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Enhanced photocatalytic activity of nanohybrids TiO_2/CNTs materials

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ABSTRACT

The nanohybrids TiO_2/CNTs materials were synthesized by hydrolysis method. The results show that, compared to pure TiO_2 or CNTs nanoparticles, nanohybrids TiO_2/CNTs materials exhibit higher catalytic activities in degradation of methylene blue (MB), or methylene orange (MO). The highest degradation percentages, observed in samples with [TiO_2]/[CNTs] ratio of 5/1, are around 33% for MO and 38% for MB, respectively. This can be attributed to the significantly enhanced visible light absorption of nanohybrids TiO_2/CNTs due to the attachment of the TiO_2 nanoparticles on the sidewall of CNTs. The density functional-theory (DFT) calculations indicate that the stability of nanohybrids TiO_2/CNTs is due to the favored bonding state between nanocrytal TiO_2 and CNTs at the interface. Hopefully, this work can help promote better understanding of the role of semiconductor-CNTs interface in increasing the efficiency of using the solar energy, by enhancing the photocatalytic performance in the visible region.

1. Introduction

Development of novel hybrid nanostructures can significantly increase the complexity and expand the functionality of nanomaterials, benefiting nanotechnology-based electronics [1], medicine [2], catalysis [3], and sensors [4]. Among the photocatalytic active materials, TiO_2 is the most widely used due to its high catalytic activity, chemical and biological stability and low cost [5]. However, the main drawback of TiO_2 materials is the large band gap (3.0–3.2 eV) which limits its application to the UV region which constitutes only about 4% of the total solar spectrum. It is therefore important and a great challenge to develop new TiO_2 photocatalytic systems that are both UV and visible light active.

The issue was further solved by doping effect which results in the sub-bandgap absorption in the visible region. The experimental works demonstrate that nonmetal or metal dopants extend photoresponse of TiO_2 from the UV to the visible light region [6–9]. Theoretical calculations also confirm that anion doping considerably affects the band gap of TiO_2 [10]. However, the high concentration of dopants is difficult to obtain and the synthesized materials are usually unstable to photo-corrosion [11]. Furthermore, dopant-mediated electron hole pair recombination in the lattice can be a significant problem, restricting practical application. Recently, some studies reported that the photocatalytic activity of some semiconductors can be improved by making composites with CNTs [12–14]. In the nanohybrids TiO_2/CNTs, a dense heterojunctions through Ti–O–CNTs structure is a reason enhanced photoactivity [15]. Not only do CNTs provide a large surface area supporting the catalysts, but they also stabilize the charge separation by trapping the electrons transferred from semiconductors and thus hinder electron–pair recombination. Therefore, TiO_2/CNTs can have applications in optical or electronic technologies. [16,17].

In this work, we report the efficiency of enhancing photocatalytic activities of nanohybrids TiO_2/CNTs materials. The nanocrystal TiO_2 was attached on the surface of CNTs via hydrolysis method. The bonding between TiO_2 nanocrystal and CNTs enhances the visible light absorption ability and photocatalytic activity for the degradation of dyes (in comparison with pure TiO_2 or CNTs). The experimental results were combined with DFT calculations of the electronic band structures and density of states (DOS) to understand the bonding states between TiO_2 and CNTs, proving the stability of the TiO_2/CNTs system.

2. Experiment

CNTs were surface-activated, using a mixture of concentrated H_2SO_4 and concentrated HNO_3 ($H_2SO_4/HNO_3 = 1/3$). After stirring vigorously for 12 h at 120 °C, the resulting solution was filtered and washed with deionized water, then dried at 80 °C in air for 24 h. $C_{12}H_{28}O_4Ti$ was then added dropwise to the prepared CNTs dispersion in an iced bath with various concentrations

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($[TiO_2]/[CNT]=3/1$, 5/1, 10/1, or 20/1). The prepared particles were dried at 80 °C for 24 h and heat treated at 400 °C for 2 h. To clarify the role of chemical oxidation of CNTs' surface by acids, another TiO_2/CNTs sample was prepared from CNTs without surface chemical oxidation.

