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Synthesis and Characterization of CNT/TiO_2/ZnO Composites with High Photocatalytic Performance

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Abstract: Novel carbon nanotubes (CNTs)/titanium dioxide (TiO_2)/zinc oxide (ZnO) composites have been successfully synthesized via a two-step solution method using titanyl sulfate as the titanium precursor. Its structural performances were researched by various characterization methods, such as X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and UV-vis diffuse reflectance spectroscopy (UV-vis DRS). The performance of the composites was tested by degrading rhodamine B (RhB) under UV-vis illumination and found to strongly rely on the content of ZnO. The experimental results showed that the CNT/TiO_2/ZnO-90 wt % expressed more outstanding photocatalytic performance compared to the corresponding binary composites and the CNT/TiO_2/ZnO-85 wt %, CNT/TiO_2/ZnO-95 wt % materials. The improved photocatalytic activity was attributed to synergistic effect of CNT, TiO_2 and ZnO, in which ZnO can absorb photons to produce electrons and holes, whereas TiO_2 and CNT can reduce the electron-hole recombination.

Keywords: carbon nanotubes; titanium dioxide; zinc oxide; photocatalyst

1. Introduction

Carbon nanotubes (CNTs), which are characterized by large surface area, high electrical conductivity and chemical stability, have attracted considerable interest because of their potential applications in CNT-based composites, nanoelectronic devices, field emitters, photocatalyst and supercapacitor [1–5]. In particular, CNT/metal oxide-based materials have become the focus of attention due to the improvement of combination technology, such as atomic layer deposition [6], self-assembly [7].

Titanium dioxide (TiO_2), with 3.2 eV band gap, is susceptible to the light wavelength (<380 nm) which is part of UV light [8]. Moreover, the cheap TiO_2-based materials were used extensively in photocatalytic degradation because of the strong stability against extreme environment. In order to improve the separation efficiency of electron-hole pairs and photocatalytic effect, compound semiconductor materials have been prepared by combining the two semiconductors with different band gap, such as CdS-TiO_2 [9], SnO_2-TiO_2 [10], V_2O_5-TiO_2 [11], and so on. This method has been proved feasible to enhance activity of TiO_2. Chen et al. [12] added nano-sized TiO_2-ZnO compound semiconductor material into anion exchange membrane layer chitosan to prepare polyvinyl alcohol-sodium alginate/TiO_2-ZnO chitosan bipolar membrane with better photocatalytic property for water decomposition, hydrophilicity, thermal stability and mechanical properties.

Raghavan et al. [13] prepared reduced graphene-oxide/titanium dioxide/zinc oxide with superior photocatalytic degradation efficiency compared with the binary materials. The reason why the enhanced properties is that the heterojunction formed between TiO_2 and the coupled semiconductor with appropriate band gap can reduce the band gap of compound semiconductor materials and the recombination efficiency of electron-hole pairs, enlarge the range of absorption wavelength [14].

Herein, we reported the synthesis of CNTs/TiO_2/ZnO by combining CNTs with TiO_2 and ZnO using the two-step solution. Firstly, CNTs were decorated with TiO_2 in chemical bath deposition, followed by a solvothermal method to incorporate the main building block ZnO. The experimental results showed that the CNT/TiO_2/ZnO-90 wt % expressed more outstanding photocatalytic performance compared to the corresponding binary composites and the CNT/TiO_2/ZnO-85 wt %, CNT/TiO_2/ZnO-95 wt % materials. The most important causes of this were the forming of compound semiconductor materials and the large surface area of CNT.

