

Research Article

Preparation and Photocatalytic Properties of SnO₂ Coated on Nitrogen-Doped Carbon Nanotubes

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SnO₂ nanoparticles coated on nitrogen-doped carbon nanotubes were prepared successfully via a simple wet-chemical route. The as-obtained SnO₂/CN_x composites were characterized using X-ray powder diffraction, scanning electron microscopy, and transmission electron microscopy. The photocatalytic activity of as-prepared SnO₂/CN_x for degradation Rhodamine B under UV light irradiation was investigated. The results show that SnO₂/CN_x nanocomposites have a higher photocatalytic activity than pure SnO₂ and SnO₂/CNTs nanocomposites. This enhanced photoresponse indicates that the photoinduced electrons in the SnO₂ prefer separately transferring to the CN_x, which has a high degree of defects. As a consequence, the radiative recombination of the electron-hole pairs is hampered and the photocatalytic activity is significantly enhanced for the SnO₂/CN_x photocatalysts.

1. Introduction

Carbon nanotubes (CNTs) have been the focus of intensive study due to their unique structural, electrical, and mechanical properties since their discovery by Iijima [1]. Their potential applications include nanodevices, quantum wires, ultrahigh-strength engineering fibers, sensors, and catalyst supports [2–4]. Recently, the study of CNT-based composites is becoming a promising and challenging area of research owing to their improved properties [5–7]. Of them, CNT-based metal oxide hybrids represent an important class and are very promising as functional materials in lithium-ion batteries, supercapacitors, and photocatalysts [8].

However, to fabricate CNT-based composites, the CNTs required a pretreatment process to modify their inert surface nature via harsh processes for activation by refluxing in concentrated acids, which destroys the π conjugation and reduces the conductance of the CNTs base [9]. Unfavorably, the harsh process would risk CNTs to some damages in their inherent properties. To bypass the drawbacks suffered by CNTs, employing nitrogen-doped carbon nanotubes (CN_x) without requiring any pretreatment to composite with the functional materials directly is a promising method, because

the nitrogen atoms on the surface of the CNTs modifies the adsorption strength of the nanotubes towards foreign elements which can influence the dispersion of active phase. Moreover, nitrogen atoms in the framework of CN_x will form chemically active points which are available for metal or metallic oxide nanoparticles anchoring. Ghosh prepared ZnO/CN_x composites via a simple wet-chemical method and studied their field emission performance [9]. Yue and coworkers obtained Pt/CN_x composites which presented obvious catalytic activity for methanol oxidation [10]. CN_x decorated with CeO₂ and SnO₂ nanoparticles showed greater activity and sensitivity than the conventional CNT-based composites for NO electrooxidation [11].

SnO₂, a stable and large n-type bandgap ($E_g = 3.6$ eV) semiconductor, has the ability to degrade dyes under UV light [12]. Recently, a nanocomposite of SnO₂ nanoparticles coated on CNTs was synthesized and exhibited excellent photocatalytic activity due to the electron transfer between SnO₂ and CNTs [13]. However, the photocatalytic properties of SnO₂ nanoparticles coated on CN_x (SnO₂/CN_x) have been scarcely investigated.

In this study, according to the unique properties of CN_x-based metal oxide, we have synthesized SnO₂/CN_x

composites via a simple and efficient room-temperature chemical route. The as-synthesized nanocomposites were well characterized and their photocatalytic activities were evaluated by the photodegradation of RhB.

2. Experimental

2.1. Synthesis of SnO₂/CN_x. Following the procedures reported previously [14], CN_x was synthesized using ethylene diamine and diethylamine as the carbon and nitrogen source.

Synthesis of SnO₂/CN_x nanocomposites was according to the following procedures, which were modified from the reference [15]. 50 g of tin (II) chloride (anhydrous, Alfa, 99%) was put into 500 mL of distilled H₂O inside a glass flask, and then 70 mL of HCl (38%) was added. We then immersed 1 g of CN_x in the above solution. This solution was sonicated for 10 min and then stirred for 60 min at room temperature. SnO₂/CN_x nanocomposites were then obtained after centrifuging, washing with ethanol and deionized water for several times, and drying at 80°C for 8 h. SnO₂/CNTs composites were synthesized using the similar procedures besides CNTs pretreated in concentrated HNO₃ in 140°C for 14 h, and pure SnO₂ sample was synthesized without adding CNTs.

