Visible-light photocatalytic activity of semiconductor composites supported by electrospun fiber

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A. Polymer–matrix composites (PMCs)
B. Synergism
C. Scanning/transmission electron microscopy (STEM)
D. Thermo-gravimetric analysis (TGA)
E. Electro-spinning

1. Introduction

Growing concerns over the threat of chemical warfare agents and exposure to toxic industrial chemicals have drawn much attention to the challenge of developing new harmless treatment methods for the toxic organic materials [1]. Photocatalytic degradation of harmful organic pollutants in the air and water using semiconductor particles, such as titanium dioxide (TiO$_2$), is one of the most widely studied methods [2]. The semiconductor particles are able to convert abundant solar energy into effective chemical energy, and mineralized the organic pollutants completely [3]. However, the photocatalytic degradation of toxic organic pollutants using semiconductor is still challenging, in terms of the low enrichment ability for organic compounds, are suitable as photocatalyst carrier [9]. The visible-light photocatalytic activity of TiO$_2$ is able to improved greatly by doping it with other elements, and the synthesis of nanocrystalline TiO$_2$ capped ZnS under hydrothermal conditions is a convent way [10].

In this paper we demonstrate a novel method to prepare visible-light photocatalytic activity TiO$_2$–ZnS particles loaded by fluoropolymer electrospun fiber composites as photocatalyst under visible-light radiation. The results show the as-prepared composites have good visible-light photocatalytic activity and stability for the potential applicability in environmental remediation.
2. Experimental

Trifluoroethyl acrylate (TFA) was obtained from Xuejia Fluorine-silicon Chemical Co., Ltd, Harbin China. Anatase Degussa P25 was purchased from Shanghai Haiyi Scientific & Trading Co., Ltd. Poly(vinylidene fluoride) (PVDF), titanium oxo-sulphate (TiOSO4), methacrylic acid (MAA), zinc sulfate (ZnSO4), thiocetamide (TAA), methylene blue, urea and other chemicals were purchased from Shanghai Chemicals Ltd., and used as received.

Perkin Elmer Spectrum 100 FTIR spectrometer was used to widely scan the synthetic products. JSM-6700F scanning electron microscopy (SEM) was utilized to study the surface morphologies of the products. The specific surface area (BET) analyzed by ASAP 2020 M + C. ESCALAB 250 X-ray photoelectron spectroscopy (XPS) was used to study the structure of composites. Transmission electron microscope (TEM) image and the selected area electron diffraction (SAED) pattern were taken on JEOl 2010. The crystal structure was detected through the X-ray diffraction (XRD), Rigaku D/MAX-rB. The thermo-gravimetric analysis (TGA), Netzsch TG-209-F3, was applied to estimate the weight loss of composites. Ultraviolet–visible (UV/VIS) absorption spectra were obtained on a Shimadzu Solidspec-3700 DUV spectrophotometer at room temperature.

The synthesis of MAA–TFA random copolymers was performed in an automated reactor system. 30 g MAA, 70 g TFA, and 0.5 g 2, 2-azobisobutyronitrile (AIBN) were added into a three-necked flask capacity 250 mL equipped with a condenser, a stirrer and a N2 inlet. After polymerizing at 80 °C for 1 h, the reaction mixture was transferred to a stainless steel plate and placed in an oven at 40 °C for 12 h. Then the reaction mixture was maintained at 100 °C for 3 h, so that the remaining monomers can polymerize. Poly(MAA-co-TFA)/PVDF electrospun fiber mats were prepared using a typical electrospinning process [11]. 10.3 g PVDF and 1.7 g poly(MAA-co-TFA) were first dissolved in 88 g N,N-dimethylformamide (DMF). The solution was electrospun at 25 kV positive voltage, 15 cm working distance (the distance between the needle and the target), and 1.0 mL h⁻¹ flow rate. The collection time was set to 2.0 h. All manipulations were carried out at room temperature. The electrospun fiber mats of fluoropolymers were cut into strips of dimension 2.0 cm × 2.0 cm for the following experiments. The above-mentioned strip of fluoropolymer electrospun fiber mats were immersed into 10.0 mL, 0.08 mol L⁻¹ aqueous solution of titanium oxo-sulphate and 1.0 mL concentrated sulfuric acid in a 50 mL Tedllo-lined stainless steel autoclave for 6 h in order to form the complex of carboxyl of fluoropolymer electrospun fiber surface and titanium ion. Then 20.0 mL, 0.08 mol L⁻¹ urea and 20 mL distilled water were added. Then 0.0 mL, 0.5 mL, 1.0 mL, 3.0 mL, 5.0 mL, 0.01 mol L⁻¹ ZnSO4 and corresponding 0.02 mol L⁻¹ TAA were added. The reactant content of hydrothermal system was shown in Table 1. The autoclave was sealed at 150 °C for 8 h, and then cooled to room temperature. The TiO2–ZnS/fluoropolymer fiber composites were washed for three times with distilled water under ultrasonic to remove the unreacted precursor and byproducts, and dried in vacuum at 80 °C for 12 h.

