Preparation of a novel nanocomposite of polyaniline core decorated with anatase-TiO$_2$ nanoparticles in ionic liquid/water microemulsion

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Polyaniline core decorated with TiO$_2$ (PANI-TiO$_2$) nanocomposite particles were successfully synthesized in ionic liquid/water (IL/water) microemulsion in the presence of anatase TiO$_2$ nanoparticles. The TiO$_2$ nanoparticles had been dispersed beforehand in OP-10 and n-butanol to weaken the strong particles agglomeration of TiO$_2$. The PANI-TiO$_2$ nanocomposites were characterized by fourier transform infrared spectroscopy (FTIR), ultraviolet visible spectroscopy (UV-vis), scanning electron microscopy (SEM), transmission electron microscope (TEM), and their electrochemical behaviors were 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-TiO$_2$ nanocomposites had a novel structure that nanocrytalline TiO$_2$ deposited onto the surface of PANI, which was different from the reported structure of TiO$_2$-PANI nanocomposites. Both FTIR and UV-Vis spectra indicate that polyaniline and nano-TiO$_2$ particles are not simply blended or mixed up. A possible reaction mechanism for this nanocomposite preparation is suggested and analyzed.

Keywords: PANI-TiO$_2$ nanocomposites; microemulsion; ionic liquid

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1 Introduction

Organic–inorganic nanocomposites for synergetic behavior and a wide range of potential use have caused great interest and concern of therelated academic organizations and researchers over the past decade [1-4]. Especially, core-shell structures nanocomposites of organic conjugated polymers and inorganic nano-crystals have attracted great attention due to a wide 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. Deng etc. [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 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-aminothiolphenol 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 as the shell wrap of the Au nanoparticle. The CeO_2-polyaniline (CeO_2-PANI) core–shell nanocomposites via chemical oxidation of aniline by CeO_2 were reported by Chuang [9]. Jing etc. [10] successfully synthesized Ag-polyaniline core-shell nanocomposites via in-situ chemical oxidation polymerization of aniline based on mercaptocarboxylic acid capped Ag nanoparticles colloid. Yu etc. [11] prepared carbon nanotube-polyaniline core-shell nanowires by in situ inverse microemulsion. Nanocomposites "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 etc. [12]. Nanosized titania because of its unique physicochemical properties [13–16], frequently combined with polyaniline. Zhang [17] synthesized PANI-TiO_2 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-TiO_2 composites are typical core-shell structure, PANI-coated crystalline TiO_2. A polyaniline-nano TiO_2 composite [18] was prepared by polyaniline for the surface modification of nano TiO_2 particles, forming a core-shell structure.

There are many researches on the metal oxide core-polyaniline shell structures, but the structures of polyaniline core decorated with metal oxide are seldom investigated. As is known, the octahedrite type TiO_2 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 electrons-holes pair. The formed holes and electrons can oxidize and reduce the H_2O, OH or O_2 adsorbed on the surface of TiO_2 to living free radicals, which can deteriorate the organic materials or undesired pollutants that adsorbed on the surface of TiO_2 catalyst resulting in generating non-poisonous CO_2, H_2O and some inorganic products. Whereas, for TiO_2 core-PANI shell composites, because of package action of polyaniline, photon absorption of TiO_2 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 TiO_2 are bated after being enwrapped by polyaniline. Hereby, polyaniline core decorated with TiO_2 (PANI-TiO_2) nanocomposite particles make it possible to develop the properties of TiO_2.

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, 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 PANI 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 TiO_2 (PANI-TiO_2) nanocomposite was prepared in a microemulsion comprised of de-ionized water as the continuous aqueous phase and an oil solution including aniline and hydrophobic IL 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF_6) as the dispersed phase in the presence of anatase TiO_2 nanoparticles. The TiO_2 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), transmission electron microscope (TEM). Moreover, the possible reaction mechanism for the preparation of PANT-TiO_2 nanocomposite is investigated here.

2 Experimental
2.1 Materials

IL 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF_6) was prepared as described in the literature [29]. Nanocrystalline TiO_2 (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 nonyphenol ethoxylates (OP-10) was obtained from 3W Industry Co., Ltd. All aqueous solutions were prepared with de-ionized water.