2. Experimental

2.1. Samples Preparation

2.1.1. Preparation of CNT/TiO_2

In our experiment, multi-walled CNTs (the diameter of 40–60 nm and the length of less than 2 μm, >97%, Shenzhen Nanotech Port Co., Ltd., Shenzhen, China) were dispersed in 200 mL of HNO_3 (6 mol/L). The solution was undergone reflux condensation (at 140 °C for 4 h) in an oil bath, afterwards, the solution was cooled, diluted, filtered, and washed until the filtrate is neutral. The solution was dried at 80 °C for 24 h [15,16]. Oxygen titanium sulfate ($TiOSO_4$) powder (93%, Aladdin Industrial Corporation, Shanghai, China) was dissolved in 50 mL distilled water. The solution was mechanically agitated for 11 h, and the precipitate was filtered. Briefly, 50 mL distilled water was added to dilute the solution. Briefly, 60 mg of CNTs was added to 10 mL of $TiOSO_4$ solution to successfully prepare CNT/TiO_2 composites through the chemical bath deposition method at 50 ~ 65 °C.

2.1.2. Preparation of CNT/TiO_2/ZnO

$Zn(CH_3COO)_2 \cdot 2H_2O$ (99.0%, Aladdin Industrial Corporation, Shanghai, China) was added into 25 mL CH_3OH to obtain a completely dissolved solution, CNT/TiO_2 composites were added in the mixture, and then sonicated for 10 min. At the same time, 0.134 g KOH was dissolved into 13.5 mL CH_3OH. The KOH-CH_3OH solution was added into the above mixture. After the reaction at 50 ~ 65 °C for 2 h, the solution was placed in the reaction kettle with a capacity of 50 mL and undergone annealing at 180 °C for 12 h. The solution was filtered, washed and dried. CNT/TiO_2/ZnO composites were successfully obtained. Three composites samples were obtained by changing the mass percentage of ZnO to 95%, 90% and 85%. The synthesized samples were marked as CNT/TiO_2/ZnO-95 wt %, CNT/TiO_2/ZnO-90 wt % and CNT/TiO_2/ZnO-85 wt %, respectively. The binary counterpart CNT/TiO_2 and CNT/ZnO was synthesized in the same way.

2.2. Characterization

The crystallization of samples were characterized by X-ray powder diffraction (XRD) performed with a Rigaku MiniFlex 600 possessed with Cu-Kα radiation (Rigaku, Tokyo, Japan). Scanning electron microscopy (SEM) images were collected by a Hitachi field-emission scanning electron microscope (Hitachi, Tokyo, Japan). The size of the composites were observed by transmission electron microscope (TEM) and high-resolution TEM (HRTEM) (TECNAI F30 at 300 kV, FEI, Hillsboro, OR, USA), respectively. Light absorption range was tested by UV-vis diffuse reflectance spectroscopy (UV-vis DRS) (Shimadzu, Tokyo, Japan). Degradation efficiency of RhB was got by UV-vis spectrophotometer (UV-2450) (Shimadzu, Tokyo, Japan).

3. Results and Discussion

In this work, CNTs/TiO_2/ZnO was synthesized by combining CNTs with TiO_2 and ZnO using the facile two-step solution method. The fabrication of the ternary CNTs/TiO_2/ZnO composites was illustrated in Figure 1. CNTs were first discontinuously decorated with TiO_2 in chemical bath deposition, followed by a solvothermal method to incorporate the main building block ZnO.

