Enhanced photocatalytic activity of wool-ball-like TiO_2 microspheres on carbon fabric and FTO substrates

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Abstract: The wool-ball-like TiO_2 microspheres on carbon fabric (TiO_2-CF) and FTO substrates (TiO_2-FTO) have been synthesized by a facile hydrothermal method in alkali environment, using commercial TiO_2 (P25) as precursors. The XRD results indicate that the as-prepared TiO_2 have good crystallinity. And the SEM images show that the wool-ball-like TiO_2 microspheres with a diameter of 2-3 μm are composed of TiO_2 nanowires, which have a diameter of ~50 nm. The photocatalytic behavior of the wool-ball-like TiO_2 microspheres, TiO_2-CF and TiO_2-FTO under ultraviolet light was investigated by a pseudo first-order kinetic model, using methyl orange (MO) as pollutant. The wool-ball-like TiO_2 microspheres obtained a degradation rate constant (K_{ap}) of 6.91×10^{-3} min^{-1}. The K_{ap} values of TiO_2-FTO and TiO_2-CF reach 13.97×10^{-3} min^{-1} and 11.80×10^{-3} min^{-1}, which are 2.0 and 1.7 times higher than that of pristine wool-ball-like TiO_2 microspheres due to the "sum effect" between TiO_2 and substrates. This study offers a facile hydrothermal method to prepare wool-ball-like TiO_2 microspheres on CF and FTO substrates, which will improve the recyclability of phtocatalysts and can be extended to other fields.

1 Introduction

With the increase of environment pollution, photocatalytic degradation of environmental pollutants has been the focus in the field of environmental applications. Titanium dioxide (TiO_2), as a well-known good photocatalyst in semiconductor nanomaterials, has been intensively investigated in photocatalysis due to its low cost, high biocompatibility and chemical inertness. Semiconductor nanomaterials are morphology dependent physicochemical properties [1]. By accurate control of size, shape, crystallinity, and degree of exposure of reactive crystal facets, one can tune the properties of nanomaterials.[2-4] Recently, the synthesis of (001) facet-dominated anatase TiO_2 based on powdered shape has attracted intensive attention in photocatalysis due to the higher reactive facets of (001) to effectively enhance surface properties.[3, 5-8] [9, 10]

Compared with powdered TiO_2 nanomaterials, one-dimensional TiO_2 nanomaterials have higher photocatalytic activity due to reduced agglomeration and increased surface area.[11] Moreover, the unique structure of one-dimensional TiO_2 nanomaterials provide longitudinal transmission channel for charge transport and inhibit the recombination of charge carriers.[12] Hence, many efforts have been devoted to synthesis of one-dimensional TiO_2 nanomaterials, including sol-gel method [13], hydrothermal method [14] and electrochemical anodic oxidation[15]. In order to obtain one-dimensional TiO_2 nanomaterials, various templates are developed [15-17]. Template-free synthesis of one-dimensional TiO_2 nanomaterials also gained great attention [18, 19]. In addition, these traditional methods of synthesizing one-dimensional TiO_2 nanomaterials often used titanium compounds (titanium alkoxide, titanium halide, et.al) as Ti precursors. Recently, TiO_2 as a starting material to prepare nanostructured TiO_2 with template-free attracted great interest of researchers [20, 21]. Li et.al used commercial P25 as precursor dissolved in a 10 M NaOH alkaline solution and gained TiO_2 nanowires after 24h hydrothermal treatment at 269°C in a Teflon-lined stainless steel autoclave.[11]

However, recycling these one-dimensional TiO_2 nanomaterials from aqueous solution after photocatalytic reactions are not easy and these photocatalysts cause secondary pollution. [5, 22-24] To address this problem, growing these one-dimensional TiO_2 nanomaterials on certain substrates is an ideal way.[25] In this work, we demonstrated a facile synthesis of wool-ball-like TiO_2 microspheres composed of one-dimensional TiO_2 nanowires on fluorine doped SnO_2 (FTO) and carbon fabric using P25 as precursor by a modified hydrothermal method. With the "sum effect" between TiO_2 and substates on decomposition of methylene

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orange (MO), TiO_2 growing on substrates exhibits better photocatalytic efficiency than that of wool-ball-like TiO_2 microspheres.

