Preparation of PANI–TiO₂ nanocomposites and their solid-phase photocatalytic degradation

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Abstract

A series of polyaniline–anatase TiO₂ (PANI–TiO₂) nanocomposite powders with different PANI:TiO₂ ratios were prepared by ‘in-situ’ deposition oxidative polymerization of aniline hydrochloride using ammonium persulfate (APS) as oxidant in the presence of ultrafine grade powder of anatase TiO₂ cooled in an ice bath. And the solid-phase photocatalytic degradation of PANI–TiO₂ nanocomposites was investigated under the ambient air in order to assess the feasibility of developing photodegradable polymers. The photodegradation of the composite powders was compared with that of pure PANI powders by performing weight loss monitoring, elemental analysis, FT-IR and UV–vis spectroscopy and X-ray photoelectron spectroscopy (XPS). The PANI–TiO₂ nanocomposite powders showed highly enhanced photodegradation and the photodegradation increased with decreasing ratios of PANI:TiO₂. A weight loss of about 6.8% was found for the PANI–TiO₂ (1:3) nanocomposite; however, the weight loss of the PANI–HCl powder was only 0.3% after being irradiated for 60 h under air. The photocatalytic degradation of the nanocomposite powders accompanied the peak intensity decrease in the FT-IR spectra at 1235 cm⁻¹, attributed to C–N stretching mode for benzenoid unit, and the depigmentation of the powders due to the visible light scattering from growing cavities. The elemental analysis and XPS analysis of the composite showed that the bulk and surface concentrations of N decreased with irradiation. A possible mechanism for the photocatalytical oxidative degradation was also mentioned.

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Keywords: Polyaniline–anatase TiO₂ nanocomposite; Preparation and characterization; Solid-phase photocatalytic degradation; UV irradiation; Mechanism

1. Introduction

It is well known that nanocrystalline TiO₂ will produce electron–hole pairs under illumination of UV light. TiO₂ photocatalyst has been successfully used to purify water and air, to degrade the organic pollutants and to kill bacteria [1–3]. Previous studies on the TiO₂ photocatalytic degradation of polymers mainly dealt with liquid-phase reactions, such as photocatalytic degradation of polyvinylchloride (PVC) particles in TiO₂ suspension aqueous solution [4]. Recently, there are a few studies on the solid-phase photocatalytic degradation of polymer–TiO₂ composite. The polymer matrices are mainly polyolefins, such as polystyrene (PS) [5], PVC [6] and so on.

Heterogeneous-conducting polymer nanocomposites, especially for organic/inorganic nanocomposite, have drawn the attention of scientists over the last few years [7]. Most recently, as one of the most intensively studied conducting polymers in the last 20 years, polyaniline (PANI) has attracted considerable attention for the preparation of its composites with inorganic particles to improve their processability, such as conducting polyaniline–BaTiO₃ composite [8], polyaniline–molybdenum trisulfide composite [9], conducting polyaniline–inorganic salt composite [10] and polyaniline–V₂O₅ composite [11]. Besides conducting materials, polyaniline–inorganic particles were also investigated for their applications in electrorheological ER fluids [12] and high-density information storage material [13].

TiO₂ has also been studied to prepare its composite with conducting polymers [14,15]. Although there are so many candidates for polymeric matrix, one particular interest is the
integration of inorganic nanoclusters with conducting polymers because the resulting nanocomposites may possess unique electrical and optical properties. Because of the combination of electrical conductivity of polyaniline and UV-sensitivity of anatase TiO₂, such nanomaterials are expected to find applications in electrochromic devices, nonlinear optical system and photoelectrochemical devices.

In this study, a series of polyaniline–anatase TiO₂ (PANI–TiO₂) nanocomposite powders with different PANI:TiO₂ ratios from 3 to 0 were prepared and their photocatalytic degradation under the ambient air atmosphere was investigated. It demonstrates that the PANI–TiO₂ composite has a potential viability to be used as a photodegradable product. The photocatalytic degradation in the solid polymer matrix proceeded much faster than the direct photolytic degradation under air. A possible mechanism for the photocatalytic oxidative degradation was also mentioned.