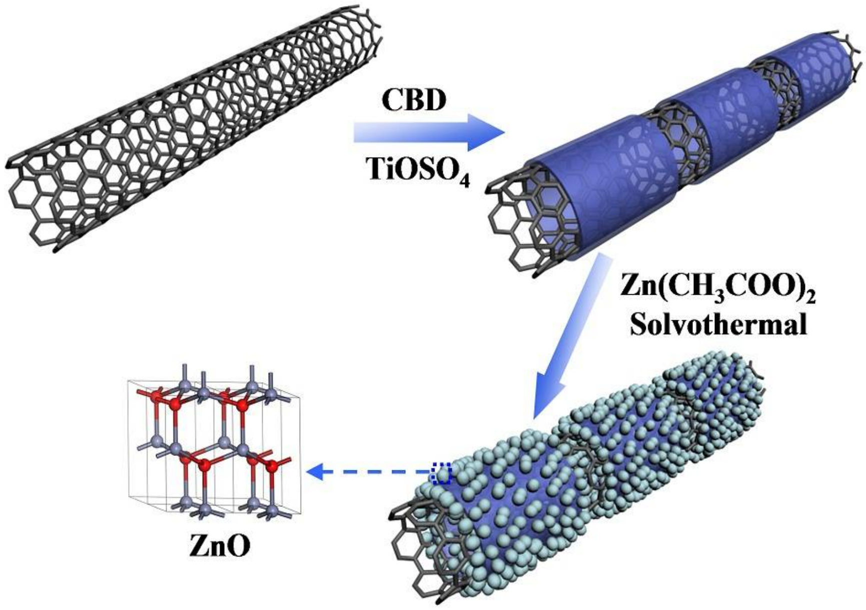

Figure 1. Schematic illustration of the ternary carbon nanotubes (CNTs)/TiO_2/ZnO composites.

Figure 2a showed the XRD patterns of CNT/TiO_2, CNT/ZnO, CNT/TiO_2/ZnO-95 wt %, CNT/TiO_2/ZnO-90 wt % and CNT/TiO_2/ZnO-85 wt %. It can be clearly seen that all of ZnO-based materials revealed semblable diffraction peaks. The 2θ peaks observed at 31.9°, 34.5°, 36.4°, 47.6°, 56.7°, 63.0°, 66.5°, 68.1°, 69.3° were corresponded to the (100), (002), (101), (102), (110), (103), (200), (112), (201) of hexagonal wurtzite structure ZnO, respectively. The more the content of ZnO, the weaker the diffraction peak intensity of 26.0° corresponded to the (002) of amorphous carbon. Moreover, no obvious diffraction peaks of anatase TiO_2 were observed at 38.2°, 47.9°, 54.4°, 62.6° corresponded to (004), (200), (105), (204), which was attributed to the stronger peak intensity of ZnO. The SEM and TEM images for the CNT/TiO_2/ZnO-90 wt % materials were exhibited in Figure 2b–d. Figure 2b showed abundant TiO_2 and ZnO nanoparticles were loaded on the surface of CNT, and there was bare CNTs. As shown in the Figure 2d, HRTEM also proved coexist of TiO_2 and ZnO nanoparticles, lattice fringes were in accordance with the XRD results.

According to the Figure 3a, the optical property of CNT/TiO_2/ZnO-95 wt %, CNT/TiO_2/ZnO-90 wt % and CNT/TiO_2/ZnO-85 wt % composites was observed. The slight red-shift of absorption range was caused by the increased of ZnO. This phenomenon was attributed to the mobility of electron and the relaxation energy [17]. The degradation efficiencies of compounds were evaluated in regard of photodegradation of RhB with the initial concentration of 5 mg/L under UV-vis light irradiation. RhB was chosen as degradation product because it is highly toxic and harmful to humankind. Figure 3b showed the change of concentration of RhB, the concentration was almost close to zero at 40 min for CNT/TiO_2/ZnO-90 wt % materials revealed the best photodegradation activity. Upon the incorporation of ZnO into CNT/TiO_2, the photodegradation activity of CNT/TiO_2/ZnO-90 wt % was higher than CNT/TiO_2/ZnO-95 wt % and CNT/TiO_2/ZnO-85 wt % composites, because the carrier delivery and separation were related to suitable mass ratio and band gap between different level semiconductor [18]. The lower photodegradation activities compared to CNT/TiO_2/ZnO-95 wt % and CNT/TiO_2, CNT/TiO_2/ZnO-85 wt % and CNT/ZnO were ascribed to superabundant or derisory content of ZnO which to some extent reduced separation efficiency of electron-hole pairs. These findings proved that the photodegradation activity of compounds depended on the synergetic effects of CNT, TiO_2 and ZnO.