2.2 Synthesis of polyaniline core decorated with TiO_2 (PANI-TiO_2) nanocomposite

The polyaniline core decorated with TiO_2 (PANI-TiO_2) composites were synthesized in microemulsion system via in-situ chemical oxidative polymerization in the presence of TiO_2 nanoparticles, and the procedure was as follows: Firstly, hydrophobic IL [bmim]PF_6 (2 mL)/aniline (1 mL) mixture was added into the OP-10 (13 mL)/n-butanol (3 mL)/HNO_3 (87 mL (0.115 mol·L^{-1})) solution, after the mixture was stirred for 1 h under magnetic stirring, a dispersion of TiO_2 nanoparticles (TiO_2: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 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 TiO_2 (PANI-TiO_2) 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 TiO_2 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 mM·L^{-1} $K_3Fe(CN)_6$, 1 mM·L^{-1} $K_4Fe(CN)_6$ and 0.2 mol·L^{-1} NaCl. The scan speed was 0.1 V·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 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-TiO_2 nanocomposite

Fig. 1 shows a supposed model describing a polyaniline core decorated with TiO_2 (PANI-TiO_2) nanocomposite formation via microemulsion polymerization. There are plenty of surface hydroxyl groups on the surface of TiO_2 nanoparticles, which are produced from the adsorbed water molecules on the surface of

TiO$_2$ 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 TiO$_2$, and thus to form a dispersion of TiO$_2$ 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 TiO$_2$ nanoparticles absorb onto the surface of the microemilsion micelles to form core-shell type nano-micelles. Afterwards, the polymerization is initiated by APS, during that some chemical bonds generate between TiO$_2$ and polyaniline chain which are stronger than the hydrogen bonds between the surface of TiO$_2$ 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 TiO$_2$ nanocomposite are prepared.
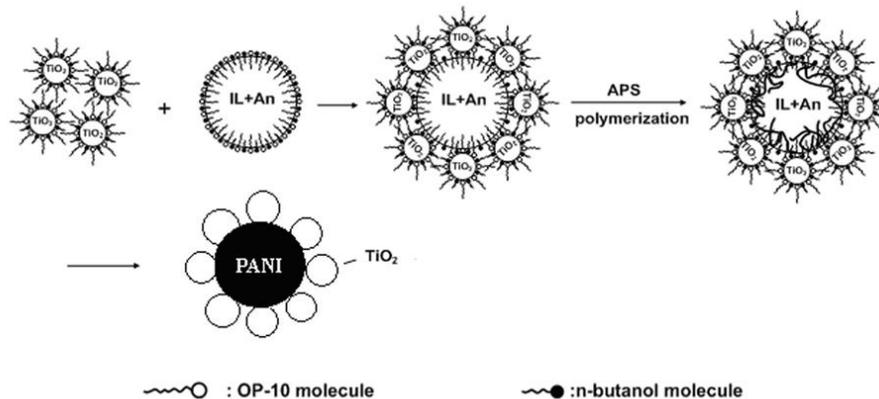

Fig. 1 The forming mechanism of PANI-TiO$_2$ nanocomposite

3.2 FTIR and UV-vis spectra of PANI-TiO$_2$ nanocomposites

The FTIR spectra of anatase-TiO$_2$ nanoparticles, PANI, and PANI-TiO$_2$ nanocomposite are shown in Fig. 2, respectively. From Fig. 2(a), the broad peak from 400-700 cm^{-1} is the characteristic band of TiO$_2$. The characteristic bands of PANI (Fig. 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 mode 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 a 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-TiO$_2$ composite shown in Fig. 2(c) contains contributions from both anatase TiO$_2$ and PANI. However, some bands of PANI have shifted due to interactions with anatase-TiO$_2$ 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-TiO$_2$ nanocomposite, while the N–H band become stronger. This is probably because of the action of hydrogen bonding between the surfaces of anatase TiO$_2$ nanoparticles and the N–H groups in PANI macromolecules. The results confirm that there is strong interaction between the PANI and nanocrystalline TiO$_2$, as well as the presence of anatase TiO$_2$ nanoparticles prompts the doping of PANI.
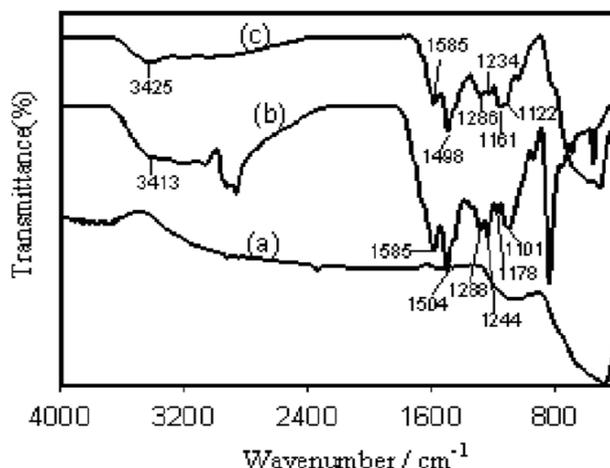
Fig. 2 FTIR spectra of (a) TiO$_2$, (b) PANI and (c) PANI-TiO$_2$