Photocatalytic degradation of methylene blue solution was performed by photochemical reactor (SGY-1, Stonetech Co., Ltd. Nanjing, China), light source is 350 W xenon lamp, and reaction system temperature was 23 ± 1 °C. The TiO2–ZnS/fluoropolymer fiber composites and 300.0 mL 16.0 mg L⁻¹ methylene blue were added to the quartz tube-500 mL. The TiO2–ZnS/fluoropolymer fiber composites can be extended well in methylene blue solution without stirring. The Degussa P25 and TiO2–ZnS powders synthesized according to Stengl et al. methods [10] were performed as stated in the previous steps with electromagnetic stirring. Prior to irradiation, the photocatalytic reaction system was stirred in a dark condition for 15 min to establish an adsorption–desorption equilbrium. The photocatalytic reaction system was sampled at regular intervals, and the semiconductor powders suspensions were centrifuged before measured. The remaining methylene blue concentration after adsorption–desorption equilibrium (C0) and photodegradation (C) was detected by UV/VIS at 665 nm, and the degradation efficiency be expressed as (C/C0)%.

3. Results and discussion

3.1. Morphology of TiO2–ZnS/fluoropolymer fiber composites

The poly(MAA-co-TFA)/PVDF electrospun fiber mats were made of random nonwoven mesh of fibers, and had an interconnected open porous structure, as shown in Fig. 1a. The SEM images of TiO2–ZnS/fluoropolymer fiber composites prepared by different proportions for 8 h at 150 °C are compared in Fig. 1b–f and the corresponding Zn content of composites is presented in Table 1. The size distribution of semiconductor particles was about 5 nm to 1 μm, and the size and agglomeration of semiconductor particles were improved with the increasing zinc ion contents in the reaction system, as shown in Table 1. The reasons are able to explained as follows: the sulfide ion was released from TAA at low temperature with high rate [12], but the TiO2 crystal prepared by hydrothermal hydrolysis of titanium oxo-sulphate with urea need multi-step reaction [13], therefore the generation and growth of ZnS crystal were faster than that of the TiO2 crystal under the same reaction system. Without zinc added, the TiO2 crystals formation and growth were controlled by carboxyl along the surface of electrospun fiber, and the about 5 nm TiO2–ZnS/fluoropolymer fiber composites were achieved, as shown in Fig. 1b. With the zinc ion added, the ZnS crystals generated on the fiber surface preceded TiO2 crystals, and then both semiconductor crystals decomposing and combining, so the TiO2–ZnS mixed crystals generated on the fluoropolymer fiber surface. When the zinc ion content of reaction system is low, the TiO2–ZnS particle size is less than 100 nm because of heterogeneous nucleation effect, as shown in Fig. 1c and d. With zinc ion content increase, ZnS homogeneous nucleation plays as a dominant role, plus, the nucleation and growth of ZnS particles accelerates under hydrothermal conditions, which inhibits the instantaneous decomposing and combining of semiconductor particles, thus semiconductor agglomerations sized over 200 nm were obtained, as shown in Fig. 1e and f.

3.2. Characterization of TiO2–ZnS/fluoropolymer fiber composites

The XRD patterns and the corresponding characteristic 2θ values of the diffraction peaks were shown in Fig. 2. It is confirmed that semiconductor composites as-prepared samples is identified as anatase-phase (JCPDS card No. 21-1272), ZnS as cubic-phase (JCPDS card No. 5-566) and the typical PVDF crystal structure [14]. Three intensity peaks only of TiO2 or ZnS have appeared in the XRD patterns and all other high angle peaks have submerged in the background due to large line broadening. The crystal
structure and figuration of semiconductor composites were further discussed using TEM analysis.

The TEM images of TiO₂-ZnS/fluoropolymer fiber composites prepared by reactants TiZn₂ demonstrate the slightly agglomerated TiO₂–ZnS particles, which are inclusive of nanocrystallites with indistinct polygonal shape of about 100 nm in size, as shown in Fig. 2a. The selected area electron diffraction (SAED) patterns of cubic ZnS and anatase TiO₂ are shown in Fig. 3b and c.

