

Research Article

Preparation of a Novel Nanocomposite of Polyaniline Core Decorated with Anatase-TiO₂ Nanoparticles in Ionic Liquid/Water Microemulsion

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Polyaniline core decorated with TiO₂ (PANI-TiO₂) nanocomposite particles was successfully synthesized in ionic liquid/water (IL/water) microemulsion in the presence of anatase TiO₂ nanoparticles. The TiO₂ nanoparticles had been dispersed beforehand in OP-10 and *n*-butanol to weaken the strong particles agglomeration of TiO₂. The PANI-TiO₂ nanocomposites were characterized by fourier transform infrared spectroscopy (FTIR), ultraviolet visible spectroscopy (UV-Vis), scanning electron microscopy (SEM), and transmission electron microscope (TEM), and their electrochemical behavior was estimated by the electrochemical workstation. SEM micrographs showed that the nanocomposites exhibited spherical morphology with particle sizes about 70 nm. The TEM result showed that the PANI-TiO₂ nanocomposites had a novel structure and that nanocrystalline TiO₂ deposited onto the surface of PANI, which was different from the reported structure of TiO₂-PANI nanocomposites. Both FTIR and UV-Vis spectra indicate that polyaniline and nano-TiO₂ particles are not simply blended or mixed up. A possible reaction mechanism for this nanocomposite preparation is suggested and analyzed.

1. Introduction

Organic-inorganic nanocomposites for synergetic behavior and a wide range of potential use have triggered great interest and concern of the related academic organizations and researchers over the past decade [1–4]. Specifically, core-shell structures nanocomposites of organic conjugated polymers and inorganic nanocrystals have attracted great attention due to a large number of potential applications such as photonics, photoelectronics, and catalysis [5]. Among the conducting polymers, conducting polyaniline (PANI) is often used as an organic part to prepare nanocomposites because of its low cost, easy preparation, controllable unique properties by oxidation and protonation state, excellent environmental stability, and potential application in electronic devices [6]. A number of different metal oxide particles have so far been encapsulated into the shell of polyaniline giving rise to a host of nanocomposites. Du et al. [7] reported an Ag-PANI

core-shell structure via one-pot redox reaction in ethanol at 250°C. The obtained Ag-PANI core-shell particles are with a large Ag core of the size of about 200 nm and relative thin polyaniline shell of the thickness of about 50 nm. Lei [8] successfully prepared Au-polyaniline nanocomposites with core-shell structure on ITO conducting electrode based on 4-aminothiophenol-capped Au nanoparticles via electrochemical synthesis, and the Au nanoparticle with a mean diameter of ca. 250 nm is the core of the nanocomposite and the polyaniline is the shell wrap of the Au nanoparticle. The CeO₂-polyaniline (CeO₂-PANI) core-shell nanocomposites prepared via chemical oxidation of aniline by CeO₂ were reported by Chuang and Yang [9]. Jing et al. [10] successfully synthesized Ag-polyaniline core-shell nanocomposites via in situ chemical oxidation polymerization of aniline based on mercaptocarboxylic-acid-capped Ag nanoparticle colloid. Yu et al. [11] prepared carbon nanotube-polyaniline core-shell nanowires by in situ inverse microemulsion. Nanocompos-

ites of “egg-like” cores and shell ranging in diameter from 40 to 80 nm and 60 to 120 nm, respectively, have been prepared successfully using hexadecyl trimethyl ammoniumbromide (CTAB) microemulsion by Asim et al. [12]. Nanosized titania, because of its unique physicochemical properties [13–16], is frequently combined with polyaniline. Zhang et al. [17] synthesized PANI-TiO₂ composite microspheres with an average diameter 2.5–3.5 μm by a template-free method in the presence of salicylic acid as dopant. The PANI-TiO₂ composites are typical core-shell structure, PANI-coated crystalline TiO₂. A polyaniline-nano-TiO₂ composite [18] was prepared by polyaniline for the surface modification of nano-TiO₂ particles, forming a core-shell structure.