2. Experimental

2.1. Materials and reagents

Aniline (ANI) (AR, Beijing Chemical Reagent Co., China) was distilled under reduced pressure and stored below 4 °C under nitrogen atmosphere prior to use. Nanocrystalline TiO₂ (anatase, 27 nm, Zhourshan Mingri Nanomaterials Ltd. Co., Zhejiang, China), 38% hydrochloric acid (AR), ammonium persulfate (NH₄)₂S₂O₈ (APS, AR), ether (AR) and ethanol (AR) were used as received.

2.2. Preparation of PANI–TiO₂ nanocomposites

The PANI–TiO₂ nanocomposites were prepared according to the following steps: 0–3.0 g of nanocrystalline TiO₂ particles, 1 mL of aniline and 90 mL of 1.0 M HCl aqueous solution were introduced into the reaction vessel. The solution was mechanically stirred for 1 h to obtain a uniform suspension containing TiO₂ particles, in an ice-water bath. The mixture was deoxygenated by bubbling oxygen-free nitrogen into the reaction vessel. After that, 100 mL of a precooled 1.0 M HCl aqueous solution containing 2.5 g of APS was added dropwise to the above cooled mixture over a period of approximately 60 min, and the resulting mixture was allowed to react in the ice bath for 4 h. During the polymerization, N₂ purging rate was kept constant. The precipitated dark-green colored PANI–TiO₂ nanocomposite powder was filtered and washed with large amount of deionized water, then with 50 mL of ethanol and 30 mL of ether, after that the powder was extracted with ethanol in order to remove the oligomers till the extracted solution became colorless. Finally, the product was dried at 80 °C till the constant mass was reached. The samples were signed as PANI–TiO₂ (X), where X is the ratio of ANI to TiO₂ in nominal.

2.3. The photocatalytic performances

The photocatalytic degradation reactions were carried out under atmospheric condition in a box reactor using a 300 W high-pressure mercury lamp (qe6, λₘₐₓ = 365 nm, Osram Corporation, Germany) as the irradiation source. The relative humidity was 40% and the temperature was 30 °C in the reaction box. All samples were a 1.00 g round mat placed in a culture dish with about 78.5 cm² area. The irradiation distance between the lamp and the sample was 15 cm. Each sample was weighed three times before and after irradiation to measure the weight loss of PANI by the photocatalytic degradation as the function of irradiation time.

2.4. Analysis and characterizations

The elemental analysis was carried out using Elementar Vario EL instrument. Fourier transform infrared (FT-IR) spectra of the polymers in KBr pellets were recorded on a Nicolet Avatar 360 FT-IR spectrometer (Nicolet Corp., USA). The spectra were collected from 4000 to 400 cm⁻¹, with a 4 cm⁻¹ resolution over 20 scans. Thermogravimetric analysis (TGA) was carried out for the measurement of thermal degradation of the polyaniline–anatase TiO₂ (PANI–TiO₂) nanocomposite powders, performed with a Perkin–Elmer TGA-7 system at a scan rate of 10 °C min⁻¹ to 800 °C in N₂. X-ray diffraction (XRD) was used for the identification of the crystalline phases. The XRD patterns were recorded in the range of 2θ = 10–80° by step scanning with a Shimadzu XRD-6000 X-ray diffractometer. Nickel-filter Cu Kz radiation (λ = 0.15418 nm) was used with a generator voltage of 40 kV and a current of 30 mA. The UV–vis absorption spectra were recorded on a UV–vis spectrometer (Lambda 35, Perkin–Elmer Corporation, USA) with an integrating sphere and 2 nm spectral resolutions at room temperature in the range of 190–1100 nm, and BaSO₄ was used as a reference. X-ray photoelectron spectroscopy (XPS) was performed on an XSAM 800 X-photoelectron spectrometer with a Mg Kz X-ray source. In the data analysis, the binding energy of the core level C1s was set at 284.8 to compensate for surface-charging effects. The microstructures of the nanocomposites were analyzed with a JEOL JXA-8800R electron-probe microanalyser (EPMA; Japan Electronic Corporation, Japan) at an accelerating voltage of 15 kV and with a beam diameter of 2 mm. Data were reduced with the Bence and Albee correction method.

