

Research Article

Facile Low-Temperature Synthesis of Carbon Nanotube/TiO₂ Nanohybrids with Enhanced Visible-Light-Driven Photocatalytic Activity

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We demonstrate a facile and novel chemical precipitation strategy for the accurate coating of TiO₂ nanoparticles on the surface of carbon nanotubes (CNTs) to form CNT/TiO₂ nanohybrids, which only requires titanium sulfate and CNTs as starting materials and reacts in the alkaline solution at 60°C for 6 h. Using this process, the as-prepared hybrid structures preserved the good dispersity and uniformity of initial CNTs. Furthermore, the CNT/TiO₂ nanohybrids show a broad blue luminescence at 469 nm and exhibit significantly enhanced photocatalytic activity for the degradation of rhodamine B (RhB) under visible-light irradiation, which is about 1.5 times greater than that of commercial Degussa P25 TiO₂ nanoparticles. It is believed that this facile chemical precipitation strategy is scalable and its application can be extended to synthesize other CNT/oxide nanohybrids for various applications.

1. Introduction

Titanium oxide (TiO₂), with a wide bandgap of 3.2 eV, is a very promising material and has received considerable attention both in fundamental and photocatalysis due to its natural abundance, nontoxicity, photostability, low-cost, physical and chemical stability, availability, and unique electronic and optical properties [1–4]. Recent studies have also revealed that TiO₂ displays excellent photocatalytic activity toward the photodegradation of rhodamine-B (RhB) under the irradiation of ultraviolet (UV) light. Due to the poor utilization of solar energy and the short diffusion length of a photogenerated electron-hole pair, TiO₂ nanoparticles show low quantum efficiency in photocatalytic reactions. Therefore, it is of great importance to extend the photoresponse of the TiO₂ to the visible region. Recently, some extensive efforts to modify the electronic band structures of TiO₂ for visible-light harvesting have been conducted, including coupling with secondary semiconductors [5, 6], metal/nonmetal doping [7, 8], and photosensitization with dyes [9, 10]. Additionally, the application of TiO₂ nanoparticles for wastewater treatment has a major

drawback, that is, an additional separation step is usually required to remove the adsorbent from the solution. Moreover, pure TiO₂ nanoparticles often show lower removal efficiencies owing to the problem of self-aggregation [11], which causes serious fast diminishment of the active surface area. To meet these requirements, TiO₂ nanoparticles are frequently immobilized on carbonaceous materials [12–15]. Particularly, carbon nanotubes (CNTs) can act as scaffolds to anchor light harvesting assemblies, due to their unique electrical and electronic properties, wide electrochemical stability window, and high surface area [16–18]. By virtue of their advantageous structural features to extend the light-response range and other distinctive features, such as facile charge separation, and increased adsorption of pollutants [19–22], we design a unique hybrid structure by directly anchoring TiO₂ nanoparticles onto CNTs for degradation of RhB under visible-light irradiation. This novel strategy for preparation of CNT/TiO₂ nanohybrids only requires titanium sulfate and CNTs as starting materials and reacts in the alkaline solution at 60°C for 6 h. As expected, the as-prepared CNT/TiO₂ nanohybrids demonstrate the excellent

photocatalytic activity toward the decomposition of RhB when exposed to visible-light irradiation. In addition, the photoluminescence (PL) properties of the as-prepared TiO₂ nanoparticles and CNT/TiO₂ nanohybrids were also studied, which exhibit a broad blue luminescence at 469 nm.

2. Experimental

All reagents were of analytical grade, purchased from the Shanghai Chemical Reagent Factory, and used as received without further purification.

2.1. Synthesis of CNT/TiO₂ Nanohybrids and TiO₂ Nanoparticles. CNTs with 40–60 nm in diameter were synthesized following our previous method [23]. For a typical synthesis, 30 mg of as-prepared CNTs were dissolved in 40 mL of distilled water with the assistance of ultrasonication for 10 min, and the appropriate quantities of NaOH (0.1 M) solution were added to adjust the pH value to 11.0. Then, 0.012 g of titanium sulfate was added, and the mixed solution was continuously stirred at 60°C for 6 h. Subsequently, the as-prepared products were washed repeatedly with distilled water and ethanol for several times and then dried in an oven at 60°C for 6 h. For comparison, the pure TiO₂ nanoparticles were obtained without addition of CNTs in the reaction process, while the other conditions remain unchanged.