2.2. Characterization. The bare CN_x and the composites were characterized by a range of analytical techniques. The degree of crystallinity of the SnO₂/CNTs composites was characterized by powder X-ray diffraction (XRD). The XRD patterns with diffraction intensity versus 2θ were recorded in a Bruker D8 ADVANCE instrument with Cu-Kα radiation (λ = 1.5418 Å) from 10° to 80° at a scanning speed of 0.02 °/s. X-ray tube voltage and current were set at 40 kV and 40 mA, respectively. Scanning electron microscopy (SEM) was carried out on Hitachi S-4800 with an acceleration voltage of 5 kV. Transmission electron microscopy (TEM) was carried out on JEOL-JEM-1005 at 200 kV. The specimens for SEM and TEM imaging were prepared by suspending solid samples in ethanol with 15 min ultrasonication and placing a drop of this mixture on a 3.05 mm diameter copper mesh (300 lines/in. mesh), which was then dried in air.

2.3. Photodegradation of RhB. The photoreactor was designed with a cylindrical quartz cell configuration and an internal light source surrounded by a quartz jacket, where RhB aqueous solution completely surrounded the light source. An external cycled cooling flow of water was used to maintain the reaction temperature constant.

Photocatalytic experiments were carried out by adding 0.02 g SnO₂ or SnO₂/CNTs composites or SnO₂/CN_x composites into photoreactor containing 30 mL RhB solution with an initial concentration of 10 mg/L. The RhB solution with catalyst was stirred in the darkroom for 10 h to reach the equilibrium of surface adsorption. Then the stirred suspensions were illuminated with a 300 W high-pressure mercury lamp 10 cm high over the solution. The solution was stirred continuously during the photocatalytic reaction. The

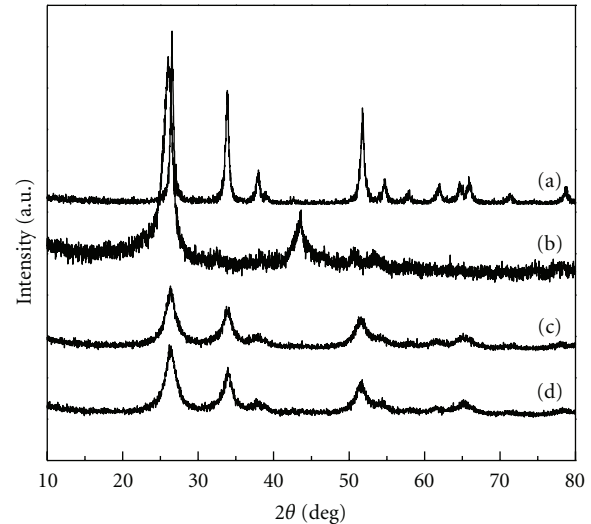


FIGURE 1: XRD patterns of (a) pure SnO₂, (b) pure CN_x and SnO₂/CN_x composites prepared with CN_x obtained from (c) ethylene diamine and (d) diethylamine.

change of RhB concentration with the illumination time was monitored by determining the absorbance at 555 nm [16], using Shimadzu UV-2550 spectrophotometer.

3. Results and Discussion

The XRD patterns of pure SnO₂, pure CN_x, and SnO₂/CN_x composites are displayed in Figure 1. The main peaks at 26.1° and 46.7° for CN_x were similar to those of graphite, which indicated that the employed CN_x were highly graphitized. The typical XRD patterns of the pure SnO₂ are illuminated in Figure 1(a). All the diffraction peaks are indexed to the tetragonal rutile structure of SnO₂ (JCPDS card no. 41–1445). No diffraction peaks from impurities are observed. Different amine for synthesis CN_x has no obvious effect on the formation of SnO₂/CN_x composites. The diffraction angle for SnO₂/CN_x composites at 2θ = 33.6°, 51.8° can be assigned to 101 and 211 planes of the cassiterite SnO₂, respectively. The peak at 26.3° attributed to the peak of the 110 planes of SnO₂ overlapped with the peak of graphitic reflection from CN_x. Average crystalline size can be estimated by Scherrer's formula:

$$D = \frac{K\lambda}{\beta \cos \theta}, \quad (1)$$

where D is the grain diameter, K (0.89) is the shape factor, λ is the X-ray wavelength of Cu Kα radiation (0.154 nm), θ is the Bragg angle, and β is the experimental full-width half-maximum (fwhm) of the respective diffraction peak. The calculated mean particle size of SnO₂ nanoparticles was calculated to be about 4 nm.

