



In situ synthesis of CNTs/Fe–Ni/TiO₂ nanocomposite by fluidized bed chemical vapor deposition and the synergistic effect in photocatalysis



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ABSTRACT

Carbon nanotube (CNTs)/Fe–Ni/TiO₂ nanocomposite photocatalysts have been synthesized by an in situ fluidized bed chemical vapor deposition (FBCVD) method. The composite photocatalysts were characterized by XRD, Raman spectroscopy, BET, FESEM, TEM, UV–vis spectroscopy, and XPS. The results showed that the CNTs were grown in situ on the surface of TiO₂. Fe(III) in TiO₂ showed no chemical changes in the growth of CNTs. Ni(II) was partly reduced to metal Ni in the FBCVD process, and the metal Ni acted as a catalyst for the growth of CNTs. The photocatalytic activities of CNTs/Fe–Ni/TiO₂ decreased with the rise of the FBCVD reaction temperature. For the sample synthesized at low FBCVD temperature (500 °C), more than 90% and nearly 50% of methylene blue were removed under UV irradiation in 180 min and under visible light irradiation in 300 min, respectively. The probable mechanism of synergistic enhancement of photocatalysis on the CNTs/Fe–Ni/TiO₂ nanocomposite is proposed.

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1. Introduction

Titanium dioxide (TiO₂) is one of the most important transition metal oxides with a broad range of applications such as the removal of organic or inorganic pollutants (Linsebigler, Lu, & Yates, 1995; Morrison, Raghavan, & Timpone, 1997; O'Regan & Grätzel, 1991; Takata & Domen, 2009; Wu, Wang, & Rusakova, 1999). However, there are still some difficulties that hamper its applications as a photocatalyst. The large band gap of 3.25 eV means that only irradiation with a wavelength less than 385 nm can be utilized. TiO₂ also shows low adsorption capacity and low quantum yield, the latter being associated with the rapid recombination of generated photoelectrons and holes.

Many attempts have been devoted to preparing a TiO₂ photocatalyst that is capable of efficiently utilizing of visible light (Soni, Henderson, Bardeau, & Gibaud, 2008; Zhu, Chen, Zhang, Chen, & Anpo, 2006). Among them, doping with transition metal cations was reported as a good strategy to improve the photocatalytic properties for the enhancement of visible light response. Fe³⁺-doped TiO₂ film deposited on fly ash cenosphere (FAC) was synthesized using the sol–gel method (Wang, Li, Wang, Li, & Zhai, 2011). Compared with TiO₂/FAC, the degradation of methyl blue using Fe³⁺-doped TiO₂ was increased by 33% under visible light irradiation.

Wu, Zhang, Xiao, and Chen (2010) prepared nanoparticles of TiO₂ modified with iron and carbon using the sol–gel method followed by solvothermal synthesis at a low temperature. The modified TiO₂ photocatalyst showed enhanced photocatalytic activity for photodegradation of acid orange 7 under visible light. The synergistic effects of iron and carbon may improve the separation of photogenerated holes and electrons. Although doping TiO₂ with transition metal cations could migrate the absorption edge to the visible light range, it cannot improve the quantum yield so effectively (Leary & Westwood, 2011). A heterojunction of TiO₂ and CNTs can provide a potential driving force for the separation of photo-induced charge carriers, retarding or hindering the recombination of electrons and holes. The CNT–TiO₂ Schottky barrier junction is also effective in increasing the recombination time, as was demonstrated by a variety of publications based on dye degradation (Woan, Pyrgiotakis, & Sigmund, 2009). The coupling of TiO₂ with carbon nanotubes has been shown to provide a synergistic effect which can enhance the quantum efficiency of a photocatalytic process (Wang, Serp, Kalck, & Faria, 2005).