2.2. Characterization. Powder X-ray diffraction (XRD) measurements of the samples were performed with a Philips PW3040/60 X-ray diffractometer using CuK α radiation at a scanning rate of 0.06° s⁻¹. Scanning electron microscopy (SEM) was performed with a Hitachi S-4800 scanning electron microanalyzer with an accelerating voltage of 15 kV. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were conducted using a JEM-2100F field emission TEM. Energy dispersive X-ray spectrometry (EDS) was performed with a spectroscope attached to HRTEM. Samples for TEM measurements were prepared for TEM by dispersing the products in ethanol and placing several drops of the suspension on holey carbon films supported by copper grids. PL spectra were recorded on an Edinburgh FLSP920 fluorescence spectrometer and the absorption spectra were measured using a PerkinElmer Lambda 900 UV-vis spectrophotometer at room temperature. UV-vis diffuse reflectance spectra (UV-vis DRS) of the as-prepared samples and Degussa P25 TiO₂ nanoparticles were recorded over the range of 200–800 nm in the absorption mode using a Thermo Nicolet Evolution 500 UV-vis spectrophotometer equipped with an integrating sphere attachment.

2.3. Photocatalytic Activity of CNT/TiO₂ Nanohybrids. Photocatalytic activities of CNTs/TiO₂ nanohybrids were evaluated by the degradation of RhB under visible-light irradiation of a 500 W Xe lamp (CEL-HXF300) with a 420 nm cutoff filter. The reaction cell was placed in a sealed black box with the top opened, and the cutoff filter was placed to provide visible-light irradiation. In a typical process, 0.05 g

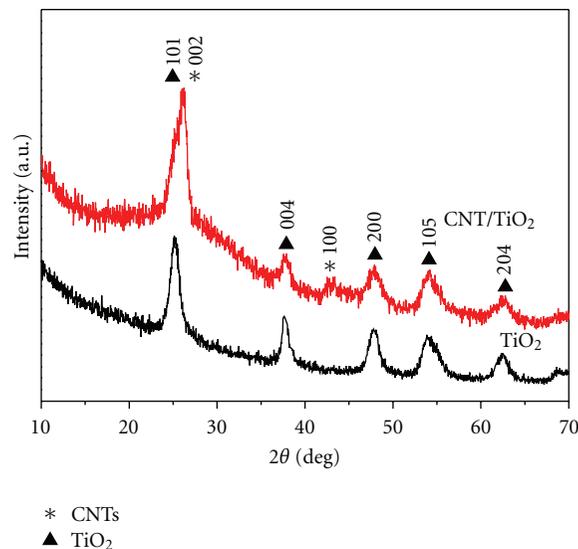


FIGURE 1: XRD patterns of the as-prepared CNT/TiO₂ nanohybrids and TiO₂ nanoparticles.

of as-prepared CNTs/TiO₂ nanohybrids as photocatalysts were added into 100 mL of RhB solution in distilled water (concentration: 5 mg/L), respectively. After being dispersed in an ultrasonic bath for 5 min, the solution was stirred for 2 h in the dark to reach adsorption equilibrium between the catalyst and the solution and then was exposed to visible-light irradiation. The samples were collected by centrifugation at given time intervals to measure the RhB degradation concentration by UV-vis spectroscopy.

3. Results and Discussion

The XRD patterns of the as-prepared CNT/TiO₂ nanohybrids and TiO₂ nanoparticles are shown in Figure 1. From the XRD patterns, the peaks at 2θ values of 26.0°, 43.0° were associated with the (002) and (100) diffractions of the hexagonal graphite structure, similar to pristine CNTs. The peaks at 2θ values of 25.5°, 37.8°, 48.1°, 54.0°, and 62.8° can be perfectly assigned to the crystal planes of the (101), (004), (200), (105), and (204) of the body-centered tetragonal TiO₂ (JCPDS standard card no.89-4921) with a cell constant of $a_0 = 0.3777$ nm, and $c_0 = 0.9501$ nm. In addition, the average size of TiO₂ nanoparticles on the surface of CNTs calculated using the Debye-Scherrer equation based on the full width at half-maximum of the diffraction peak is about 3.5 nm.