The UV-vis absorption spectra of anatase TiO$_2$, PANI and the PANI-TiO$_2$ composite are shown in Fig. 3. Clearly, the resulted PANI-TiO$_2$ composite can strongly absorb not only the near ultraviolet light but also the visible light, whereas the TiO$_2$ can absorb light with wavelengths below 250 nm only. As shown in Fig. 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]. Specially, the absorption peaks of the PANI-TiO$_2$ nanocomposite at characteristic peaks of PANI become stronger, moreover the characteristic absorption peak at 535 nm become unconspicuous because of being covered by a new absorption peak at 680nm in visible region. This result further proves that it is not a simple mixing action between the PANI and nanocrystalline TiO$_2$, and the resulted PANI-TiO$_2$ nanocomposite could have a potential use as photocatalysis material.
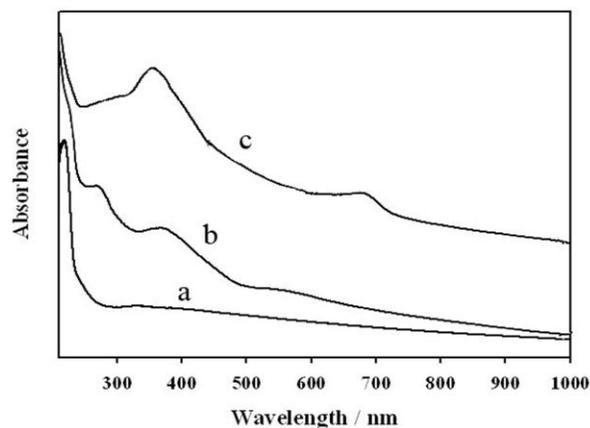

Fig. 3 UV-vis spectra of (a) TiO$_2$, (b) PANI and (c) PANI-TiO$_2$

3.3 electrochemical characteristics of PANI-TiO$_2$ nanocomposite

The electrochemical characteristics of different samples were also investigated in relevant electrolyte. Cyclic voltammograms (CV) of PANI and PANI-TiO$_2$ nanocomposite are shown in Fig. 4 The reversible CV curves are observed obviously, which is related to the electrochemical probe of $Fe(CN)_6^{4-}$/$Fe(CN)_6^{3-}$. Although both shapes seem to be similar to each other, the oxidation and reduction peak current density (3.13 mA·cm^{-2}, -3.45 mA·cm^{-2}) of the PANI-TiO$_2$ nanocomposite are higher than those of the PANI (2.30 mA·cm^{-2}, -2.70 mA·cm^{-2}).The better electrochemical catalytic activity of the PANI-TiO$_2$ nanocomposite should be attributed to its special structure. When TiO$_2$ nanoparticles are mixed into the RTIL/water microemulsion under stirring, they assemble at the RTIL/water interface. Morever, nano TiO$_2$ exhibit electropositive in the acidic medium.

They can attract a lot of anions, namely nitrate ions, to assemble at the interface of the micromulsion. The anions are doped into the PANI chains as counterions when the polymerization is processed. Thus, the doping degree of the PANI-TiO_2 nanocomposite is improved, and a better electrochemical activity is exhibited.
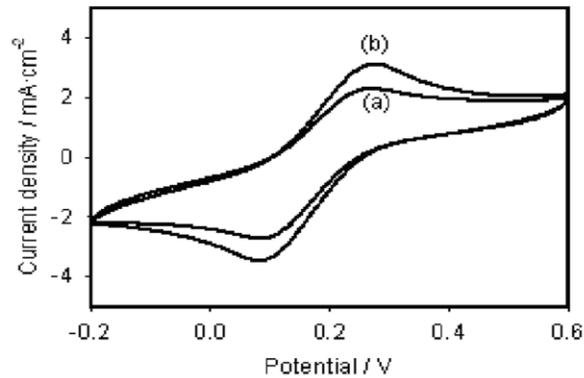

Fig. 4 Cyclic voltammograms of different samples at a potential scan rate of 50 mV·s^{-1}.