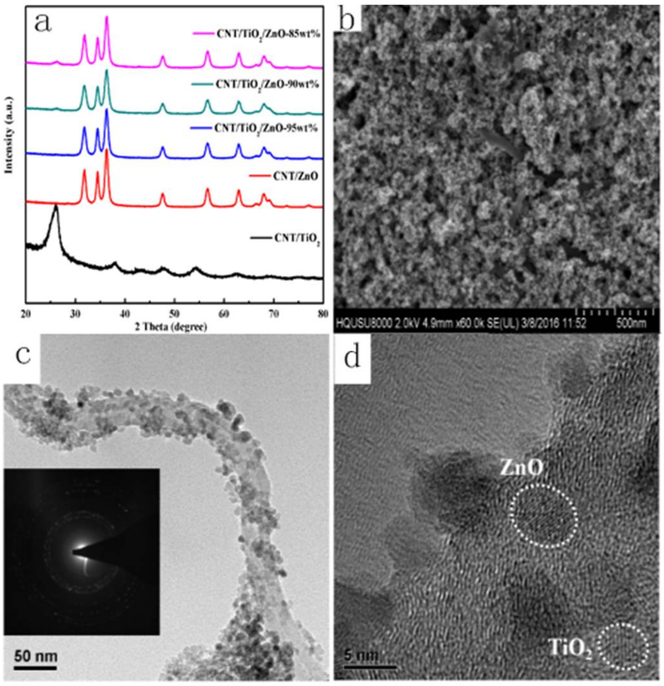

Figure 2. (**a**) X-ray powder diffraction (XRD) patterns of CNT/TiO_2, CNT/ZnO, CNT/TiO_2/ZnO-95 wt %, CNT/TiO_2/ZnO-90 wt % and CNT/TiO_2/ZnO-85 wt %; (**b**) SEM image of CNT/TiO_2/ZnO-90 wt %; (**c**) Transmission electron microscopy (TEM) image with SAED pattern (inset) of CNT/TiO_2/ZnO-90 wt %; (**d**) HRTEM image of CNT/TiO_2/ZnO-90 wt %.

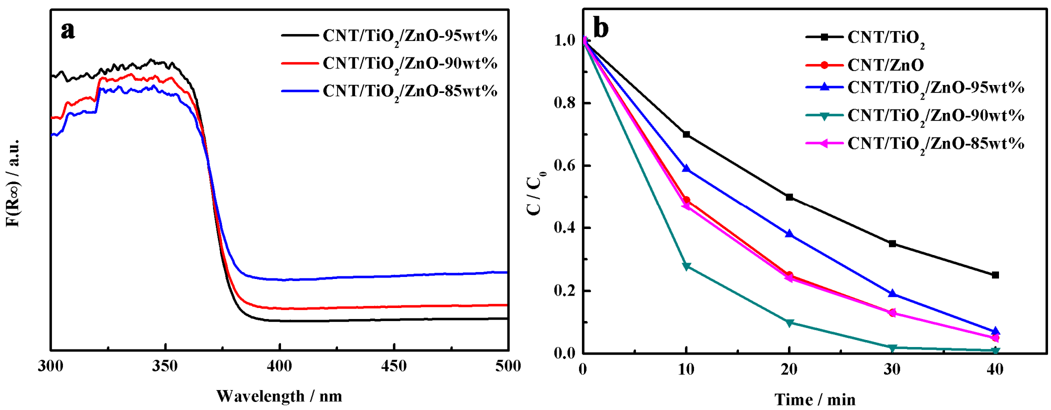

Figure 3. (**a**) UV-vis diffuse reflectance spectroscopy (DRS) patterns of CNT/TiO_2/ZnO-95 wt %, CNT/TiO_2/ZnO-90 wt % and CNT/TiO_2/ZnO-85 wt %; (**b**) change of concentration of rhodamine B (RhB) during degradation process in UV-vis light irradiation of CNT/TiO_2, CNT/ZnO, CNT/TiO_2/ZnO-95 wt %, CNT/TiO_2/ZnO-90 wt % and CNT/TiO_2/ZnO-85 wt %.