The typical SEM and TEM images of the as-prepared CNT/TiO₂ nanohybrids and TiO₂ nanoparticles are shown in Figure 2. A panoramic view by SEM reveals that the sample consists of sinuous and highly entangled CNTs uniformly decorated with TiO₂ nanoparticles on the entire surface (Figure 2(a)). The formation of CNT/TiO₂ nanohybrids is further evidenced by TEM observation (Figure 2(b)), as characterized by radial assembly of high density TiO₂ nanoparticles with an average diameter of about 3.5 nm on the long CNT surface. From these images, it can be seen

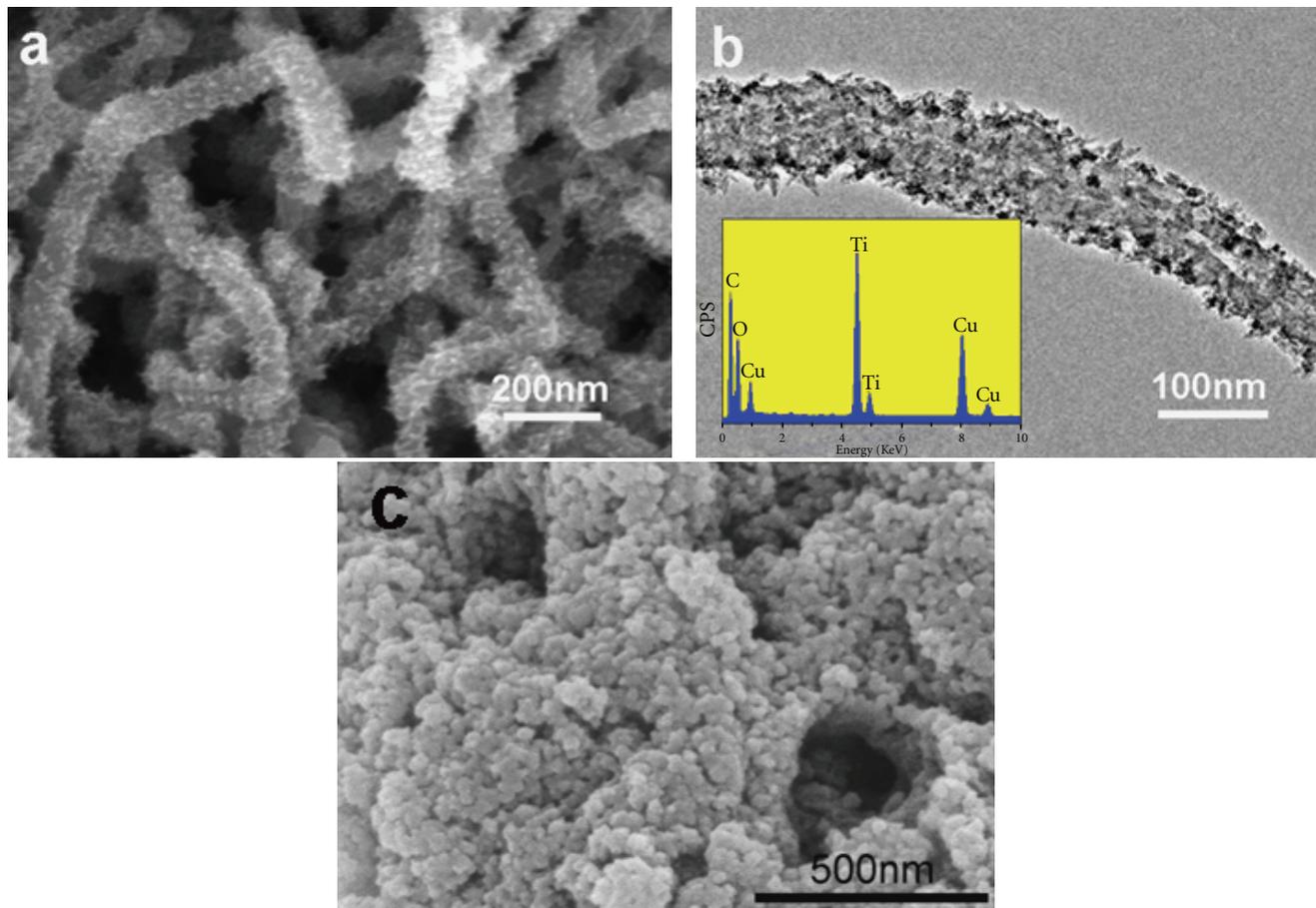


FIGURE 2: (a) Typical SEM image, (b) TEM image and EDS pattern (inset) of as-prepared CNT/TiO₂ heterostructures. (c) SEM image of the as-prepared TiO₂ nanoparticles.

that the as-prepared hybrid structures preserved the good dispersibility and uniformity of the initial CNTs, which may endow the hybrids a high specific surface area and the application potential as the photocatalyst for water treatment. Additionally, the EDS pattern (inset in Figure 2(b)) of surface layer of as-prepared CNT/TiO₂ also confirms the existence of TiO₂ nanoparticles on the CNTs. From SEM image (Figure 2(c)), the as-prepared TiO₂ nanoparticles show some agglomerated forms.

To investigate the optical properties of the as-prepared CNT/TiO₂ heterostructures and their potential application as photonic materials, the UV-vis DRS spectrum (in Figure 3(a)) were recorded at room temperature. For comparison, the optical property of the as-prepared TiO₂ nanoparticles and Degussa P25 were also obtained at the same conditions. From Figure 3(a), TiO₂ nanoparticles and Degussa P25 show the characteristic