One-pot Preparation of Core–Shell Structure Titania/Polyaniline Hybrid Materials: The Effect of Sodium Dodecyl Sulfate Surfactant

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Polyaniline (PANI)-coated titania (TiO_2) have been prepared with ammonium persulfate (APS) as an oxidant in aqueous sodium dodecyl sulfate (SDS) micellar solution. The addition of a small amount of TiO_2 nanoparticles greatly increased electrical conductivity from 5.89 to 14.2 S/cm. The effect of SDS for TiO_2@PANI composites was studied in terms of morphology of the core–shell structure, dispersibility of TiO_2 in composites, and electrical conductivity.

Polyaniline was firstly synthesized in 1862,[1] and important evidence of the electrical properties for PANI film was found by Diaz and Logan.[2] The studies of MacDiarmid et al.[3] recognized the significance of PANI as a conducting polymer because of its superior electrical, optical, and photoelectrical properties, as well as its simple preparation and excellent environmental stability.[4] Nanocomposites exhibit unique physical and chemical properties over their single-component counterparts[5] and, hence, are potentially useful in a wide range of applications.[6] One important class of nanocomposites is organic/inorganic hybrids in which the organic phase is a conductive polymer.[7] Numerous studies have been conducted to prepare PANI/TiO_2 composites because of their well-matched band gap for charge transfer and of various applications of their photocatalytic activity and as gas sensor.[8]

Although PANI is expected to have one of the highest environment stabilities, its conductivity can be strongly degraded by accelerated aging tests.[9] Such decrease in conductivity can be related to two factors, intrinsic and extrinsic, such as dedoping, loss of conjugation, oxidation, crosslinking, and other chemical reactions. Schnitzler et al.[10] have reported that TiO_2 could improve the thermal stability of PANI. Several groups investigated the effect of TiO_2 on electrical conductivity in PANI/TiO_2 nanocomposites.[11] They have found that the combination of TiO_2 with PANI slightly increases the conductivity of the PANI/TiO_2 nanocomposite by inducing conformation change to form an efficient network for charge transport. Yavuz and Gök[12] reported that some surfactants affected thermal stability of PANI/TiO_2 composite. However, most studies of PANI/TiO_2 composites have used functionalized protonic acid surfactants, such as dodecylbenzenesulfonic acid (DBSA, $CH_3(CH_2)_{11}C_6H_4SO_3H$) only as a doping agent to improve dispersibility of inorganic particles and to provide thermal stability. Up to now, there has been no report on the effect of sodium dodecyl sulfate (SDS, $C_{12}H_{25}SO_4Na$) surfactant on the electrical properties of PANI and PANI/TiO_2 nanocomposite as well. SDS is an anionic surfactant and has similar molecular structure except for existing sulfate group and shorter carbon chain in contrast to DBSA.

In this paper, we report a one-pot preparation of core–shell structure PANI/TiO_2 hybrid materials with high conductivity. Also, the effect of SDS surfactant in respect to thickness of the shell, dispersibility of TiO_2 in composites, and electrical conductivity at different concentrations is discussed.

TiO_2@PANI was prepared by the chemical oxidation of aniline in an acidic medium dispersing TiO_2 (average size 21 nm). To examine the effect of SDS surfactant, 0.2 M of aniline monomer and some amount of TiO_2 were added to 190 mL of 1 M aqueous HCl solution containing SDS micelles. The polymerization was carried out at 30 °C by adding 0.01 mol APS. After 2 h, the solution was washed with methanol and centrifuged at 2000 rpm for 5 min to separate the powder and supernatant. The obtained powder was observed by TEM. Figure 1 showed core–shell-structured TiO_2@PANI prepared under different concentration of SDS. The particle size distributed in the range of diameter 26–45 nm. The thickness of the PANI-coated TiO_2 was 2.3 nm at 0.05 M SDS, 3.2 nm at 0.08 M SDS, 9.4 nm at 0.10 M SDS, and 10.6 nm at 0.20 M

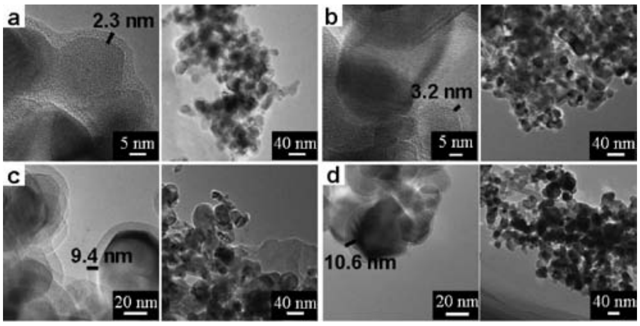

Figure 1. TEM images of TiO_2@PANI prepared with varying SDS concentrations at 3 g TiO_2: (a) 0.05, (b) 0.08, (c) 0.10, and (d) 0.20 M of SDS.

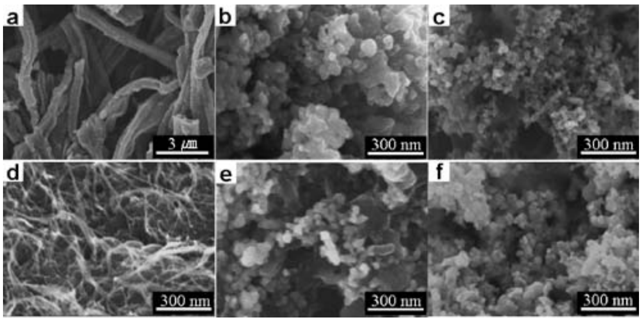

Figure 2. SEM images: (a), (d) PANI, (b), (e) TiO_2@PANI with 1 g TiO_2, (c), (f) TiO_2@PANI with 3 g TiO_2; (a), (b), (c) prepared with 0.08 M SDS, (d), (e), (f) prepared with 0.20 M SDS.