Figure 4 showed the schematic electron-hole separation process of CNT/TiO_2/ZnO composites. ZnO particles absorbed photons to produce electrons and holes with the light of a certain wavelength [19]. On the one hand, the band gaps of TiO_2 and ZnO are 3.2 eV and 3.37 eV, respectively, which suggested the possible transfer of the photo-generated carriers. This phenomenon restrained the recombination between electrons and holes in ZnO to some extent. On the other hand, a larger surface area was provided by CNTs. In addition, CNTs have larger work function to absorb electrons of ZnO or TiO_2 and thus promote further separation between electrons and holes. In other words, CNTs influence the lifetime of electron-hole pairs [20]. Consequently, electrons and holes on the surface were reacted with H_2O, OH^-, or O_2 of solution to form OH· radical and others, which are responsible for the degradation of RhB. Superficial holes were combined with radicals to destroy the aromatic structure of RhB and degrade RhB to CO_2 and H_2O [21,22].

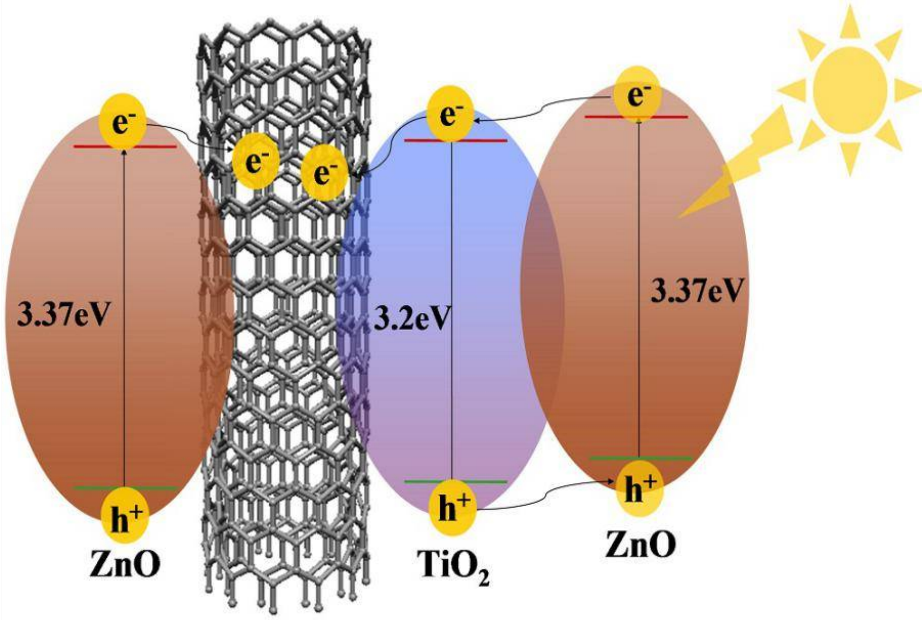

Figure 4. Schematic electron-hole separation process of CNT/TiO_2/ZnO composites.

4. Conclusions

In this study, two facile routes, namely, chemical bath deposition and solvothermal route were developed to synthesize the ternary CNT/TiO_2/ZnO composite. The CNT/TiO_2/ZnO-90 wt % expressed more outstanding photocatalytic performance compared to the corresponding binary composites and the CNT/TiO_2/ZnO-85 wt %, CNT/TiO_2/ZnO-95 wt % materials. The improved photocatalytic activity was attributed to the synergistic effect of CNT, TiO_2 and ZnO, in which ZnO can absorb photons to produce electrons and holes, whereas TiO_2 and CNT can reduce the electron-hole recombination, CNT can enhance redox ability of electrons and holes and reduce recombination efficiency of electron-hole pairs. This work may provide new insights into the development of compound semiconductor photocatalysts, which attracts great interest in scientific circles.

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Conflicts of Interest: The authors declare no conflict of interest.

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