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Full Length Article

Enhanced photocatalytic activity towards degradation and H_2 evolution over one dimensional TiO_2@MWCNTs heterojunction

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ABSTRACT

With the distinct electronic and optical properties, multiwall carbon nanotubes (MWCNTs) are identified as an outstanding catalyst support, which can effectively improve the performance of the TiO_2 photocatalysts. Herein, the unique one dimensional TiO_2@MWCNTs nanocomposites have been prepared by a facile hydrothermal method. The TiO_2 coating layers are extremely uniform and the thickness is adjustable for different nanocomposites. XPS measurements confirm that intimate electronic interactions are existed between MWCNTs and TiO_2 via interfacial Ti—O—C bond and the photoluminescence intensity of the TiO_2@MWCNTs nanocomposites are effectively quenched compared with pure TiO_2, suggesting the fast electron transfer rates. The thickness of TiO_2 coating layers of the TiO_2@MWCNTs nanocomposites plays a significant role in the photocatalytic degradation of organic pollutants, such as methylene blue (MB) and Rhodamine B (RhB), and photocatalytic H_2 evolution from water. Due to the formation of one dimensional heterojunction of TiO_2@MWCNTs nanocomposites and the positive synergistic effect between TiO_2 and carbon nanotubes, it is found that the photocatalytic activity of the system is significantly improved.

1. Introduction

With the increasingly serious environmental pollution and energy shortage, converting clean solar energy into chemical energy to obtain hydrogen [1–6] and dispose pollutants [7] are the attractive and challenging issues. Semiconductor photocatalysts, which possess suitable physical and photochemical properties, have attracted considerable interest over the past decades. Among all of the photocatalysts, titanium dioxide (TiO_2) has become the most widely investigated and suitable one [8,9] since the breakthrough of water splitting on TiO_2 photoelectrode reported by Fujishima and Honda [10]. Based on its unique properties, such as strong oxidizing power, non-toxicity, inexpensive and long-term photostability [9,11,12], TiO_2 has been widely used in many filed such as environmental purification [13,14], photocatalytic H_2 evolution [1,15–17], CO_2 reduction [18,19], sensor [20], photovoltaic [21], Li-ion battery [22,23] and so on. Various efforts have been paid to improve the photocatalytic activity of TiO_2, such as self-structural modification, tailored facets, non-metal doping as well as combining with other materials to form hetero-junctions [24–39].

Carbon nanotubes (CNTs), which process special 1 D structure and excellent conductive property, is considered as one of the promising materials to promote the photogenerated electron transfer [39–42]. In particular, the use of CNTs as substrates to form nanocomposites and thus to enhance the photocatalytic activity of TiO_2 has attracted considerable attention [43–49]. It is proposed that CNTs can transfer the electron away from TiO_2 and lead to an effective separation of photo-induced electron-hole pairs. Furthermore, CNTs could provide spatial confinement for TiO_2 nanoparticles and thus effectively hinder the aggregation on the CNTs surface.

In all of the composite structure, tailored uniform core-shell structure could provide the most efficient photo-induced electron transfer from TiO_2 photocatalyst to the CNTs due to the maximum effective contact between the TiO_2 and CNTs. Up to now, although much research have reported to construct TiO_2-CNTs composite systems and achieved positive results [50–54], the facial and controllable synthesis of TiO_2@MWCNTs core-shell structure still suffers from great challenges due to the fact that the morphology of TiO_2 is hard to control and easy to agglomerate on the CNTs.

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Table 1
Sample labels for the composites prepared by different $TiCl_4$ concentration.

Sample name	$TiCl_4$ concentration	TiO_2 (wt%)	CNT (wt%)
T@C-12	0.025 mol/L	12	88
T@C-56	0.050 mol/L	56	44
T@C-66	0.075 mol/L	66	34

Herein, to synthesis uniform core-shell TiO_2@CNTs composite with an enhanced catalytic activity is still an urgent need.

In this work, we report a facial and controllable method to prepare one dimensional highly uniform coaxial core-shell TiO_2@MWCNTs nanocomposites with different TiO_2 coating thickness. The photocatalytic results reveal a new insight to investigate the influence of the thickness of TiO_2 coating layer on the photocatalytic activity. It is worth noting that, the TiO_2 coating layers are extremely uniform and its thickness could be controlled by the concentration of Ti precursors. Photocatalytic degradation methylene blue (MB) and Rhodamine B (RhB) solution as well as photocatalytic H_2 evolution from water are used as probes to evaluate the photocatalytic activity of different TiO_2@MWCNTs nanocomposites. The results indicate the electron transfer efficiency not only depends on the thickness but also the amount of the loaded TiO_2 on MWCNTs. Under optimized conditions, the one dimensional TiO_2@MWCNTs exhibits higher photocatalytic activity than that of anatase TiO_2 and P25.