There are many researches on the core/shell-metal oxide/polyaniline structures, but the structures of polyaniline core decorated with metal oxide are seldom investigated. As is known, the octahedrite-type TiO₂ has better chemical properties and photon characteristics, due to its good absorbability and lower electron/holes recombining rate [19]. The ultraviolet excitation (wavelength <380 nm) can overcome the energy gap of pristine titanium dioxide for photocatalysts for electrons to jump to conduction band to form the electron-hole pair. The formed holes and electrons can oxidize and reduce the H₂O, OH⁻, or O₂ adsorbed on the surface of TiO₂ to living free radicals, which can deteriorate the organic materials or undesired pollutants that adsorbed on the surface of TiO₂ catalyst resulting in generating nonpoisonous CO₂, H₂O, and some inorganic products. However, for TiO₂ core-PANI shell composites, because of package action of polyaniline, photon absorption of TiO₂ nanoparticles is blocked and the living free radicals generated from holes and electrons are hard to transfer onto the surface of polyaniline to oxidize organic materials; moreover, the living free radicals may react to the polyaniline in course of transfer. Thus, in fact, the photoelectric capabilities of TiO₂ are bated after being enwrapped by polyaniline. Hereby, polyaniline core decorated with TiO₂ (PANI-TiO₂) nanocomposite particles makes it possible to develop the properties of TiO₂.

Ionic liquids (ILs) are organic salts with low melting points [20] and have a stable liquid range temperature of over 300°C. Typical ILs have unusual properties including nonvolatility, nonflammability, wide electrochemical windows, higher ionic conductivity, and excellent thermal and chemical stability. More recently, synthesis of PANI has been advocated by electrochemical [21] and interfacial [22] polymerization in ILs. All of the PANIs exhibit excellent physical and chemical properties. Another potential advantage of synthesis in ILs is their unique solvent capabilities, which can avoid organic solvent volatilizing.

Microemulsions are thermodynamically stable dispersions of two or more immiscible liquids that are stabilized by an adsorbed surfactant film at the liquid-liquid interface. They are an effective method to prepare nanoparticles, nanowires, and nanorods [23]. Furthermore, it has been demonstrated that ILs could substitute water or conventional organic solvents to form novel microemulsion systems in the presence of surfactant, and these novel microemulsions

incorporate the advantages of ILs and microemulsion [24–26]. Our research group has successfully prepared PANI nanoparticles in IL/water emulsion systems [27, 28].

In the present study, a polyaniline core decorated with TiO₂ (PANI-TiO₂) nanocomposite was prepared in a microemulsion comprised of deionized water as the continuous aqueous phase and an oil solution including aniline and hydrophobic IL 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF₆) as the dispersed phase in the presence of anatase TiO₂ nanoparticles. The TiO₂ nanoparticles were dispersed beforehand in OP-10 and *n*-butanol. The nanocomposites were characterized by fourier transform infrared spectroscopy (FTIR), ultraviolet visible spectroscopy (UV-Vis), scanning electron microscopy (SEM), and transmission electron microscope (TEM). Moreover, the possible reaction mechanism for the preparation of PANI-TiO₂ nanocomposite is investigated here.

2. Experimental

2.1. Materials. IL 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF₆) was prepared as described in the literature [29]. Nanocrystalline TiO₂ (anatase <10 nm) was synthesized based on a sol-gel technique as described in the previous procedure [30]. Aniline, *n*-butanol, ammonium persulfate (APS), nitric acid, and other chemicals were analytical grade (Sinopharm Chemical Reagent Co., Ltd) and were used as received. The emulsifier nonylphenol ethoxylates (OP-10) was obtained from 3W Industry Co., Ltd. All aqueous solutions were prepared with deionized water.

