (0.01 M) with 1 wt% PSS, and the stable Pd/PEDOT:PSS dispersion was formed after the reaction.

The products were characterized using FTIR (Bruker Tensor27), UV/vis/NIR spectrometer (Spec20), powder X-ray diffraction (XRD, Rigaku Ultima Plus), and transmission electron microscopy (Hitachi H-7000 FA).

To measure the sensing property of the nanocomposite, the Pd/PEDOT:PSS colloid was mixed with commercially available PEDOT:PSS (1:1 weight ratio), and was spin-coated on a glass substrate. The spin-coated film was patterned by wiping off the excess material to form a 5 mm wide, 25 mm long stripe, and baked in a vacuum oven at 150 °C for 30 min. The electrical contacts were made at the ends of the Pd/PEDOT:PSS stripe using the silver paste. The device was fixed in a chamber with electric feedthrough, and the current of the device at the applied bias of 5 V was recorded using Keithley 2612 SourceMeter for 1600 s. During the measurement, the device was exposed to ammonia vapor and N_2 gas alternatively.

3. Results and discussion

3.1. Morphology and formation mechanism

The formation mechanism of Pd/PEDOT nanocomposite is shown in Fig. 1. The Pd/PEDOT nanocomposite was formed because of the simultaneous oxidation–reduction reaction: the EDOT monomers were oxidized by the Pd^{2+} ions to PEDOT polymers, whereas the Pd^{2+} ions were reduced to neutral nanoparticles at the same time [18,21]. The morphology of the Pd/PEDOT nanocomposite with or without PSS surfactant was characterized using TEM (Fig. 2). Without the PSS as the stabilizer during the reaction, Pd/PEDOT participated out of the reaction solution, and the Pd nanoparticles were aggregated together to form Pd/PEDOT spherical particles of ∼ 50 nm diameter (Fig. 2a). The internal structures of the spherical particles were not revealed due to the limitation of our TEM instrument. The spherical particles were most likely composed of small Pd nanoparticles connected together by PEDOT polymer chains [19]. Addition of PSS during the "one-pot" simultaneous oxidation–reduction reaction stabilized the Pd nanoparticles, and a Pd/PEDOT:PSS colloid was obtained. In the TEM image of Pd/PEDOT:PSS (Fig. 2b), the Pd nanoparticles were spherical with diameters about 3–5 nm, and were well-dispersed in PEDOT:PSS matrix. The Pd/PEDOT:PSS colloid could be stable for more than 6 months.

3.2. Structural characterization

The Pd/PEDOT nanocomposite was characterized using XRD. XRD diffraction pattern of Pd/PEDOT powder sample (Fig. 3a) showed a weak peak at 40°, which was assigned to the (1 1 1) reflection of the faced-centered cubic Pd(0) crystal [19]. The weak XRD signal in Pd/PEDOT indicated that the Pd nanoparticles in Pd/PEDOT were very small, and therefore implied that the spherical particles in Pd/PEDOT (Fig. 2a) contained small and aggregated Pd nanoparticles, which likely had similar sizes to the Pd nanoparticles in Pd/PEDOT:PSS (Fig. 2b).

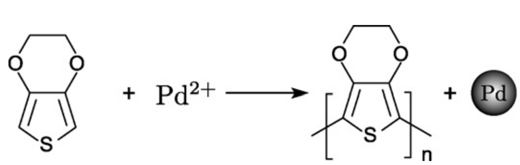

Fig. 1. Mechanism of simultaneous oxidation–reduction reaction between $Pd(NO_3)_2$ and EDOT.

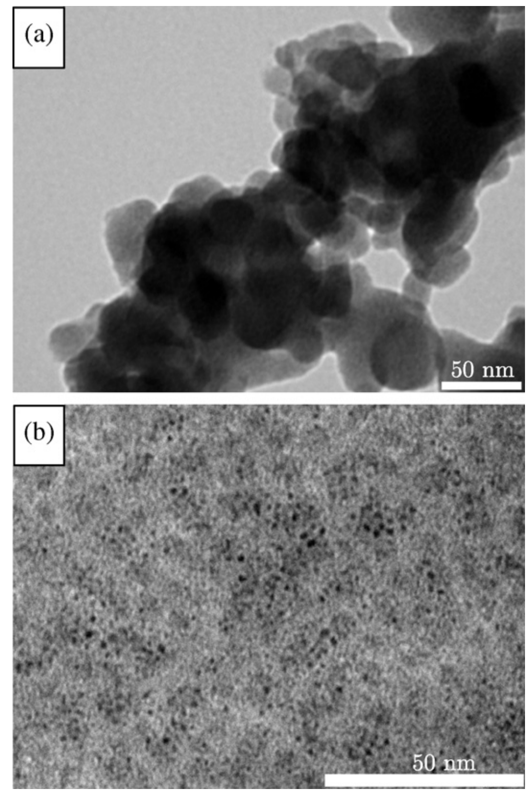

Fig. 2. TEM images of (a) Pd/PEDOT and (b) Pd/PEDOT:PSS.

The FTIR spectra of pure EDOT and Pd/PEDOT were shown in Fig. 3b. In the spectrum of pure EDOT, the =C–H in-plane and out-of-plane deformation vibrations were observed at 1186 cm^{-1} and 892 cm^{-1}, respectively [18,20]. After the reaction, the two vibrational modes disappeared in the spectrum of Pd/PEDOT, indicating that the thiophene rings were polymerized by α–α' coupling [22]. Other peaks could be attributed to the –C–S bonds (840 cm^{-1}, 988 cm^{-1}), the –C–O–C– stretching (1090 cm^{-1}, 1234 cm^{-1}), and the C–C and C= C stretching of quinoidal structure (1360 cm^{-1}) [23].

The Pd/PEDOT:PSS colloid was further characterized by UV/vis/NIR spectroscopy (Fig. 3c), and the result was compared to that of the commercial PEDOT:PSS solution. In PEDOT:PSS, the PEDOT polymers were oxidized and doped by PSS to form $PEDOT^+$ and PSS^- complexes [3]. The oxidized $PEDOT^+$ displayed a broad absorption in the visible and near-infrared region, due to the bipolaron formation in the doped conducting polymer [24]. In the spectrum of Pd/PEDOT:PSS colloid, a broad absorption similar to that of PEDOT:PSS was observed, suggesting that the "one-pot" reaction lead to the formation of highly oxidized PEDOT. Further, the spectrum of Pd/PEDOT:PSS displayed high absorption at short wavelength and a shoulder band around 340 nm. The absorption around 340 nm was attributed to the valence-conduction band transition of the Pd nanoparticles [25,26]. The result confirmed the formation of the Pd nanoparticles simultaneously with polymerization of EDOT during the reaction.