The structures of samples were determined by X-ray diffraction (XRD). The chemical and structural properties of samples were analyzed with Fourier transformation infrared spectroscopy (FT-IR). The morphologies of the samples were observed using a scanning electron microscope (SEM), and high resolution transmission electron microscopy (HR-TEM). The optical properties were studied by UV–Vis spectroscopy. For a typical photodecomposition experiment, 25 mg of photocatalyst is mixed with 50 ml of 10 ppm dyes solution. The light source for decomposition of dyes used was a 150 W high-pressure Xenon lamp with a cut-off filter of 420 nm. Before turning on the light, the suspension containing dyes and photocatalyst was magnetically stirred continuously in dark until no change in the absorbance of the solution is observed. The concentration change of dyes as a function of time was characterized by UV–vis spectroscopy. The DFT was also used to calculate the electronic structures at the interface of the nanohybrids TiO_2/CNTs.

3. Results and discussions

Fig. 1(a) shows the XRD patterns of the nanohybrids TiO_2/CNTs materials. The peaks in 2θ of XRD patterns were indexed as anatase TiO_2 phase and hexagonal graphite structure, similar to pristine CNTs. The peak at 26.0° of CNTs is absent in the samples with TiO_2/CNTs ratios of 20/1, 10/1, and 5/1. However, the broadening and asymmetry of the 25.5° peak of TiO_2 in the samples with the ratios of 3/1 and 1/1 clearly show the effect of CNTs on XRD spectrum of TiO_2. This indicate that our samples contain both anatase TiO_2 phase and CNTs as expected. Furthermore, Fig. 1 (b) shows the FT-IR spectroscopy of nanohybrids TiO_2/CNTs with various $[TiO_2]/[CNTs]$ ratios. The sharp peak at 1632 cm^{-1} is associated with the deformation of C=O bonds. The peaks at 1104 cm^{-1} and 1385 cm^{-1} are ascribed to the C–O stretching mode. Simultaneously, the band associated with the Ti–O stretching and O–Ti–O bending modes of the TiO_2 (which usually appears at 611 cm^{-1}) is broader and shifted to 480 cm^{-1}. This is probably due to the inclusion of CNTs.

Fig. 2(a)–(c) show the SEM images of nanohybrids TiO_2/CNTs materials at various $[TiO_2]/[CNTs]$ ratios. The result indicates that TiO_2 nanoparticles with an average diameter of around 8 nm are attached along the surfaces of CNTs. Evidences of some clusters of nanoparticles TiO_2 were also observed in Fig. 2(a) and (b). The attachment of TiO_2 on CNTs was further confirmed by a typical TEM image, as shown in Fig. 2(d). It is seen that the CNTs have a diameter of around 30 nm. The HR-TEM image in Fig. 2(e) show that the nanohybrids TiO_2/CNTs are highly crystalized. The $<101>$ direction of TiO_2 is determined to be 3.33 Å and the spacing of the carbon nanotube tube is of 3.57 Å. For comparison and to see the role of H_2SO_4/HNO_3 in the chemical oxidation process, the SEM image of TiO_2/CNTs prepared from CNT without oxidization was shown in Fig. 2(f) which shows that the TiO_2 nanoparticles are independent with CNTs. This indicates that high absorbency of TiO_2 on the surface CNTs results from surface acid modification of the CNTs.