2.2. Synthesis of Polyaniline Core Decorated with TiO₂ (PANI-TiO₂) Nanocomposite. The polyaniline core decorated with TiO₂ (PANI-TiO₂) composites was synthesized in microemulsion system via in situ chemical oxidative polymerization in the presence of TiO₂ nanoparticles, and the procedure was as follows: Firstly, hydrophobic IL [bmim]PF₆ (2 mL)/aniline (1 mL) mixture was added into the OP-10 (13 mL)/*n*-butanol (3 mL)/HNO₃ (87 mL (0.115 mol·L⁻¹)) solution; after the mixture was stirred for 1 h under magnetic stirring, a dispersion of TiO₂ nanoparticles (TiO₂: aniline = 25 wt%) in a mixed solution of 3 mL OP-10 and 2 mL *n*-butanol was in one time introduced into the mixture; after another 1 h of magnetic stirring, a transparent oil-in-water microemulsion was obtained. Then, the polymerization was initiated by adding 6 mL of 3 mol·L⁻¹ APS aqueous solution into the above microemulsion droplet within 30 min under magnetic stirring. The polymerization was allowed to proceed for 4 h under stirring. Finally, the obtained sap-green polyaniline core decorated with TiO₂ (PANI-TiO₂) nanocomposite powder was filtrated and rinsed with acetone and water repeatedly and then dried in vacuum at 55°C for 24 h. For comparison, polyaniline nanoparticles were also prepared under the same condition, but without TiO₂ nanoparticles added.

All the experimental procedures proceeded at room temperature except the drying of samples.

2.3. Characterization. The morphology of nanocomposites was examined by a JSM-6700F scanning electron microscope (SEM) and a JEM-3010 high-resolution transmission electron microscope (TEM). Fourier transform infrared (FT-IR) spectra were recorded on a Perkin Elmer Fourier transform infrared spectrometer. The ultraviolet visible (UV-vis) absorption spectra were recorded on a LabTech UV-240 spectrophotometer. Cyclic voltammetric studies of PANI and nanocomposites were performed by using an Iviumstat electrochemical working station (Ivium Technologies BV). A one-compartment cell was used with a platinum mesh as counter electrode and a saturated calomel electrode (SCE) as reference electrode. The electrolyte was composed of $1 \text{ mM} \cdot \text{L}^{-1} \text{ K}_3\text{Fe}(\text{CN})_6$, $1 \text{ mM} \cdot \text{L}^{-1} \text{ K}_4\text{Fe}(\text{CN})_6$ and $0.2 \text{ mol} \cdot \text{L}^{-1} \text{ NaCl}$. The scan speed was $0.1 \text{ V} \cdot \text{s}^{-1}$, and the potential range was from -200 mV to 600 mV . A certain volume of PANI or nanocomposite ethanol solution was added dropwise by an injector to the surface of graphite disk (0.7 cm^2). After having been dried in air at room temperature, the PANI/graphite or nanocomposite/graphite electrode was used as the working electrode.

3. Results and Discussion

3.1. A Possible Reaction Mechanism for PANI-TiO₂ Nanocomposite. Figure 1 shows a supposed model describing a polyaniline core decorated with TiO₂ (PANI-TiO₂) nanocomposite formation via microemulsion polymerization. There are plenty of surface hydroxyl groups on the surface of TiO₂ nanoparticles, which are produced from the adsorbed water molecules on the surface of TiO₂ nanoparticles. The hydrogen bonding interactions between the surface hydroxyl groups and the ether groups in OP-10 or the hydroxyl groups in *n*-butanol make it possible to weaken the strong particles agglomeration of TiO₂ and thus to form a dispersion of TiO₂ nanoparticles. When the above dispersion is added into the (IL+An)/water microemulsion, under the traction of lipophilic groups of OP-10 and *n*-butanol, the dispersed TiO₂ nanoparticles adsorb onto the surface of the microemulsion micelles to form core-shell-type nanomicelles. Afterwards, the polymerization is initiated by APS, during which some chemical bonds generate between TiO₂ and polyaniline chain which are stronger than the hydrogen bonds between the surface of TiO₂ and hydrophilic groups of OP-10 or *n*-butanol. After the polymerization ends, OP-10, *n*-butanol and IL can be washed down; finally, the polyaniline core decorated with TiO₂ nanocomposite are prepared.