3. Results and discussion

3.1. Preparation and characterizations of PANI–TiO₂

For the polyaniline–anatase TiO₂ (PANI–TiO₂ (1:3)) nanocomposite powders, the elemental analysis (Table 1) showed that the organic/inorganic (PANI–TiO₂) weight ratio was near to 1:2.5. The loss of TiO₂ may be caused by the dispersed TiO₂ in the solution. This indicated that the addition of a mass of TiO₂ had little influence on the conversion of aniline.

The FT-IR spectra of PANI doped with HCl and PANI–TiO₂ composites are shown in Fig. 1. All characteristic bands of PANI in the PANI–HCl (Fig. 1a) before UV irradiation,
PANI–HCl (Fig. 1b) after UV irradiation and PANI–TiO2 (1:3) (Fig. 1c) were observed. The main characteristic peaks of doped PANI are assigned as follows: the band at 3457 and 3230 cm\(^{-1}\) can be attributed to the free (non-hydrogen bonded) N–H stretching vibration and hydrogen-bonded N–H bond between amine and imine sites [16], C==N and C==C stretching modes for the quinonoid and benzenoid units occur at 1560 and 1483 cm\(^{-1}\), the bands at 1297 and 1235 cm\(^{-1}\) have been attributed to C–N stretching mode for benzenoid unit, while the band at 1112 cm\(^{-1}\) to quinonoid unit doped PANI, and the peak at 793 cm\(^{-1}\) is associated with C–C and C–H for benzenoid unit. The characteristic peaks of TiO\(_2\) at 1103 and 452 cm\(^{-1}\) were also found in the spectrum of PANI–TiO\(_2\) nanocomposite. The characteristic peaks from the PANI around 1297, 1483 and 1560 cm\(^{-1}\), corresponding to the stretching modes of C–N and C==N bonds, reveal the presence of leucoemeraldine and pernigraniline components. After titania was introduced, all peaks shifted to higher wavenumbers: 1299, 1491 and 1573 cm\(^{-1}\). Meanwhile, the characteristic peak of N–H stretching mode at 3457 cm\(^{-1}\) of PANI shifted to a lower wavenumber (3432 cm\(^{-1}\)) in the PANI–TiO\(_2\) composite, and the hydrogen bond absorption at 3230 cm\(^{-1}\) is strengthened after TiO\(_2\) was introduced. These findings reveal that the hydrogen bonding in the PANI complex became stronger after complexing with TiO\(_2\). The results also suggest that there is strong interaction between the polyaniline and nanocrystalline TiO\(_2\) [17,18].

The UV–vis absorption spectra of the PANI–TiO\(_2\) composites with various aniline:TiO\(_2\) weight ratios prepared with the proposed method are shown in Fig. 2. Clearly, the prepared PANI–TiO\(_2\) composites not only can strongly absorb the UV light but can also absorb the visible and near-IR light. The hybrid samples present characteristic bands of polyaniline–emeraldine salt at ~320 nm, ~415 nm and ~650–690 nm, which are attributed to \(\pi–\pi^*\) transition of benzenoid ring, polaron–polaron and \(\pi–\pi^*\) transition of the quinonoid rings, respectively [19], whereas electronic spectra of PANI–TiO\(_2\) composites exhibited bands at 415 and 650 nm presumably due to the formation of new composite [20]. And the peak at about 650 nm is shifted to higher wavelengths of 690 nm with the increase in TiO\(_2\):aniline weight ratio. This result indicates that there is strong interaction between polyaniline and nanocrystalline TiO\(_2\) [20].

