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Visible light photocatalytic behavior of manganese carbonate/titanium dioxide nanocomposites based on photoinduced interfacial charge transfer



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ARTICLE INFO

Article history:

Received 23 March 2015

Accepted 21 April 2015

Available online 30 April 2015

Keywords:

Nanocomposites

MnCO₃

Semiconductor

Visible-light-active photocatalyst

IFCT

ABSTRACT

Here, a novel visible-light-driven photocatalyst MnCO₃/TiO₂ heterostructure nanocomposite has been prepared *via* a precipitation method. The synthesized MnCO₃/TiO₂ exhibited superior activity for the degradation of propylene under visible light compared to bare P25 TiO₂ and pure MnCO₃. This high visible light activity is due to the interfacial charge transfer (IFCT) from the MnCO₃ to the conduction band of TiO₂. After repeated cycles of photo-oxidation of propylene, the photocatalytic behavior of MnCO₃/TiO₂ exhibited no loss of activity. This work provides new perspective to fabricate visible-light-active photocatalyst by use of IFCT effect between carbonate and semiconductor.

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1. Introduction

Titanium dioxide has been widely applied as a promising photocatalyst due to its high oxidization ability, chemical stability, low cost and non-toxicity. However, owing to the large band gap, it can be activated only by UV light accounting for about 5% of solar light. Therefore, many efforts have been developed to extend the absorption of TiO₂ into visible region. Research found that modifying TiO₂ with noble metals, such as Au and Ag, can efficiently extend the photo-response to visible light [1–3]. Under visible light irradiation, Au or Ag particles can be excited owing to plasmon resonance and the excited electrons would migrate from noble metal to the conduction band of TiO₂, leading to the visible light activity. However, the noble metals are expensive and rare. Another widely used strategy is combining TiO₂ with narrow band gap semiconductor, such as CdSe, CdS and PbS [4–6], to extend the absorption into visible light region. However, the toxicity and harmful effect of cadmium or lead on the environment and human beings restricts their practical application. Hence, it is imperative to develop environmentally friendly photocatalyst with high visible light activity.

MnCO₃, the representative of transition-metal carbonate, is extensively used in electronics industry, medicine and ceramics, owing to its low cost, environment-friendly property and abundance in nature. Furthermore, manganese carbonate can be obtained by recycling the industrial waste water containing manganese [7], but it is seldom

reported having any application in photocatalysis for degrading organic pollutants. In this paper, we combine MnCO₃ on the surface of P25 TiO₂ by a precipitation method and find that the resultant MnCO₃/TiO₂ heterostructure exhibits excellent performance, far superior to P25 TiO₂ and pure MnCO₃, in photo-oxidation of propylene under visible light irradiation. The good photocatalytic activity of MnCO₃/TiO₂ is ascribed to the interfacial charge transfer (IFCT) from MnCO₃ to the conduction band of TiO₂.

2. Experimental

MnCO₃/TiO₂ heterostructures with different mass ratios were synthesized *via* a precipitation method. Briefly, 0.5 g of P25 was firstly dispersed in distilled water and then mixed with 0.1 M Na₂CO₃ under magnetic stirring, forming a mixed suspension. Subsequently, the same volume of MnCl₂ solution was dripped into above suspension to yield MnCO₃/TiO₂ precipitate. By changing the amount of Na₂CO₃ and MnCl₂ added, MnCO₃/TiO₂ composites with different ratios (1:10, 1.5:10 and 2:10) have been prepared and labeled as MnCO₃/TiO₂ (X:Y), where X:Y means the mass ratio of MnCO₃ to TiO₂ in the composite. For comparison, pure MnCO₃, prepared with MnCl₂ and Na₂CO₃, and Degussa P25 TiO₂ are also used.

The morphology and structure of samples were characterized using scanning electron microscopy (SEM, NOVA NANOSEM-450), transmission electron microscopy (TEM, JEOL JEM-2010) and X-ray diffraction (XRD, DX-2500 diffractometer). The absorption property and chemical state of samples were investigated using diffuse reflectance spectroscopy (DRS, CARY5000) and X-ray photoelectron

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spectroscopy (XPS, Kratos Amicus apparatus, Mg K_{α}), respectively. The binding energies were calibrated with reference to the adventitious C 1s line at 284.8 eV.

The photocatalytic activity of samples was evaluated by monitoring the oxidation of propylene under visible light irradiation. In all experiments, each sample was spread on a glass plate located in a flat quartz tube reactor surrounded with a water channel to eliminate infrared light. A 500 W xenon lamp was used as the visible light source (intensity ($\lambda \geq 420$ nm): ca. 25 mW/cm²) and an ultraviolet cut 420 filter was inserted between the lamp and reactor to eliminate UV light. The feed gas was composed of C₃H₆ and air and stored in a high-pressure cylinder. Prior to irradiation, the feed gas was allowed to flow (200 mL/h) through the reactor continuously until the adsorption/desorption equilibrium was established. Considering the volume of reactor (55 ml) and the irradiation area (15 cm²), the actual residence time of feed gas is ca. 8 min. The removal rate of C₃H₆ is calculated as $(C_0 - C_t)/C_0 \times 100\%$. Where, C_0 and C_t are the initial and the residual C₃H₆ concentrations at any time t , respectively. C_t was determined by a gas chromatograph (GC7900) equipped with a flame ionization detector (FID).