3.2. FTIR and UV-Vis Spectra of PANI-TiO₂ Nanocomposites. The FTIR spectra of anatase TiO₂ nanoparticles, PANI, and PANI-TiO₂ nanocomposite are shown in Figure 2, respectively. From Figure 2(a), the broad peak from 400 to 700 cm^{-1} is the characteristic band of TiO₂. The characteristic bands of PANI (Figure 2(b)) are assigned as follows: the band at 3413 cm^{-1} is attributable to N-H stretching mode; C=N and C=C stretching modes for the quinoid and benzenoid rings occur at 1585 cm^{-1} and 1504 cm^{-1} ; the bands at about 1288 cm^{-1} and 1244 cm^{-1} have been attributed to C-

N stretching mode for the benzenoid ring, while the band at 1101 cm^{-1} is assigned to an in-plane bending vibration of C-H (mode of N=Q=N, Q=N⁺H=B and B-N⁺H-B), which is formed during protonation [31]. It is evident that the FTIR spectrum of the PANI-TiO₂ composite shown in Figure 2(c) contains contributions from both anatase TiO₂ and PANI. However, some bands of PANI have shifted due to interactions with anatase TiO₂ nanoparticles. For example, the bands at 1585 cm^{-1} , 1504 cm^{-1} , and 1288 cm^{-1} , corresponding to the stretching mode of C=N, C=C, and C-N, all shift to lower wavenumbers, and N-H stretching band at 3413 cm^{-1} shifts to higher wavenumber. Similarly, the band at 1101 cm^{-1} also shifts to 1120 cm^{-1} . These changes suggest that C=N, C=C and C-N bands become weaker in PANI-TiO₂ nanocomposite, while the N-H band becomes stronger. This is probably because of the action of hydrogen bonding between the surfaces of anatase TiO₂ nanoparticles and the N-H groups in PANI macromolecules. The results confirm that there is strong interaction between the PANI and nanocrystalline TiO₂, and the presence of anatase TiO₂ nanoparticles prompts the doping of PANI.

The UV-Vis absorption spectra of anatase TiO₂, PANI and the PANI-TiO₂ composite are shown in Figure 3. Clearly, the resulting PANI-TiO₂ composite can strongly absorb not only the near ultraviolet light but also the visible light, whereas the TiO₂ can absorb light with wavelengths below 250 nm only. As shown in Figure 3, we can clearly observe the characteristic bands of polyaniline at 366–373 nm and 535 nm, which are attributed to π - π^* transition of benzenoid ring, polaron- π^* , respectively [32]. Specifically, the absorption peaks of the PANI-TiO₂ nanocomposite at characteristic peaks of PANI become stronger; moreover, the characteristic absorption peak at 535 nm becomes un conspicuous because of being covered by a new absorption peak at 680 nm in visible region. This result further proves that it is not a simple mixing action between the PANI and nanocrystalline TiO₂, and the resulting PANI-TiO₂ nanocomposite could have a potential use as photocatalysis material.

3.3. Electrochemical Characteristics of PANI-TiO₂ Nanocomposite. The electrochemical characteristics of different samples were also investigated in relevant electrolyte. Cyclic voltammograms (CVs) of PANI and PANI-TiO₂ nanocomposite are shown in Figure 4. The reversible CV curves are observed obviously, which is related to the electrochemical probe of $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$. Although both shapes seem to be similar to each other, the oxidation and reduction peak current density ($3.13 \text{ mA} \cdot \text{cm}^{-2}$, $-3.45 \text{ mA} \cdot \text{cm}^{-2}$) of the PANI-TiO₂ nanocomposite are higher than those of the PANI ($2.30 \text{ mA} \cdot \text{cm}^{-2}$, $-2.70 \text{ mA} \cdot \text{cm}^{-2}$). The better electrochemical catalytic activity of the PANI-TiO₂ nanocomposite should be attributed to its special structure. When TiO₂ nanoparticles are mixed into the RTIL/water microemulsion under stirring, they assemble at the RTIL/water interface. Moreover, nano-TiO₂ exhibits electropositive properties in the acidic medium. They can attract a lot of anions, namely, nitrate ions, to assemble at the interface of the microemulsion. The anions are doped into the PANI chains