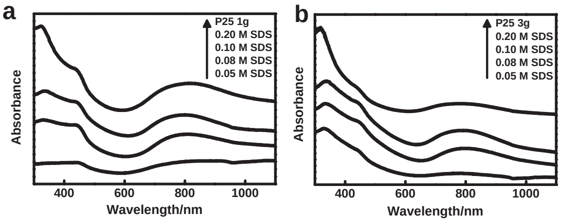

Figure 3. UV–vis spectra of TiO_2@PANI with various SDS concentration at constant TiO_2: (a) 1 g TiO_2, (b) 3 g TiO_2.

SDS. It was found that increasing the SDS concentration improved the layer thickness of the PANI on TiO_2.

Yavuz and Gök[12] reported that surfactants were incorporated into PANI/TiO_2 composites owing to the interaction between the polycations and surfactants. It was suggested that the SDS incorporated into the composite resulted in increasing the thickness. The SEM images of the TiO_2@PANI nanocomposite are given in Figure 2. Figures 2a and 2d show the morphology of PANI at 0.08 and 0.20 M SDS, respectively, where the former system formed nanotube phase PANI, and the latter formed nanofiber PANI. These nanostructures might be closely related to the formation of anilinium–dodecyl sulfate complex generated by mixing aniline and SDS that acts as a template. Details will be appeared elsewhere.[13] As the TiO_2 content increased, nanocomposites prepared at 0.08 M SDS and 0.20 M SDS transformed in morphology from tube or fiber PANI to particles. This suggests that the TiO_2 nanoparticles acted as a nucleus for core–shell structures in the polymerization and that the large amount of TiO_2 made a homogeneous PANI shell on their surface.

The UV–vis spectra of TiO_2@PANI were investigated with varying SDS concentration at constant TiO_2 contents (Figure 3). Three characteristic absorption bands of PANI are shown at 330, 440, and 800 nm. The peak at 330 nm is related to the amount of TiO_2 coated by PANI. The absorption at 330 nm increased with high TiO_2 nanoparticle loading. However, at low SDS concentration, the intensity at 330 nm was weaker than that at high SDS concentration. When the amount of TiO_2 is kept the same, it is thought that composites must show the same intensity regardless of SDS concentration. This indicates that at low SDS, TiO_2 is not dispersed homogeneously. In the case of TiO_2 particles, it is known that the UV scattering or the hiding power increases with increasing degree of dispersion.[14]

Figure 4b shows the electrical conductivity of TiO_2@PANI composites prepared with different TiO_2 contents. TiO_2@PANI composites with 100 to 20 wt % PANI showed the same order of magnitude of conductivity. And the value of composite with 20 wt % PANI was about 70000 times higher than that of raw TiO_2. Compared to neat PANI, the addition of a small amount of TiO_2 improved the electrical conductivity from 5.89 to 14.2 S/cm in the 0.08 M SDS system and from 5.01 to 6.92 S/cm in the 0.20 M SDS system, respectively. Previous studies attributed this to the conformation change of stiff PANI backbones contact with TiO_2 nanoparticles, which is believed to facilitate the formation of a more efficient network for charge transport, thus enhancing the conductivity of the composites.[11] However, it is difficult to explain the present conductivity to be increased above twice. As shown in Figure 4a, it was confirmed that the electrical conductivity was decreased drastically by incorporating the SDS into the PANI. Now we can consider a plausible reaction mechanism of the TiO_2@PANI composite as depicted in Figure 5. The SDS surfactant was used to disperse TiO_2 nanoparticles, homogeneously. This means that the surfactant molecules were adsorbed on the TiO_2 surface. After adding aniline monomer, they were adsorbed on the surfactant coated onto TiO_2. And then PANI polymerized forming a shell around the TiO_2. Therefore, the TiO_2@PANI nanocomposites were polymerized with a lower amount of SDS than those used to prepare neat PANI. In the present report, it is demonstrated that this resulted in a drastic increase of the conductivity.

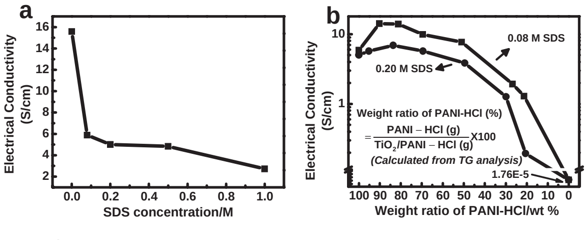

Figure 4. The electrical conductivity of (a) neat PANI prepared with varying SDS concentrations, (b) TiO_2@PANI with various amount of TiO_2 at 0.08 M SDS and 0.20 M SDS.

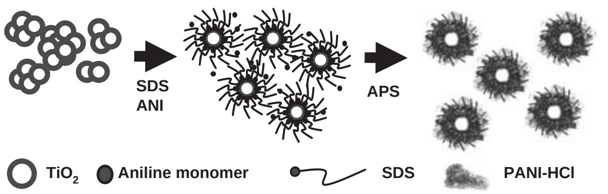

Figure 5. The schematic diagram of the mechanism for TiO_2@PANI.

In conclusion, TiO_2@PANI hybrid composites were prepared using a one-pot reaction. By increasing the SDS concentration, the shell thickness was increased by incorporating the surfactant into the PANI and the TiO_2 was well dispersed into the composites. The addition of a small amount of TiO_2 nanoparticles drastically increased the electrical conductivity. It should be noted that the improvement in the conductivity of TiO_2@PANI composite resulting from SDS as dispersant for TiO_2 as well as interaction between TiO_2 and PANI.

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