spectra with typical absorption sharp edge rising at 400 nm, which is attributed to the band-band transition. However, CNT/TiO₂ nanohybrids exhibit extended absorption range to the visible region. This result implies an increase of surface electric charge of the TiO₂ in the composite catalysts due to CNTs introduction, resulting in modifications of the

fundamental process of electron/hole pair formation under the visible-light illumination [24]. Thus, the photocatalytic activity of as-prepared CNT/TiO₂ nanohybrids could be improved. Figure 3(b) shows the PL spectra of the as-prepared TiO₂ nanoparticles and CNT/TiO₂ nanohybrids, which all feature a broad blue emission at 469 nm under an excitation wavelength of 320 nm. According to previous reports, the blue luminescence at 469 nm may result from the surface defects on the TiO₂ nanoparticles [25]. The as-prepared CNT/TiO₂ nanohybrids show obviously diminished PL intensity as compared to TiO₂ nanoparticles, indicating reduced charge recombination [21]. Therefore, CNTs in here have an important role to act as an electron reservoir to trap electrons emitted from TiO₂ particles, which result in hindering electron-hole pair recombination and improving the photocatalytic activity of TiO₂.

Figure 4(a) displays the photodegradation behaviour of RhB dye in the absence of any photocatalyst (the blank test), and in the presence of the as-prepared TiO₂ nanoparticles, commercial Degussa P25 and CNT/TiO₂ hybrids after exposure to visible light irradiation, where C is the concentration of RhB after different light irradiation times and C_0 is the initial concentration of RhB before dark adsorption. About