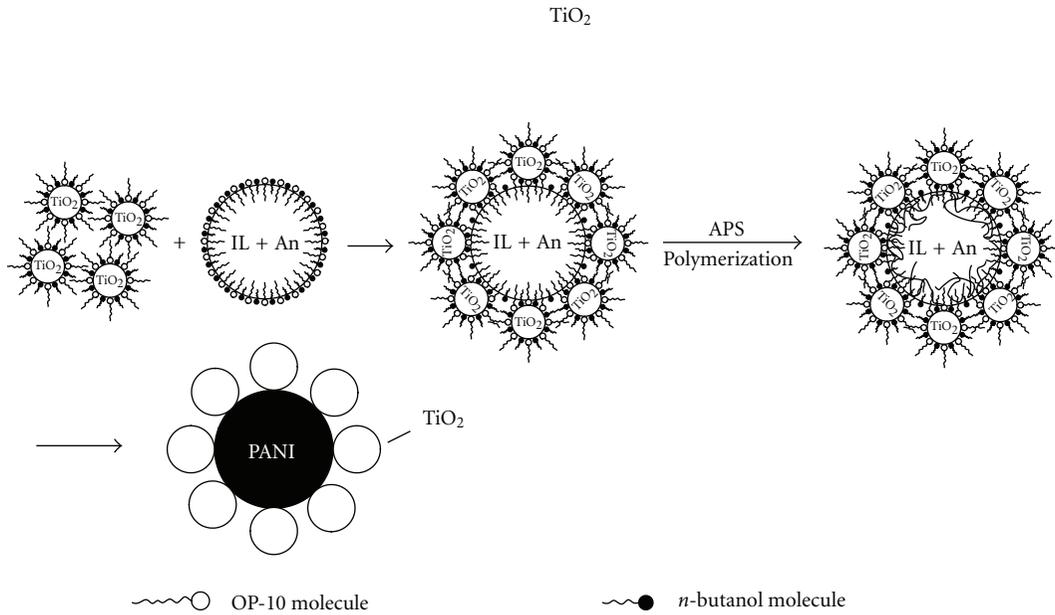


FIGURE 1: The forming mechanism of PANI-TiO₂ nanocomposite.

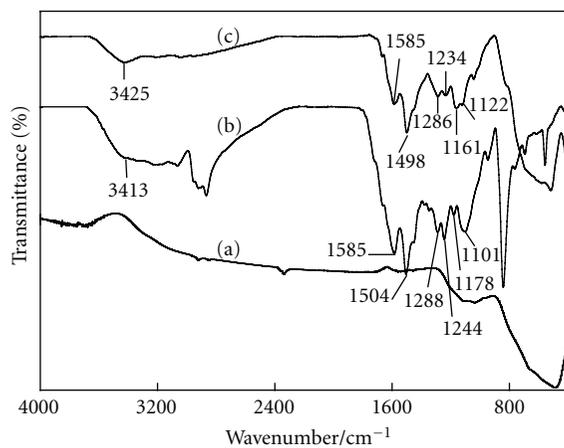


FIGURE 2: FTIR spectra of (a) TiO₂, (b) PANI, and (c) PANI-TiO₂.

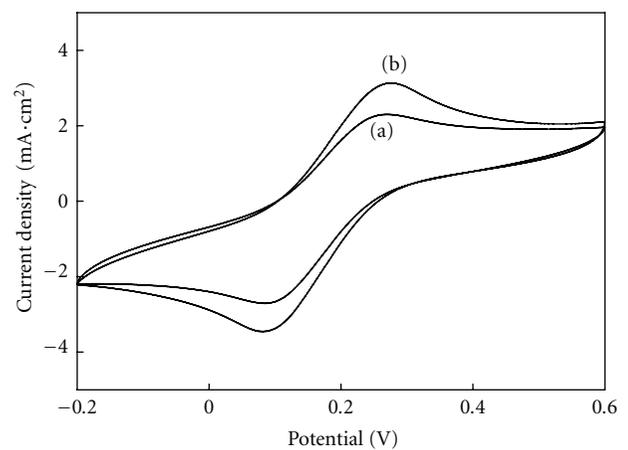


FIGURE 4: Cyclic voltammograms of different samples at a potential scan rate of 50 mV·s⁻¹. (a) PANI, (b) PANI-TiO₂.