X-ray diffractions of the TiO\(_2\) PANI and PANI–TiO\(_2\) (1:3) composites are presented in Fig. 3. It can be seen from Fig. 3a that the titania powder was anatase crystal, and the positions of all peaks are in good agreement with the results reported by Tang et al. [21]. In the pattern of PANI (Fig. 3b), the Bragg diffraction peaks of 2\(\theta\) ~ 9.4, 14.0, 15.7, 16.9, 26.5 and 27.4° can be found. It indicated that the pure PANI was in partial orthorhombic structure [22]. The other two broad peaks centered at 2\(\theta\) ~ 20.8 and 25.4° are ascribed to the periodicity parallel and perpendicular to the polymer chain and indicated that the pure PANI was in semi-crystalline phases [23]. In the pattern of PANI–TiO\(_2\) (1:3) composite, the peaks of 2\(\theta\) ~ 9.4, 14.0, 15.7, 16.9 and 27.4° of PANI disappeared and the peak at 20.8° of PANI became weaker. The result suggests that the addition of nanocrystalline TiO\(_2\) hampers the crystallization of the polyaniline molecular chain. This is because when the deposited polyaniline is absorbed onto the surface of the nano-TiO\(_2\) particle, the molecular chain of absorbed polyaniline is tethered, and the degree of crystallinity decreases [20].

The thermal behavior of the PANI–TiO\(_2\) (1:3) composite sample was investigated by thermogravimetric analysis (TGA), and the result is shown in Fig. 4. From Fig. 4a, it is evident that the release of ethanol and water (from both the titania

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**Table 1**

<table>
<thead>
<tr>
<th>Samples</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before UV irradiation</td>
<td>23.04</td>
<td>2.380</td>
<td>4.356</td>
</tr>
<tr>
<td>After UV irradiation for 60 h</td>
<td>18.40</td>
<td>1.689</td>
<td>2.691</td>
</tr>
</tbody>
</table>
and polymer surface) occurs from 50 to 100 °C, and thereafter a plateau appears up to about 210 °C. The mass loss occurred between 210 and 245 °C with an exothermic peak probably due to the expulsion of the dopant [24]. In the temperature range of 330 e 650 °C, a strong weight loss occurred, which is attributed to the degradation of the skeletal polyaniline chain structure [24]. The amount of polyaniline (28.7%) in the PANI e TiO2 (1:3) composite sample estimated by CHN elemental analysis (Table 1) is close to that stipulated by the weight loss in the 330 e 650 °C range (26.0%) on TGA curves.

3.2. Solid-phase photocatalytic degradation and possible mechanism

For the PANI—TiO2 (1:3) nanocomposite, that had the highest inorganic/organic ratio, it was found in the FT-IR spectra (Fig. 5) that the peak intensity at 1235 cm \(^{-1}\) attributed to C—N stretching mode for benzenoid unit decreased with the increase in irradiation time and disappeared after a UV irradiation time of 60 h. The FT-IR spectrum in Fig. 5b also showed the existence of C=O bond by a peak at 1680 cm \(^{-1}\) [25]. The peak intensity at 1097 and 448 cm \(^{-1}\) attributed to the characteristic peaks of TiO2 was strengthened by increasing the UV irradiation time. This observation indicated that the characteristics of TiO2 increased and the characteristics of PANI decreased as the irradiation time increased due to the degradation of PANI in the composite sample. However, for the FT-IR spectra of the PANI—HCl (Fig. 1a and b), the peak intensity at 1235 cm \(^{-1}\) changed little with the UV irradiation and the FT-IR spectra were almost same before and after UV irradiation. The experiment result indicated that the C—N bonds of the benzenoid unit had been photocatalytically oxidatively degraded in the presence of the photocatalyst of nano-TiO2 in the PANI—TiO2 nanocomposites, but the changes in the pure PANI sample were little.

The evidence for degradation and erosion of PANI in the PANI—TiO2 nanocomposites was obtained by electron-probe microanalyser (EPMA). The surface morphologies of the composite before and after irradiation are shown in Fig. 6. It can be seen that after irradiation for certain time, the cavities formed on the surface of the composite particles, and the surface became more coarse. With the prolonging of the UV irradiation, the nanocomposites’ structure was destroyed, and the chalking phenomenon took place [5]. This indicates that TiO2 nanoparticles will greatly enhance the photocatalytic degradation of the PANI material. It can also be found that the PANI—TiO2 (1:3) sample after UV irradiation for 60 h had poorer thermo-stability than that before UV irradiation (Fig. 4b). The organic compounds had been decomposed completely at the temperature range of 330—640 °C. The weight loss of sample after UV irradiation was lower than that before UV irradiation. Accordingly, the C, N and H elemental contents in the composites decreased after UV irradiation (Table 1).
All these results indicated that parts of PANI in the composites had been photodegraded.