2 Experimental Procedures

2.1Material preparation

In a typical synthesis process of wool-ball-like TiO_2 microspheres on substrates, 1.4 g of P25 (Degussa Industries) was dissolved in a 10 M NaOH alkaline solution; after the solution had been stirred for 1 h, the fully mixed solution was transferred into a Teflon-lined stainless steel autoclave. Next, the treated substrates (FTO, CF) were immersed into the mixed solution and the hydrothermal reaction was carried out under 120℃ for 24 h. Finally, the product was obtained after being washed by MilliQ water (resistivity: 17 MΩ*cm) for several times and dried in an oven at 80℃ overnight. To get Anatase TiO_2, the dried product was calcined at 550℃ for 5 h.

2.2 Characterizations and measurements

The phase and microstructure of as-prepared samples were examined using powder X-ray diffraction (XRD) on a PANalytical X-ray diffractometer (Cu K_α radiation, 45kV, 40mA) and Field Emission Scanning Electron Microscopy (FESEM, JSM-7100F, JEOL). The ultraviolet light photocatalytic activity of as-prepared samples was investigated by the photodegradation of methylene orange (MO) in aqueous solution. In a typical experiment[11], 50 mg of photocatalysts were dispersed into 50 mL of MO solution (10 mg/L). Next, the mixed solution was kept in the dark at room temperature under stirring for 1 h to get the balance of adsorbing-desorbing. Photocatalytic activity was estimated in the presence or absence of ultraviolet light irradiation provided by XPA photochemical reaction apparatus equipped with 100 W mercury lamp. During the photoreaction process, 5 mL of solution was collected every 10 minutes. The collected solution was centrifuged at 8000 rpm to remove remaining photocatalysts and the concentration of MO was determined by UV-Vis spectroscopy at 465 nm using a standardized calibration curve.

3 Results and discussion

3.1 Characterization of crystal structure and morphology

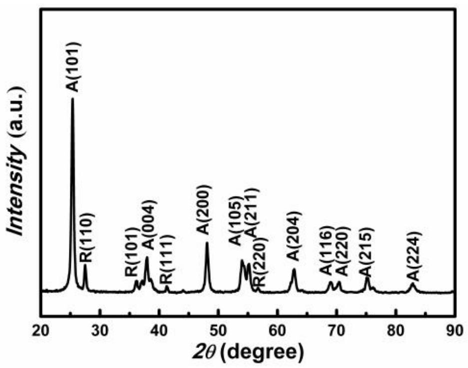

Fig. 1. X-ray diffraction spectra of as-prepared wool-ball-like TiO_2 microspheres.

Fig. 1 shows the X-ray diffraction (XRD) patterns of as-prepared wool-ball-like TiO_2 microspheres, indicating that the main phase is Anatase. The 2θ values of 25.3°, 37.9°, 48.0°, 54.0°, 55.1°, 62.8°, 68.8°, 70.3°, 75.2° and 82.7° are characteristic of Anatase (JCPDS Card no. 21-1272) and correspond to (101), (004), (200), (105), (211), (204), (116), (220), (215) and (224) crystal planes[11, 26]. It is noted that the 2θ value of 25.3° has the highest peak in all diffraction peaks, which is considered an index of good crystallinity for Anatase. The low-energy (101) crystal facets, approximately 0.44 J m^{-2},[27] leads to the highest peak at 2θ = 25.3°. Additionally, small amounts of rutile phase are observed. For example, Rutile (JCPDS Card no. 21-1276) peaks are found at 2θ values of 27.5°, 36.0°, 41.1° and 56.8°, which correspond to crystal planes of (110), (101), (111), and (220). [11, 26]