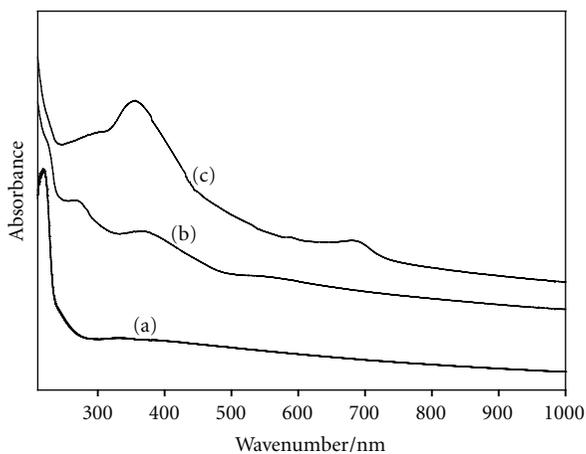


FIGURE 3: UV-Vis spectra of (a) TiO₂, (b) PANI, and (c) PANI-TiO₂.

as counterions when the polymerization is processed. Thus, the doping degree of the PANI-TiO₂ nanocomposite is improved, and a better electrochemical activity is exhibited.

3.4. Morphology of PANI-TiO₂ Nanocomposite. The morphology and particle sizes of PANI and PANI-TiO₂ nanocomposite were determined by SEM and shown in Figure 5. It can be found from Figure 5(a) that the PANIs exhibit spherical morphology with particle sizes of about 50 nm, while after combination with TiO₂ the morphology of PANI-TiO₂ nanoparticles approaches spherical with particle size of about 70 nm (Figure 5(b)). It implies that TiO₂ nanoparticles enwrap the polyaniline.

Figure 6 shows the typical TEM images of PANI and PANI-TiO₂ nanocomposite. It can be found that the

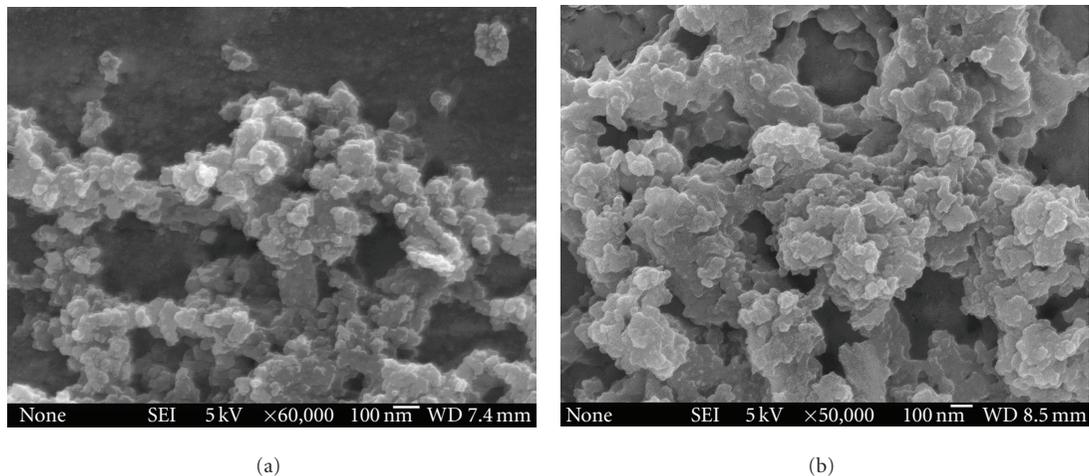


FIGURE 5: SEM images of (a) PANI and (b) PANI-TiO₂.