Figures 2 and 3 show the SEM and TEM images of pure CN_x and SnO₂/CN_x composites. CN_x with relatively homogeneous (external) diameter (30 ~ 60 nm) were obtained, and the nanomaterial was composed of individual

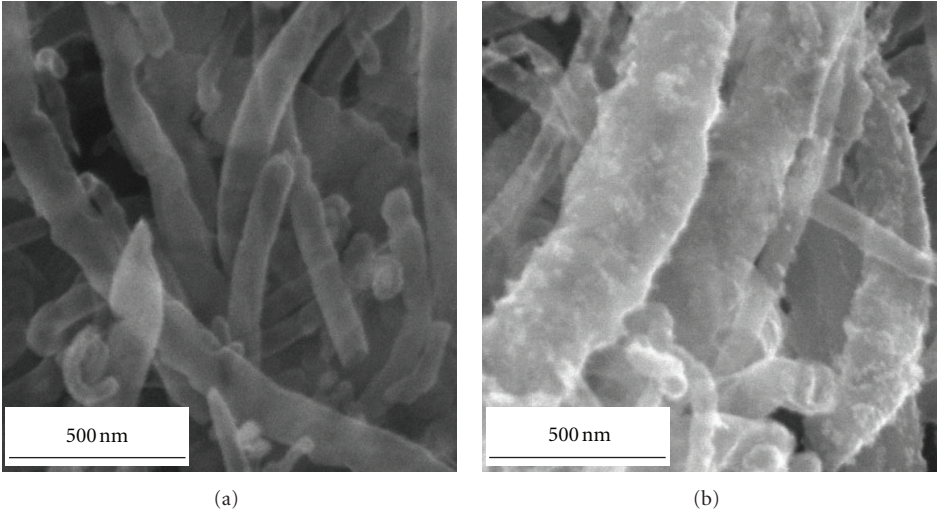


FIGURE 2: SEM image of (a) pure CNx and (b) SnO₂/CNx composites.

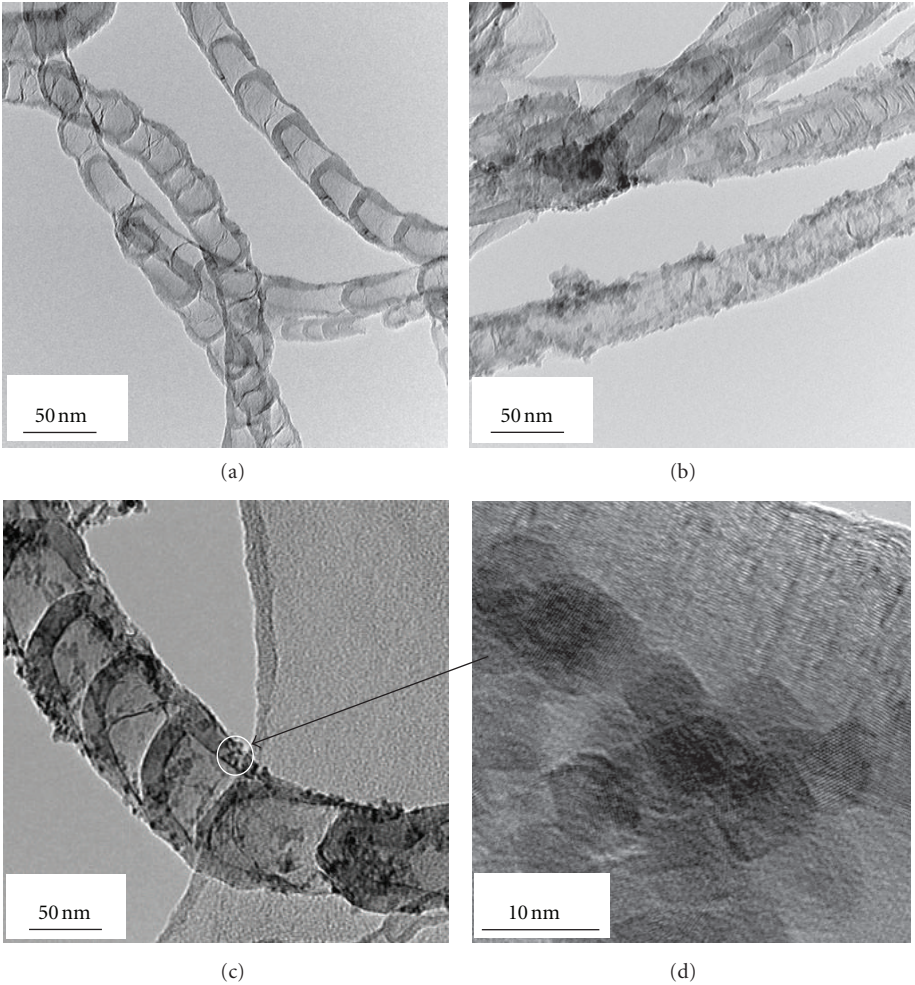


FIGURE 3: (a) TEM image of pure CNx. (b) Low-resolution TEM image of CNx bundles fully coated with SnO₂. (c) Low-resolution TEM image of an individual CNx fully coated with SnO₂. (d) High-resolution TEM image in selected location.