Therefore, it can be expected that the simultaneous introduction of the two modification methods of doping with transition metal cations and of coupling with CNTs may greatly enhance the photocatalytic performance of TiO₂. The composites comprising Fe and carbon nanotubes on TiO₂ were prepared using a modified sol–gel method (Zhang, Meng, & Oh, 2010; Zhang, Xiong, & Zhao, 2010). Cr₂O₃–CNT/TiO₂ composites derived from chromium acetylacetonate, multi-walled carbon nanotubes, and titanium

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n-butoxide were also prepared by solution method (Chen, Cho, & Oh, 2010). In all these works, the CNTs were functionally modified to combine with the metal oxides. A major drawback of these reported methods is that CNTs were functionally modified using mixed strong acids or other corrosive chemicals, which normally results in extensive changes in electronic properties caused by the destruction of the original graphite structure of CNTs. In this work, we demonstrated the successful synthesis of a CNTs/Fe–Ni/TiO₂ nanocomposite photocatalyst using an in situ fluidized bed chemical vapor deposition (FBCVD) method. This method is different from the generally reported methods for preparing CNTs/TiO₂ nanocomposite in a solution phase (Chen, Ho, Guo, Huang, & Pan, 2009; Eder & Windle, 2008; Tian, Ye, Deng, & Zan, 2011; Wang et al., 2005) because the CNTs were grown in situ on the surface of the TiO₂ particles doped with Fe (III) and Ni (II) in a FBCVD process. Furthermore, the synergistic effect among CNTs, Fe ions, and Ni is beneficial to expanding the absorption region to visible light, enhancing the separation of photo-generated electrons and holes of the TiO₂, and providing large adsorption capacity. All of these had been proved favorable for improving the photocatalytic activity of TiO₂. The photocatalytic activity of the prepared CNTs/Fe–Ni/TiO₂ composite photocatalysts was evaluated by the degradation of methylene blue under visible and UV light irradiation, respectively.

2. Experimental

2.1. Preparation of TiO₂ doped with Fe (III) and Ni (II)

The preparation of TiO₂ doped with Fe (III) and Ni (II) and the optimal dosage of iron and nickel were reported in our previous work (Ma, Chen, Lu, He, & Li, 2012). Briefly, 68 mL of tetrabutyl-orthotitanate (TBOT) were added to 377 mL ethanol at room temperature. Nitric acid (HNO₃) was then added to the solution in drops to prevent the hydrolysis of TBOT. Nitrate salts solution mix (0.202 g Fe(NO₃)₃·9H₂O and 2.765 g Ni(NO₃)₂·6H₂O dissolved in 215 mL distilled water) was then added slowly into the acidized TBOT ethanol solution. The mixed solution was stirred for 2 h and aged for 20 h at room temperature to form wet gel. Following aging, the wet gel was dried overnight in oven at 110 °C. Then, the dry powder was calcined at 500 °C in muffle furnace for 3 h. The prepared catalyst was denoted as FNT.

2.2. In situ synthesis of CNTs/Fe–Ni/TiO₂ nanocomposite

CNTs/Fe–Ni/TiO₂ nanocomposite was synthesized by FBCVD method (Ma, Chen, Lu, He, & Li, 2012). 10 g of FNT catalyst were packed into the reactor. After purging the system with N₂ from room temperature to reaction temperature, acetylene (C₂H₂), as a carbon source reactant, was introduced into the fluidized bed reactor. The gas mixture containing C₂H₂ reactant entered into the bottom vessel of the reactor by passing through the bed of zirconium spheres and the FNT catalyst was fully fluidized. The flow rate of the C₂H₂ feed was 0.025 m³/h diluted with 0.3 m³/h of nitrogen. After FBCVD processing at different temperatures for 10 min, CNTs/Fe–Ni/TiO₂ composites were collected after cooling to room temperature in N₂ atmosphere. The FBCVD temperature was set from 500 to 650 °C. The CNTs/Fe–Ni/TiO₂ nanocomposite catalysts were denoted as C-FNT-*x*, respectively, in which '*x*' represents the different reaction temperature in the FBCVD process.