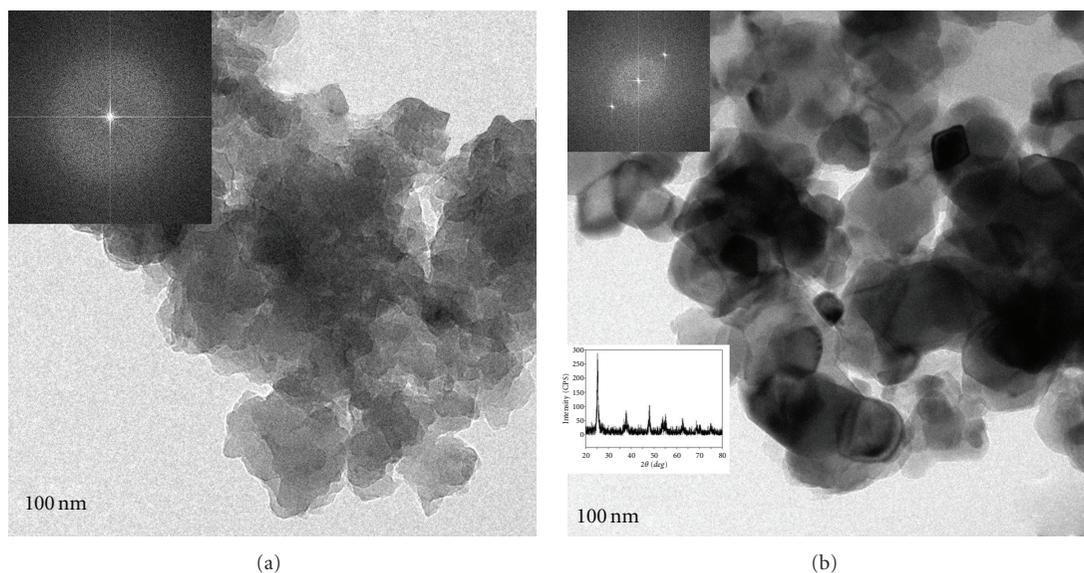


FIGURE 6: TEM images of (a) PANI and (b) PANI-TiO₂ (The insets are the selected area electron diffraction patterns and the X-ray diffraction pattern of TiO₂.)

polyaniline is amorphous in Figure 6(a), which has great difference from Figure 6(b). Figure 6(b) gives the TEM image of the polyaniline core decorated with anatase TiO₂ shell nanocomposite. One can find that the polyaniline with a mean diameter of about 50 nm is the core of the nanocomposite and the TiO₂ nanoparticles deposit onto the surface of the polyaniline, which is different from the reported structure of TiO₂-PANI nanoparticles that TiO₂ is wrapped by polyaniline. The diffraction pattern from the edge of particles of PANI-TiO₂ composite in Figure 6(b) suggests that the TiO₂ nanoparticles deposited on the surface of polyaniline are typical anatase phase, and this agrees well with the X-ray diffraction result of the separate TiO₂ nanoparticle sample.

4. Conclusion

Polyaniline core decorated with TiO₂ (PANI-TiO₂) nanocomposite has been successfully prepared in IL/water microemulsion in the presence of nanocrystalline TiO₂ particles. TiO₂ nanoparticles dispersed on the (IL + An)/water interface could deposit uniformly onto the surface of PANI. It is confirmed that the diameter of the resulted PANI-TiO₂ nanoparticles is about 70 nm, and the interactions between two components are strong. FTIR and UV-Vis spectra indicate that polyaniline and nano-TiO₂ particles are not simply blended or mixed up, while the strong interactions which exist at the interface of polyaniline macromolecules and nano-TiO₂ particles need further investigations in the future. CV curves show that the PANI-

TiO₂ nanocomposite has better electrochemical catalytic activity than PANI.

Therefore, it can be expected that PANI-TiO₂ nanocomposite should be useful in photocatalysis and electrical and electrochemical fields. Furthermore, this method is simple and environmentally friendly and has a great potential for the commercialization of the technology.

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