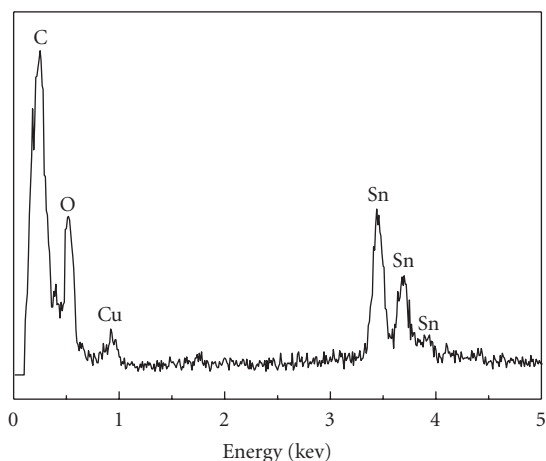


FIGURE 4: Typical EDS spectrum of SnO_2/CN_x composites.

nanobamboo stacked together to form the long nanofibers. However, after coating with SnO_2 , all CN_x are uniformly coated with a layer of SnO_2 nanoparticles, and no free nanoparticles were found. The SnO_2 nanoparticles deposited on the surface of CN_x are separated and the particle size is uniform. Figure 3(c) is TEM image of an individual CN_x fully coated with SnO_2 . The bamboo-like morphology of CN_x can be also clearly observed, and its surface is entirely and homogeneously covered by SnO_2 nanoparticles. The intimate contact between CN_x and SnO_2 favors the formation of junctions between the two materials, as a result, being helpful for improving the charge separation and thus the photocatalytic activity.

The size of SnO_2 nanoparticles on the surface of CN_x is about 4 nm, which is consistent with the XRD result. Chemical analysis using EDS further confirms the presence of Sn, O, C, and Cu in the SnO_2/CN_x composites (Figure 4). The C signal originates from the supporting CN_x .

The photocatalytic activity of SnO_2/CN_x composites was evaluated for the degradation of RhB in aqueous solution. Figure 5 shows that the spectrum changes during RhB (10 mg/L) photodegradation by SnO_2/CN_x photocatalysts with reaction time. With the increase of irradiation time, the intensity of the maximum adsorption peak located near 555 nm decreased gradually, indicating the degradation and mineralization of the RhB dye solutions.

Figure 6 presents the degradation profiles of RhB in the presence of SnO_2/CN_x composites under UV light irradiation, together with CN_x , SnO_2 , and SnO_2/CNTs composites for comparison. Almost no degradation was detected when CN_x alone was used as the catalyst. The photocatalytic activity of SnO_2/CNTs and SnO_2/CN_x composites is much higher than that of the sole SnO_2 . SnO_2/CNTs with higher photocatalytic activity than pure SnO_2 has been also observed in the literature [13]. It is noteworthy that SnO_2/CN_x composites show superior activity to SnO_2/CNTs composites. With the reaction time at 50 min, the RhB degradation efficiencies of pure SnO_2 and SnO_2/CN_x composites catalysts are about 70% and 80%, respectively. However, the value of SnO_2/CN_x is 89%. Hence, SnO_2/CN_x is an excellent photocatalyst in our experiment.

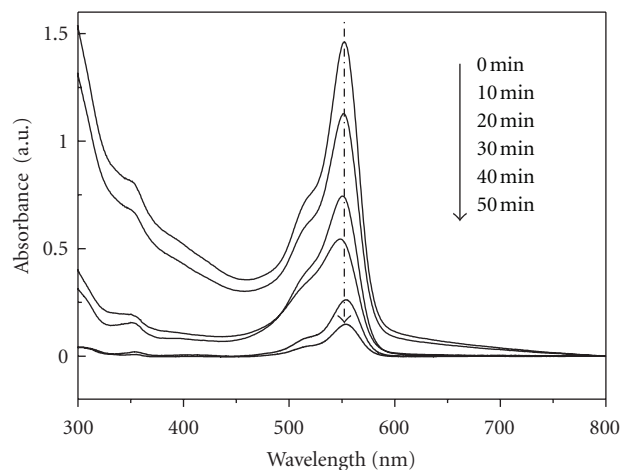


FIGURE 5: Temporal UV absorption spectral changes of RhB solution as a function of irradiation time (RhB = 10 mg/L).