2.3. Characterization analysis

X-ray diffraction (XRD) analysis of the prepared samples was carried out at room temperature with a Rigaku D/max 2550

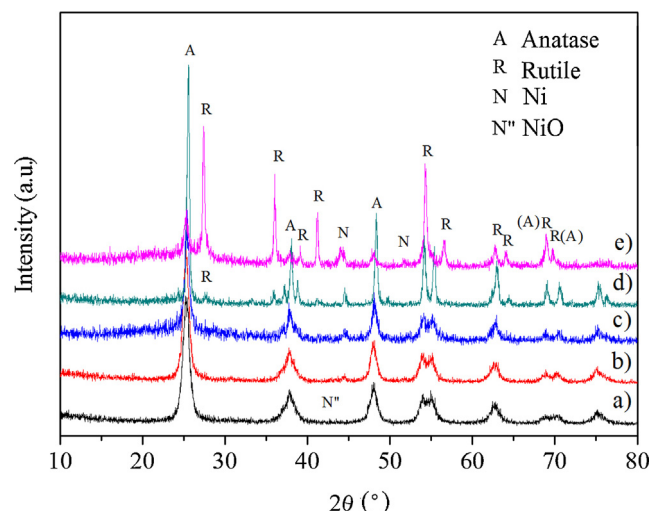


Fig. 1. XRD patterns of FNT and C-FNT-*x* samples: (a) FNT, (b) C-FNT-500, (c) C-FNT-550, (d) C-FNT-600, and (e) C-FNT-650.

VB/PC apparatus. To analyze the light absorption of the photocatalysts, UV–vis absorption spectra (DRS) were obtained using a scan UV–vis spectrophotometer (Varian Cary 500). The structure and morphology of samples were investigated using field emission scanning electron microscopy (FESEM, JEOL-JSM-6700F) and transmission electron microscopy (TEM, JEOL-JSM-2100F). Raman spectra (Via + Refex Renishaw) were obtained to analyze the structure of CNTs grown in the FBCVD process. X-ray photoelectron spectroscopy (XPS) was recorded with a Perkin Elmer PHI 5000C ESCA System with Al K α radiation operated at 250 W. The *S*_{BET} of the samples was determined with Micromeritics ASAP 2010.

2.4. Photocatalytic activity test

The photocatalytic activity of samples was evaluated by the degradation of methylene blue (MB) under visible and UV light irradiation, respectively. The photocatalytic reactions were carried out in a lab-made device. A 1000 W Xe lamp equipped with UV cut-off filters ($\lambda > 420$ nm) and a 150 W high-pressure mercury lamp ($\lambda_{\text{max}} = 365$ nm) were used as visible light source and UV light source, respectively. For each catalyst preparation, 0.1 g of powder was dispersed in 100 mL MB solution (20 mg/L) within a 150 mL quartz photo-reactor. After ultrasonic treatment for 10 min, the mixture was stirred for 1 h in the dark to reach the adsorption-desorption equilibrium. Afterwards, the quartz reactors were placed under visible light irradiation or UV irradiation with stirring. The distance between the light sources and the photo-reactor was 10 cm. 4.5 mL of the solution were taken out of the reactor during the photocatalytic process and immediately centrifuged. The concentration of solutions without catalyst particles was analyzed by UV–vis spectrophotometer (Unico, UV-2102), checking the absorbance at 665 nm. All photocatalytic reactions were executed at room temperature. The reproducibility was checked by repeating the measurements at least three times and was found to be within the acceptable limit ($\pm 2\%$).

3. Results and discussion

3.1. Photocatalyst characterization

3.1.1. Structure analysis

Fig. 1 shows the XRD pattern of the investigated samples of FNT and C-FNT-*x* (*x* = 500, 550, 600, 650). The FNT sample shows

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