Fig. 3(a) shows the UV–vis spectra of the nanohybrids TiO_2/CNTs materials with various $[TiO_2]/[CNTs]$ ratios. As can be seen, the red shifts were obtained when the CNTs amount increases. These shifts are due to the modification of the electronic structure of TiO_2/CNTs. Additionally, the increase in the based line absorption was observed, which may be due to the contribution of the wide range of absorption wavelengths of CNTs. To investigate photocatalytic activities of nanohybrids TiO_2/CNTs materials in visible region, photodecomposition of MB and MO dyes was monitored. Fig. 3(b) displays photo-degradation behaviors of these dyes in the presence of TiO_2 nanoparticles, CNTs, and TiO_2/CNTs materials. Almost no degradation is detected when pure CNTs are used. TiO_2 exhibits higher photocatalytic activity, allowing 7% of MB, or 6% of MO after to be removed after 4 hours. The percentage of dyes removed by the samples with $[TiO_2]/[CNT]$ ratios of 1/1, 3/1, and 5/1 are about 3–5 times larger than that decomposed by pure nanocrystal TiO_2. The sample with $[TiO_2]/[CNT]=5/1$ shows the highest photocatalytic activity, allowing degradation of 38% of MB or 33% of MO after 4 h. A large surface area of the nanohybrids TiO_2/CNTs results in an increase in photocatalytic performance. Additionally, due to the high capacity of CNTs to adsorb the dye molecules, the concentration of the dyes in the vicinity of CNTs is higher than those in other places of the reaction system. This allows a fast process called slip-induce surface diffusion, in which the dye molecules on the CNTs surface can transfer to the residual vacancies when some of the MB molecules on the surface of TiO_2

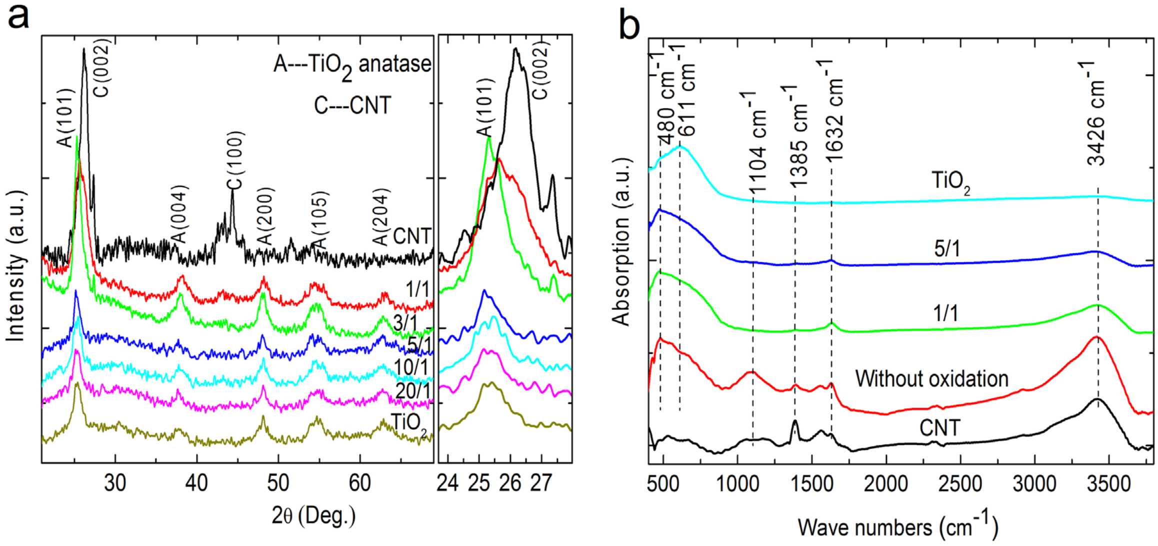

Fig. 1. (a) X-ray diffraction of pure TiO_2, pure CNTs, and TiO_2 on CNTs with ratio $[TiO_2]/[CNT]=1/1$, 3/1, 5/1, 10/1, and 20/1, and (b) the FT-IR spectra of TiO_2, CNTs, TiO_2/CNTs composite with a ratio $[TiO_2]/[CNT]=1/1$, 5/1, the FT-IR spectra of the TiO_2/CNTs prepared from CNT without surface chemical oxidation process.