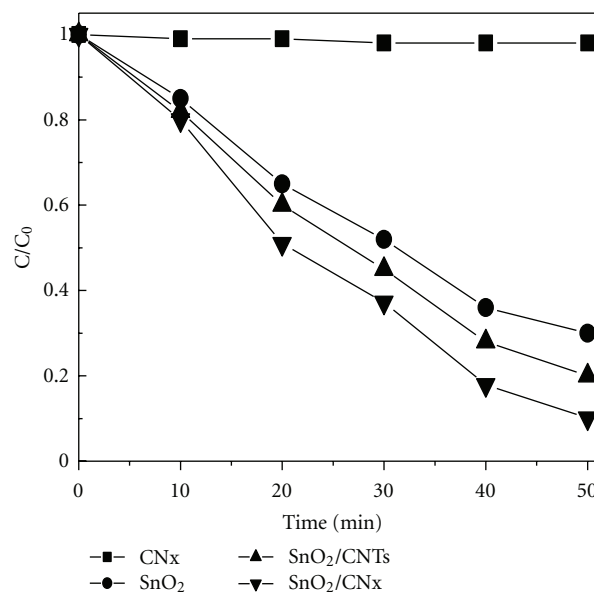


FIGURE 6: Comparison of photocatalytic degradation rate between pure SnO_2 , SnO_2/CN_x composites, and SnO_2/CNTs composites.

On the basis of the literature [13], a band configuration at the interface of the SnO_2/CN_x composites is proposed, as shown in Figure 7. Under UV irradiation, the valence band electrons of SnO_2 can be excited to its conduction bands, giving rise to the formation of high energy electron-hole pairs. Heterojunction promoting the photocatalytic activity has been reported in several cases of semiconductor oxides and carbon nanotubes [17, 18]. They attributed the improvement of photocatalytic performance to the promotion of separation rate of photogenerated electron and hole by the formation of heterostructure.

As regards CN_x , N not only acts as a direct substitute impurity, but also affects the CNTs properties in distinctive manners. In our work, the enhanced photocatalytic activity of CN_x may attribute to the following two possible reasons.

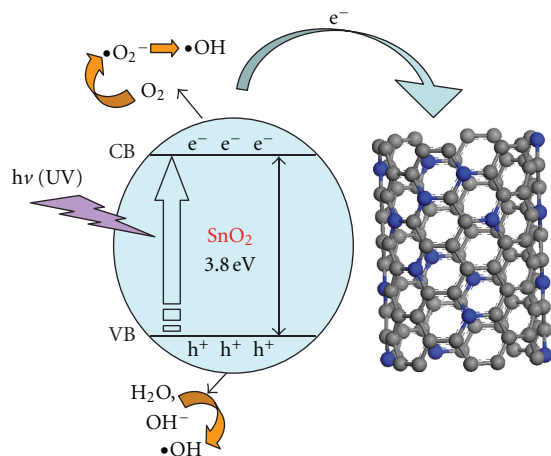


FIGURE 7: Schematic diagram showing band configuration and electron-hole separation at interface of SnO_2/CN_x nanocomposites under UV irradiation (CB—the bottom of conduction band, VB—the top of valence band).

Firstly, a high degree of defects were introduced by nitrogen doping [19], the electrons generated by SnO_2 can transfer into CN_x , which could be taken for a larger capacity container of electron in comparison with the usual CNTs. The high separation efficiency of electron-hole pairs lead to the dramatically enhanced photoactivity. Secondly, compared to carbon, nitrogen has an extra electron, and from an electronic point of view it is natural to expect an excess of donors in the N-rich areas of the CNTs upon doping [20, 21]. This in fact occurs if N substitutes for a C atom generating an n-type semiconductor with localized states above the Fermi level. That is to say, impurities significantly enhanced the CN_x metallic/conductive character [22]. Hence, the photoinduced electrons transport to the surface of the composites much easily to prevent the recombination between photogenerated electrons and holes, leading to enhanced photoactivity of SnO_2/CN_x , as also found for N-graphene/ CdS nanocomposites [23]. Further investigation on the mechanism of enhanced photocatalytic properties is underway.

4. Conclusions

SnO_2 nanoparticles were successfully coated on CN_x via a simple wet-chemical method. The composites showed excellent photocatalytic activity compared with pure SnO_2 and SnO_2/CNTs . The rapid transferring of electron and high separation efficiency of electron-hole pairs lead to the dramatically enhanced photoactivity. The SnO_2/CN_x composites would be promising for practical use in pollutant decomposition as effective photocatalysts.

Acknowledgments

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