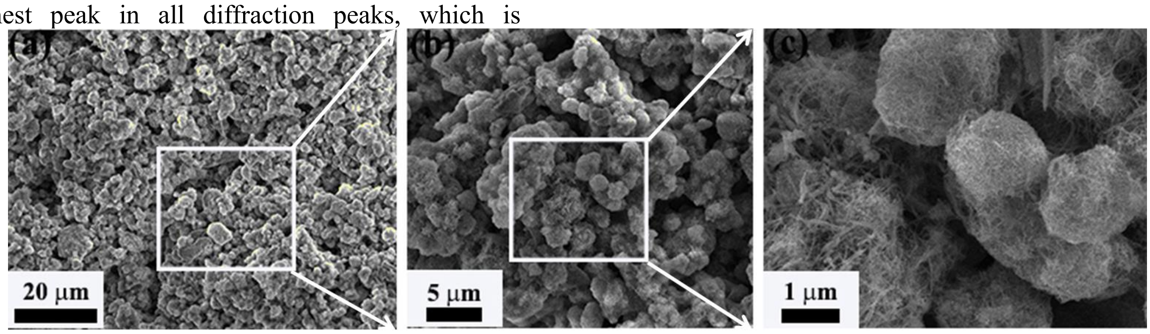

Fig. 2 SEM images of as-prepared wool-ball-like TiO_2 microspheres. (a) The wool-ball-like TiO_2 microspheres; (b) the magnification image of specific area in (a); (c) the magnification image of specific area in (b), the wool-ball-like TiO_2 microspheres are composed of TiO_2 nanowires.

Fig. 2 depicts the scanning electron microscopy (SEM) morphologies of the wool-ball-like TiO_2 microspheres. As shown in Fig. 2a, the large-scale synthesis of wool-ball-like TiO_2 microspheres can be realized by this facile hydrothermal method. Fig. 2b represents the wool-ball-like TiO_2 microspheres that have a diameter of 2-3 μm. These wool-ball-like TiO_2 microspheres are composed of one-dimensional TiO_2 nanowires with a diameter of ~50 nm (as shown in Fig. 2c), which increase the specific surface area. Due to the large specific surface area and multiple active sites provided by this 3D hierarchical structure, these wool-ball-like TiO_2 microspheres would enhance their photocatalytic properties[28].

3.2 Evaluation of photocatalytic activity

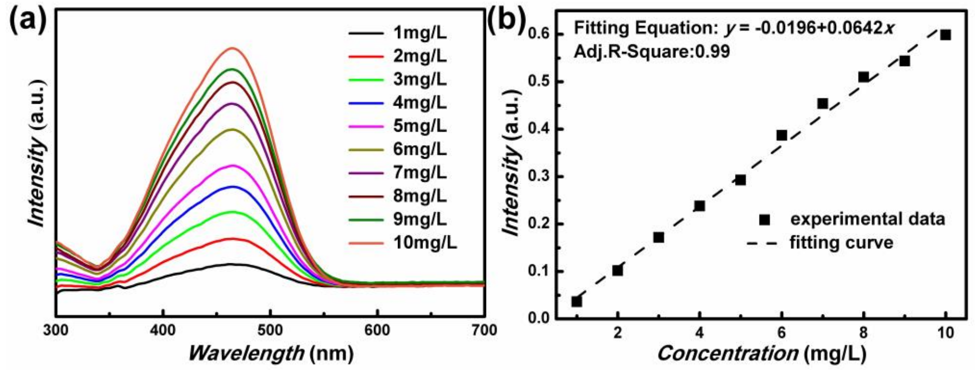

Fig. 3 (a) The absorbance curve of different MO concentration; (b) the calibration curve for MO concentration.