2. Experimental section

2.1. Materials synthesis

The hydroxyl multi-walled carbon nanotubes (MWCNTs) were purchased from Chengdu Organic Chemicals Co. Ltd. and used without further processing. In a typical synthesis, the MWCNTs were dispersed in ethanol (AR) by ultrasonic treatment for about 15 min, and then $TiCl_4$ ethanol solution was added to the alcoholic solution. After sonication for other 30 min, the black suspension was then transferred to a 100 mL Teflon-lined autoclave and heated in an oven at 150 °C for 3 h. After cool down to room temperature, the product was collected by centrifugation, washed with ethanol and deionized water several times, respectively, and then dried through freeze drying. Then the as-synthesized TiO_2@MWCNTs nanocomposites was further calcined in N_2 at 600 °C for 5 h and the heating rate was 5 °C/min. The $TiCl_4$ concentration of different sample is varied as listed in Table 1. It should be worthy note that the TiO_2 bulk agglomerates can be easily formed when water existed in the $TiCl_4$ precursor solution. Furthermore, the reaction temperature also plays a significant role for the formation of well dispersed TiO_2 nanoparticles on MWCNTs. Under optimized conditions, we successfully obtained the TiO_2@MWCNTs core-shell structure, which possess extremely uniform TiO_2 coating layers. The accurate weight content of the loaded TiO_2 NPs are measured by thermogravimetric (TG) analysis and the three samples containing different TiO_2 are 12%, 56% and 66% weight percent and labeled as T@C-12, T@C-56 and T@C-66, respectively.

2.2. Materials characterization

The morphology and structure of the samples were examined by using a field emission scanning electron microscopy (FE-SEM, Hitachi S-4800, and 5 kV) and transmission electron microscopy (TEM, Tecnai G2 20 S-TWIN, 200 kV). The X-ray powder diffraction (XRD) patterns were obtained on a Bruker D8 Advance diffractometer with Cu Kα radiation ($\lambda = 1.54056$ Å). Raman spectrum was recorded on a Renishaw inVia Raman microspectrometer and laser excitation wavelength was 633 nm. UV–vis diffuse reflectance spectra (DRS) of the samples were collected using a UV–vis spectrometer (Hitachi U-3900) with an integrating sphere at room temperature. Nitrogen adsorption-desorption isotherms were collected on a nova 3200e at 77 K. Thermo gravimetric analysis (TGA, thermal analyzer, Perkin Elmer Diamond TG) was performed at a heating rate of 10 °C/min from room temperature to 800 °C under an air flow. X-ray photoelectron spectroscopy (XPS) was carried out on an Escalab 250 Xi X-ray photoelectron spectrometer with Mg Kα X-rays as the excitation source. Photoluminescence (PL) spectra of the samples were recorded using a fluorescence spectrophotometer (Horiba Instrument, Fluoromax-4, excitation at 300 nm).

2.3. Photocatalytic activity measurements

The photocatalytic activities of the synthesized TiO_2@MWCNTs nanocomposites, pure anatase TiO_2 nanoparticles and Degussa P25 (reference photocatalysts) were investigated using methylene blue (MB) and Rhodamine B (RhB), (Sinopharm Chemical Reagent Beijing Co., Ltd) as model pollutant under ultraviolet (UV) light irradiation. Prior to irradiation, 0.01 g of the samples and 50 mL 10 mg/L of MB or RhB solution were mixed by sonication for 3 min and then continuously stirred in the dark for 30 min to ensure the establishing of an adsorption-desorption equilibrium. Then the suspension was irradiated by Xe lamp (CEL-HXUV300) with a 365 nm light filter and the emission light was in the range of 345–375 nm 3 mL solution was taken out every 5 min and centrifuged at 10000 r/min for 10 min twice to remove the solid catalysts. The concentration of MB and RhB was monitored by a UV–vis spectrometer (Hitachi U-3900) from the absorbance at 663.5 and 553 nm, respectively.

Photocatalytic H_2 production experiments were conducted in a sealed vessel connected to a glass-enclosed gas circulation system (LABSOLAR-H_2 III AG, Perfect Light, China). 0.7% Pt was loaded on samples as a cocatalyst by in situ photoreduction of chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) using methanol as scavenger. In a typical experiment, 0.02 g of sample loaded with Pt was suspended in 100 mL 20% methanol aqueous solution under magnetic stirring, and the reaction temperature was maintained at 5 °C with a recirculation cooler. A 300W Xe lamp (CEL-HXUV300) with a light filter (365 nm) was used in the photocatalytic reactions, and the distance between the lamp and the vessel was 16 cm. The amount of H_2 was analyzed by a gas chromatography (TechcoMp, GC 7900) with a thermal conductivity detector (TCD), 5 Å molecular sieve columns and N_2 carrier.

2.4. Photoelectrochmical measurements

The photocurrent and electrochemical impedance spectroscopy (EIS) were performed on an electrochemical workstation (Wuhan corrtest CS310, China) in a typical three-electrode system with prepared samples as the working elctrode, a Pt plate as counter electrode and Ag/AgCl as reference electrode. 0.5 M Na_2SO_4 aqueous solution was used as the electrolyte. A 300W Xe lamp served as a UV-light source with the centre wavelength of 365 nm. Working elctrode containing tested catalysts were prepared as follows: 2 mg of investigated catalysts were dispersed in 0.2 mL of water/ethanol (v/v = 1:1) solution containg 10 μL of Nafion solution (5 wt%) and then coated onto a 1 cm × 1 cm ITO glass by doctor blade method.

3. Results and discussion

The external morphology of TiO_2@MWCNTs nanocomposites was firstly studied by SEM measurement. Fig. 1 shows representative SEM images of the pristine MWCNTs and the nanocomposites prepared with different TiO_2 contents. From the low-resolution SEM images (Fig. 1a, c, e and g), the samples have a similar external