3. Results and discussion

Fig. 1a shows SEM image of the as-synthesized MnCO₃ microspheres with a diameter of ca. 1 μ m. As shown in the inset, the color of MnCO₃ is brownish yellow, which is consistent with what is reported elsewhere [8]. Fig. 1b displays the morphology of as-prepared MnCO₃/TiO₂ heterostructure. It can be seen that the majority of MnCO₃ is nanoparticle (NP) with average size of ca. 4–5 nm uniformly dispersed on the surface of TiO₂, leaving the minority with nanotubular (NT) morphology crossing on the

surface of TiO₂. A variety of morphologies of manganese carbonate, including cube [8], sphere [9], spindle, block, nanorod [10] and so on, have been reported. The shapes of manganese carbonate can be affected by the reaction time, reaction temperature and the ratio of reactants. In this work, different morphologies of MnCO₃ on the surface of P25 TiO₂ may be resulted from different local concentration of reactants. It is to be noted that, all the MnCO₃ NPs are firmly attached to P25 TiO₂, resulting in darker color (nigger-brown) of MnCO₃/TiO₂ (the inset of Fig. 1b) than that of pure MnCO₃ (brownish yellow) and TiO₂ (white). This indicates the strong interaction formed between MnCO₃ NPs and TiO₂ substrate, facilitating the visible-light-induced interfacial charge transfer.

Fig. 1c shows the XRD patterns of MnCO₃ microspheres and MnCO₃/TiO₂ nanocomposites. The diffraction peaks of MnCO₃ can be indexed to a hexagonal phase [JCPDS no. 44-1472], which is in agreement with what is reported elsewhere [11]. For MnCO₃/TiO₂ series, showing a miscible structure covering hexagonal phase MnCO₃, anatase (A) and rutile (R) phase TiO₂, the intensity of MnCO₃ peak (104) is gradually stronger with the increase of mass ratio of MnCO₃ to TiO₂ from 1:10 to 2:10. The diffuse reflectance spectra of pure P25, MnCO₃, and MnCO₃/TiO₂ samples are comparatively shown in Fig. 1d. Due to the wide band gap, P25 have no visible light absorption. While, pure MnCO₃ shows apparent ultraviolet–visible light absorption. Comparing with P25 and MnCO₃, MnCO₃/TiO₂ heterostructures exhibit much stronger visible light absorption, especially in 400–500 nm region. The bigger the mass ratio of MnCO₃ to TiO₂ is, the stronger the absorption is. The absorption band at 400–500 nm can be assigned to the interfacial charge transfer (IFCT) from MnCO₃ to the conduction band of TiO₂. Jun Zhang and their coworkers studied the absorption property and TEM result of CuS/ZnS nanosheet [12], and pointed that the intimate contact between CuS and ZnS is crucial

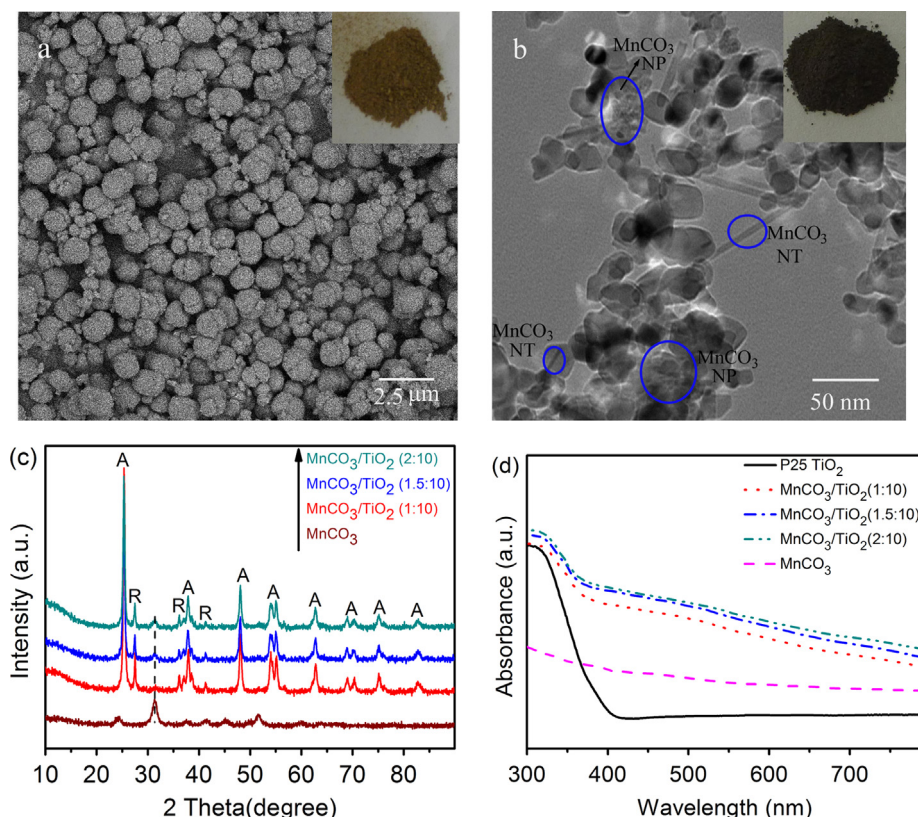


Fig. 1. SEM and TEM image of MnCO₃ (a) and MnCO₃/TiO₂ (1:10) (b) as well as their pictures (inset). XRD patterns (c) and UV-vis DRS (d) of as-prepared samples. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

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