Typical FTIR spectra of poly(MAA-co-TFA)/PVDF electrospun fiber and TiO₂–ZnS/fluoropolymer fiber composites prepared by reactants TiZn₂ are compared in Fig. 4. It is evident that the poly(MAA-co-TFA)/PVDF electrospun fiber mats have peaks at ~3350 and ~1670 cm⁻¹, corresponding to hydroxyl and carbonyl stretching of the carboxyl groups of poly(MAA-co-TFA). The corresponding hydroxyl and carbonyl absorption peaks of TiO₂–ZnS/fluoropolymer fiber composites have been broadened and slightly

Fig. 1. SEM images of (a) poly(MAA-co-TFA)/PVDF electrospun fiber mats, and TiO₂–ZnS/fluoropolymer fiber composites prepared by different reactants. (b) TiZn₀, (c) TiZn₁, (d) TiZn₂, (e) TiZn₃, (f) TiZn₄.

Fig. 2. XRD patterns of (a) poly(MAA-co-TFA)/PVDF electrospun fiber and the TiO₂–ZnS/fluoropolymer fiber composites prepared by different reactants. (b) TiZn₀, (c) TiZn₁, (d) TiZn₂, (e) TiZn₃, (f) TiZn₄.
shift to the low wavenumber. This may be due to that the metal ion was complexation adsorbed by the carboxyl on the surface of fluoropolymer electrospun [15,16], and then the semiconductor nuclei formed and grew into compound particles on the surface of fluoropolymer fiber by hydrothermal precipitation, so the chemical interaction exists between fluoropolymer fiber and semiconductor particles.

The surface properties of TiO$_2$–ZnS/fluoropolymer fiber composites were further investigated by XPS analysis, as shown in Fig. 5. The Ti2p$_{3/2}$ bonding energy is 458.6 eV and has 0.6 eV shift compared with the typical anatase TiO$_2$ (459.2 eV) [17], which resulted from the interaction between semiconductor particles and fluoropolymer [18], as shown in Fig. 5a. There are peaks appeared at around 282.3 eV, 286.5 eV, 288.7 eV, in the C$_1$s spectrum and 531.7 eV, 532.8 eV in the O$_1$s spectrum, shown in Fig. 5b and c, and the peaks were also able to ascribe to the influence of carboxyl coordinated with nonbonding metal ion of semiconductor [19]. As a result, the semiconductor particles were able to immobilize tightly on the surface of fluoropolymer fibers.

UV/Vis spectra show the photosensitive properties of TiO$_2$/ZnS–fluoropolymer fiber composites. The poly(MAA-co-TFA)/PVDF electrospun fiber mats have no evident absorption above 250 nm wavenumbers (Fig. 6a). This reveals the poly(MAA-co-TFA)/PVDF electrospun fiber mats do not disturb the light absorption of semiconductor of TiO$_2$/ZnS–fluoropolymer fiber composites during the photocatalytic process. The UV/Vis absorption spectrum of the TiO$_2$–fluoropolymer fiber composites reflects that the absorption edge is about 382 nm, as shown in Fig. 6b. The UV/Vis absorption edge of TiO$_2$–ZnS/fluoropolymer fiber composites have obviously shift to the long wavelength, as shown in Fig. 6c–f. It is due to the S of ZnS surface change the light absorption character of TiO$_2$–ZnS, reduce the band gap, [20] and result in the improvement of the visible-light response ability of TiO$_2$–ZnS/fluoropolymer fiber composites. When the reaction system have lower content zinc ion, the TiO$_2$ crystals were compounded and mixed very well with ZnS through heterogeneous nucleation, and the TiO$_2$–ZnS particles have strong compound effect, therefore the respectively absorption edge is about 473 nm and 450 nm, as shown in Fig. 6c and d. However, with the zinc ion content of reaction system increased, the ZnS agglomeration generation, and ZnS crystals were hard to decompose for TiO$_2$ crystals combining, so the TiO$_2$ crystals are not capped very well with ZnS crystals, therefore the compound effect reduces, the respectively absorption edge is about 402 nm and 390 nm, as shown in Fig. 6e and f.

TGA curve of poly(MAA-co-TFA)/PVDF electrospun fiber shows several thermal decomposition stages, but TiO$_2$–ZnS/fluoropolymer fiber composites prepared by TiZn$_2$ does not show thermal decomposition stage until 450 °C, as shown in Fig. 7. This phenomenon may be due to that the low-molecular weight substances of poly(MAA-co-TFA)/PVDF electrospun fiber mats dissolved or fused connected under long-time hydrothermal condition, and the interaction between semiconductors particles and fluoropolymer fibers may also improve the thermal stability of TiO$_2$–ZnS/fluoropolymer fibers.
fiber composites. Semiconductor particles content of TiO₂–ZnS/fluoropolymer fiber composites was measured through the weight loss after fluoropolymer electrospun fiber was fully decomposed at 700 °C, and the TiO₂–ZnS content of TiO₂–ZnS/fluoropolymer fiber composites calculated was 24.9%.