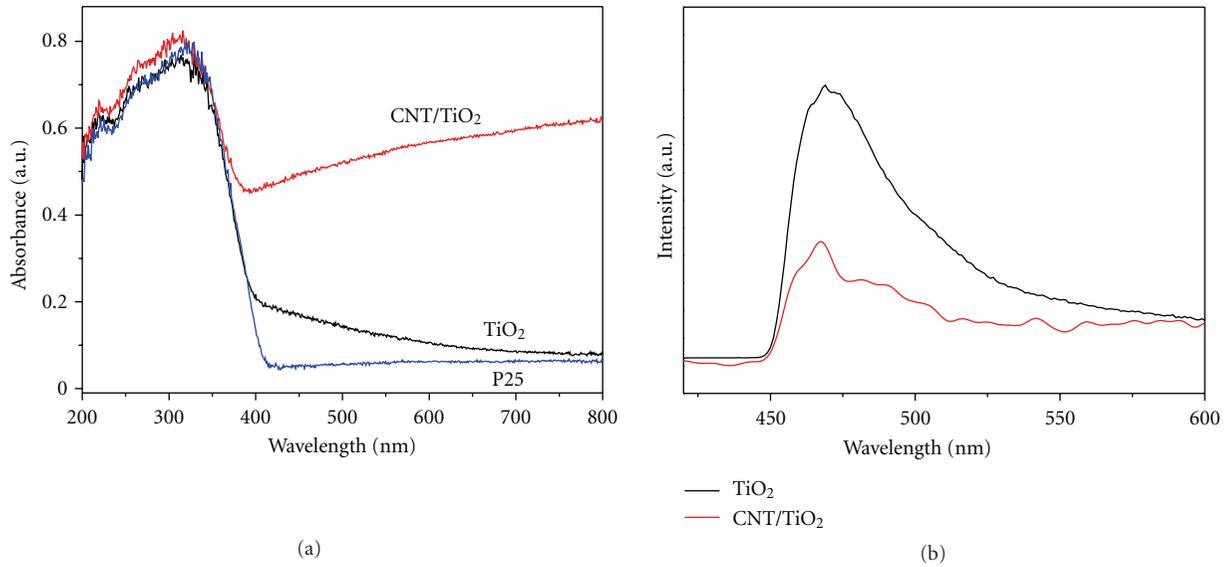


FIGURE 3: (a) UV-vis DRS spectra of the as-prepared TiO₂ nanoparticle, CNT/TiO₂ nano hybrids, and P25. (b) PL spectra of TiO₂ nanoparticle and CNT/TiO₂ nano hybrids.

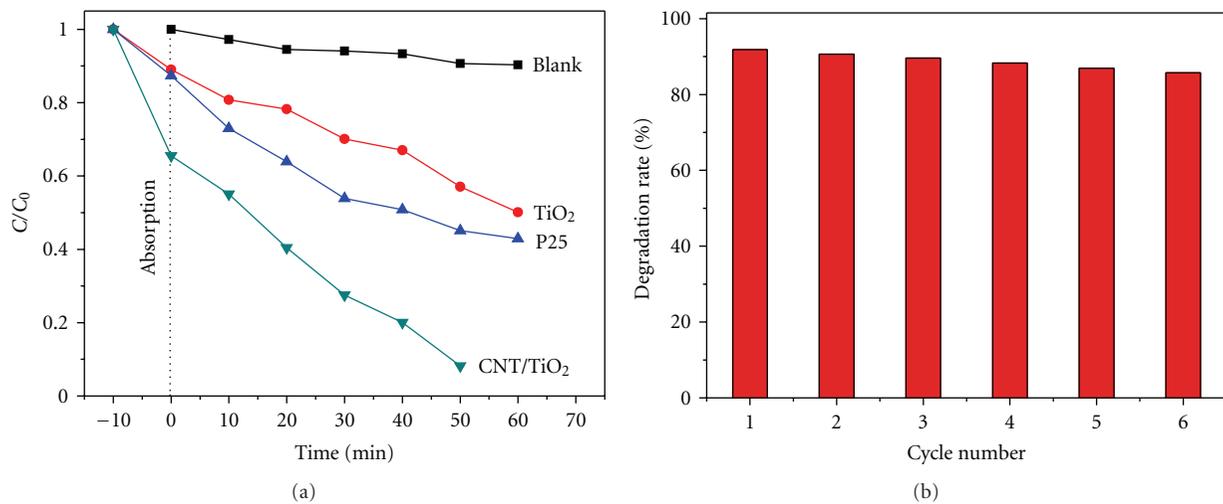
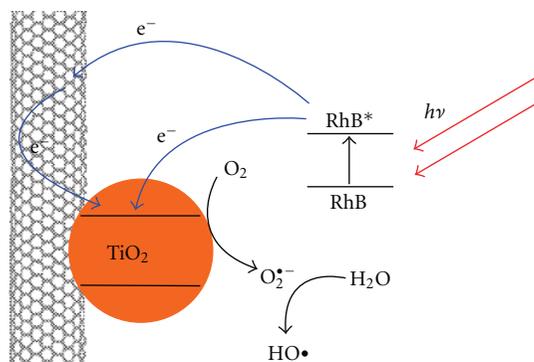