The UV–vis absorbances of the PANI–TiO$_2$ (1:3) composites after different UV irradiation times were measured and the results are shown in Fig. 7. Clearly, the adsorption of UV light, visible and near-IR light of the PANI–TiO$_2$ (1:3) nanocomposite increased with the prolonging of UV irradiation time. It resulted from the cavities formed not only on the surface, but also inside the nanocomposites due to photodegradation of PANI. Since the cavities formed as a result of the photocatalytic degradation scattered visible light, depigmentation of the irradiated composites was observed.

The XRD analysis also showed that the Bragg diffraction peak at 20.8° of PANI which is ascribed to the periodicity parallel and perpendicular to the polymer chain became weaker after irradiation under UV for 60 h (Fig. 3c and d). This indicates that chain scission in the backbone of polymer has taken place by 60 h of photocatalytic degradation, and it resulted in the vanishing of the crystalline phase in the PANI polymer.

The photoinduced weight losses of the samples with different PANI:TiO$_2$ ratios for different UV irradiation times up to 60 h are shown in Fig. 8. The weight losses increased with the decrease in PANI:TiO$_2$ ratio and the weight loss rates of the PANI–TiO$_2$ composites were much higher than that of
the PANI–HCl particles. The weight of the nanocomposite PANI–TiO2 (1:3) steadily decreases with irradiation under air and led to the total of 6.8% reduction in 60 h; however, the PANI–HCl particles showed only 0.3% weight loss under the identical experimental condition. It indicated that the more nano-TiO2 added, the higher absorption in UV region (Fig. 2), and the faster photocatalytical oxidative degradation rate were achieved. The above weight loss data implied that some degradation products volatilized into the air.

The elemental analysis showed that the C, N and H elemental contents of the samples decreased after the UV irradiation and N elemental content was the fastest to decrease (Table 1). The surface compositional data of the PANI–TiO2 (1:3) from XPS also showed that the surface N elemental content had been decreased to 0 and that of C and O elements increased after UV irradiation for 60 h (Table 2). And the surface Ti elemental content had been also decreased.

So a mechanism for the solid-phase photocatalytical oxidative degradation is emerged as following: TiO2 particles that absorbed light with energy higher than 3.2 eV under UV irradiation generate electron–hole pairs in the conduction bond (CB) and valence bond (VB), respectively. Subsequent reactions with O2 lead to the formation of active oxygen species such as hydroxyl radical and hydroperoxyl radical. The active oxygen species attacked neighboring polymer chains, the C–N bonds of the benzenoid unit were broken up and the PANI chains had been cut up into pieces with end-group of hydroxybenzene hydroxyl groups originating from the C–N bonds of the benzenoid unit, and this caused the decrease in the surface N elemental content to 0, vanishing of the crystalline phase in the PANI polymer and appearance of 1680 cm−1 peak in FT-IR spectra. The chain pieces cleaved were absorbed onto the surfaces of nano-TiO2 and then oxidised to p-benzoquinone [25,26], to quinone and to CO2 and H2O finally [25,27]. The adsorption of cleaved chain pieces onto the surface of nanotitania caused a significant increase in the concentration of carbon atoms and decrease in Ti element.

4. Conclusions

The polyaniline–TiO2 (PANI–TiO2) composites with different inorganic/organic ratios prepared by an in situ polymerization method could be degraded by photocatalytic oxidation under UV irradiation. The present study reveals that photocatalytic method can be effective for solid-phase PANI degradation and the PANI–TiO2 composite has a potential viability to be used as a photodegradable product. The photocatalytic degradation in the solid polymer matrix proceeded much faster than the direct photolytic degradation under air. A possible mechanism for the photocatalytical oxidative degradation emerged from the analytical results of the elemental analysis, FT-IR and XPS.

References


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