The specific surface area of TiO₂–ZnS of TiO₂–ZnS/fluoropolymer fiber composites prepared by TiZn₂ is considerably higher than that of Degussa P25 and poly(MAA-co-TFA)/PVDF electrospun fiber mats, but is lower than that of TiO₂–ZnS powders, as shown in Table 2.

### 3.3. Photocatalytic degradation of methylene blue

Photocatalysis of TiO₂–ZnS/fluoropolymer fiber composites prepared by TiZn₂, TiO₂–ZnS powders, Degussa P25, fluoropolymer electrospun fiber mats and blank sample were performed for the methylene blue degradation under visible-light irradiation, as shown in Fig. 8. Near-complete degradation of methylene blue occurred in 120 min in the presence of TiO₂–ZnS/fluoropolymer fiber composites, as shown in Fig. 8a. A slight change of the methylene...
blue concentration was observed for the blank sample, as shown in Fig. 8e. The remaining methylene blue is 0.01 wt.% in the presence of TiO$_2$–ZnS/fluoropolymer fiber composites, and it is 75.6 wt.% in the presence of Degussa P25 after 110 min visible-light irradiation, as shown in Fig. 8a and c. So the TiO$_2$–ZnS/fluoropolymer fiber composites exhibited higher photocatalytic efficiency than that of TiO$_2$ powder in the almost same TiO$_2$ concentration (Table 3). The reason is that the specific surface area and visible-light re- spond ability of TiO$_2$–ZnS/fluoropolymer fiber composites were higher than that of Degussa P25 (Table 2). The specific surface area of TiO$_2$–ZnS/fluoropolymer fiber composites prepared by TiZn$_2$ was lower of than that of TiO$_2$–ZnS powder, as shown in Table 2, but the remaining methylene blue is 20.2 wt.% after 110 min visible-light irradiation in the presence of TiO$_2$–ZnS powders. There may be adsorption–migration–photodegradation [21] exists in the photocatalysis reaction: methylene blue was first adsorbed onto the surface of fluoropolymer fibers because of its hydrophobicity, and then migrated to semiconductor particles surface, finally was pho- tocatalytic degraded by semiconductor particles, so deduce the TiO$_2$–ZnS/fluoropolymer fiber composites possess higher photocat- alytic efficiency than that of TiO$_2$–ZnS powders for the degradation of methylene blue with the same concentration.

Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Photocatalyst concentration (mg L$^{-1}$)</th>
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<tbody>
<tr>
<td>TiO$_2$–ZnS/fluoropolymer fiber composites (TiZn$_2$)</td>
<td>34.2</td>
</tr>
<tr>
<td>TiO$_2$–ZnS powders</td>
<td>34.7</td>
</tr>
<tr>
<td>Degussa P25</td>
<td>35.1</td>
</tr>
<tr>
<td>(MAA-co-TFA)/PVDF electrospun fiber mats</td>
<td>–</td>
</tr>
<tr>
<td>Blank</td>
<td>–</td>
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Fig. 8. Photocatalytic degradation of methylene blue by (a) TiO$_2$–ZnS/fluoropoly- mer fiber composites prepared by TiZn$_2$, (b) TiO$_2$–ZnS powders, (c) Degussa P25, (d) (MAA-co-TFA)/PVDF electrospun fiber mats; (e) blank sample.

Fig. 9. SEM image of TiO$_2$–ZnS/fluoropolymer fiber composites prepared by TiZn$_2$ after 10 times degradation of methylene blue solution under UV irradiation for 2.0 h each.

4. Conclusion

The TiO$_2$–ZnS composites with diameters from 15 nm to 1 μm were immobilize on the surface of fluoropolymer fiber under differ- ent reaction system, and the chemical interaction existed between TiO$_2$–ZnS composites and fluoropolymer fibers. When the molar ra- tio of zinc ion and titanic ion in reaction system was 1:80, the TiO$_2$–ZnS/fluoropolymer fiber composites possess good visible-light pho- tocatalytic activity because of its strong visible-light response activity, quite high specific area and synergistic effect. The repeated photocatalysis tests show the TiO$_2$–ZnS/fluoropolymer fiber com- posites possess good visible-light photocatalytic stability.

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References