FIGURE 4: (a) The photocatalytic degradation of RhB in the absence of any photocatalysts (the blank test) and in the presence of different photocatalysts. (b) 6 cycles of degradation of RhB using CNT/TiO₂ nano hybrids as the photocatalyst.

11.3% of the RhB is adsorbed for TiO₂ nanoparticles and Degussa P25 after stirring for 2 h in the dark. However, the as-prepared CNT/TiO₂ nano hybrids adsorb about 34.6% of the RhB under the same condition. After exposure to visible-light irradiation for 50 min the decolorization rates of TiO₂ nanoparticles, Degussa P25, the CNT/TiO₂ hybrids as photocatalysts are 42.8%, 55.3%, 92.3%, indicating the significantly enhanced photocatalytic activity of the CNT/TiO₂ nano hybrids. The reusability of the CNT/TiO₂ nano hybrids as photocatalyst is also investigated by collecting and reusing the same photocatalyst for multiple cycles. As shown in Figure 4(b), after 6 runs of photodegradation of RhB, the photocatalytic activity of the CNT/TiO₂ nano hybrids shows a slight deterioration due to incomplete recollection

and loss during washing. Thus, the as-prepared CNT/TiO₂ nano hybrids used as photocatalyst are quite stable and have great potential application in water treatment.

The schematic diagram representing the charge transfer process in CNT/TiO₂ heterostructures is illustrated in Scheme 1. First, the dye of RhB as a sensitizer can absorb visible light to be excited. Then, the excited species can directly inject electrons into the conduction band or through CNT indirect inject electrons into the conduction band of the TiO₂ semiconductor, forming conduction band electrons (e_{cb}^-) and the oxidized RhB to realize the charge separation [9, 26]. This process extends the photoresponse of wide bandgap TiO₂ semiconductors from the UV to the visible region and opens a unique route to utilize visible-light from



SCHEME 1: Schematic diagram representing the charge-transfer process in CNT/TiO₂ nanohybrids.

the sun. Furthermore, the photogenerated electrons can be captured by the adsorbed oxygen molecules and holes can be trapped by the surface hydroxyl, both resulting in formation of high oxidative hydroxyl radical species ($\cdot\text{OH}$) [27]. The $\cdot\text{OH}$ shows little selectivity for the attack of dye molecules and can oxidize the pollutants due to their high oxidative ability. Additionally, high surface area and strong adsorption ability of CNTs will also help to enhance photocatalytic activity. Thus, the as-prepared hybrids exhibit the superior photocatalytic performance.

4. Conclusions

In summary, we demonstrated a facile and novel low-temperature chemical precipitation route to synthesize CNT/TiO₂ nanohybrids. This method only requires titanium sulfate and CNTs as starting materials and reacts in the NaOH solution at 60°C for 6 h. With this method, the as-prepared hybrids show good dispersity and uniformity of initial CNTs. In addition, these nanohybrids exhibited a broad blue luminescence at 469 nm and a significantly higher photocatalytic activity on the degradation of rhodamine B (RhB) in water, which was 1.5 times greater than that of the commercial Degussa P25 nanoparticles under visible-light irradiation. It is expected that this strategy can be scalable and its application can be extended to synthesize other CNT/oxide nanostructures for different applications, and the CNT/TiO₂ nanohybrids should be ideal photocatalysts in the removal of dyes and other organic pollutants.

Authors' Contribution

Y. Xie and H. Qian contributed equally to this work.

Acknowledgments

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