(a) PANI, (b) PANI-TiO_2

3.4 Morphology of PANI-TiO_2 nanocomposite

The morphology and particle sizes of PANI and PANI-TiO_2 nanocomposite were determined by SEM and shown in Fig. 5. It can be found from Fig. 5(a) that the PANI exhibit spherical morphology with particle sizes about 50 nm, while after combined with TiO_2 the morphology of PANI-TiO_2 nanoparticles approaches spherical about 70 nm (Fig. 5(b)). It implies that TiO_2 nanoparticles enwrap the polyaniline.
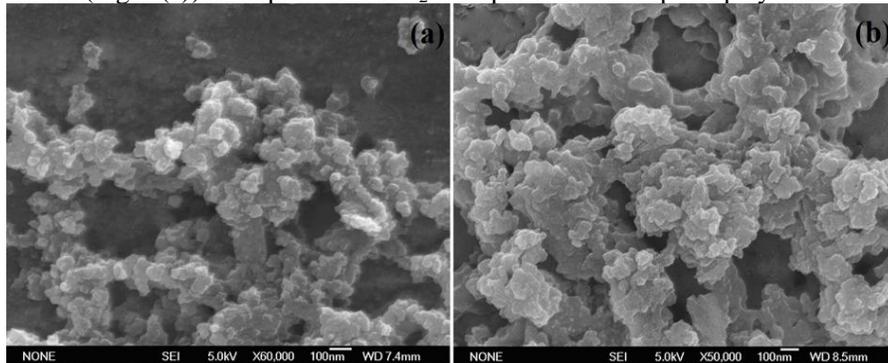

Fig. 5 SEM images of (a) PANI and (b) PANI-TiO_2

Fig. 6 shows the typical TEM images of PANI and PANI-TiO_2 nanocomposite. It can be found that the polyaniline is amorphous in Fig. 6(a), which has great difference from Fig. 6(b). Fig. 6(b) gives the TEM image of the polyaniline core decorated with anatase TiO_2 shell nanocomposite. One can find that the polyaniline with a mean diameter of about 50 nm is the core of the nanocomposite and the TiO_2 nanoparticles deposit onto the surface of the polyaniline, which is different from the reported structure of TiO_2-PANI nanoparticles that polyaniline wrap of TiO_2. The diffraction pattern from the edge of particles of PANI-TiO_2 composite in Fig. 6(b) suggests that the TiO_2 nanoparticles deposited on the surface of polyaniline are typical anatase phase, and this agrees well with the X-ray diffraction result of the separate TiO_2 nanoparticle sample.
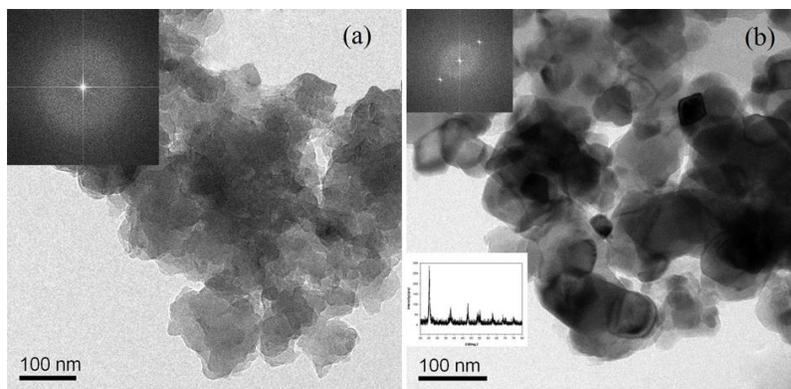
Fig. 6 TEM images of (a) PANI and (b) PANI-TiO$_2$ (The insets are the selected area electron diffraction patterns and the X-ray diffraction pattern of TiO$_2$)

4 Conclusion

Polyaniline core decorated with TiO$_2$ (PANI-TiO$_2$) nanocomposite have been successfully prepared in IL/water microemulsion in the presence of nanocrytalline TiO$_2$ particles. TiO$_2$ 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-TiO$_2$ nanoparticles are about 70 nm, and the interactions between two components are strong. FTIR and UV-Vis spectra indicate that polyaniline and nano-TiO$_2$ particles are not simply blended or mixed up, while the strong interactions which exist at the interface of polyaniline macromolecules and nano-TiO$_2$ particles need further investigations in the future. CV curves show that the PANI-TiO$_2$ nanocomposite has better electrochemical catalytic activity than PANI.

Therefore, it can be expected that PANI-TiO$_2$ nanocomposite should be useful in photocatalysis, electrical and electrochemical fields. Further more, this method is simple and environmentally friendly, and has a great potential for the commercialization of the technology.

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