The ultraviolet light photocatalytic activity of all samples was studied using MO as pollutant. As shown in Fig.3a, the absorbance intensity at 465 nm, which is the characteristic absorption wavelength of MO, increases systematically with increasing MO concentration. Based on the data provided by Fig.3a, the calibration curve for the MO concentration was generated (as shown in Fig.3b).

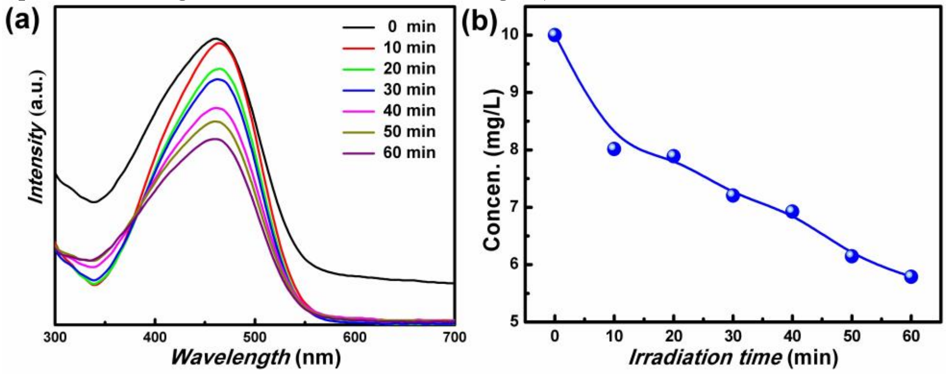

Fig. 4 (a) The absorbance curve of the wool-ball-like TiO_2 microspheres after different irradiation time; (b) MO concentration in TiO_2 microspheres solution as a function of irradiation time, in which the MO concentration was estimated by the calibration curve.

Fig. 4a shows the absorbance curve of the wool-ball-like TiO_2 microspheres after different irradiation time from 0 min to 60 min. The intensity of peak at ~ 465 nm decreases with prolonging radiation, implying the photocatalytic behavior under ultraviolet light. As shown in Fig. 4b, the MO concentration in TiO_2 microspheres solution decreases nearly linearly with increasing radiation time, indicating the good photocatalytic activity.

However, the recyclability of these TiO_2 microspheres is not very good [5, 22-24]. Growing these TiO_2 nanomaterials on certain substrates, such as FTO and CF [27], is an ideal way to address this problem.[25]

3.3 Optimization of photocatalytic activity

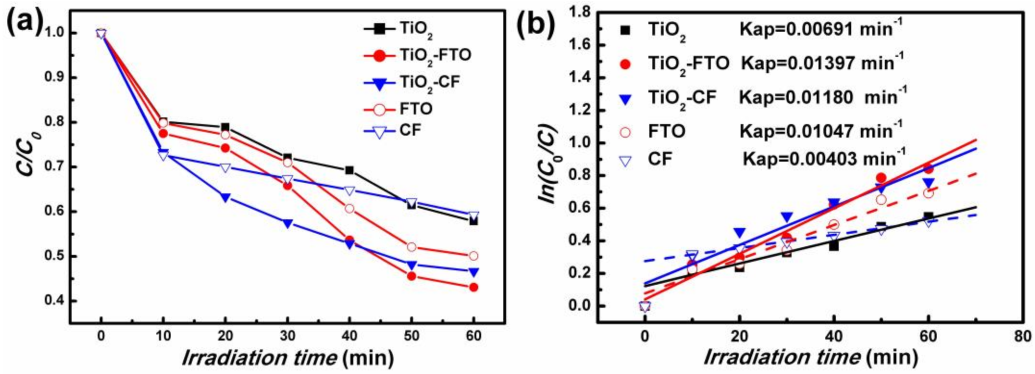

Fig.5 The photocatalytic kinetics of TiO_2, TiO_2-FTO, TiO_2-CF, FTO and CF.

In this work, the wool-ball-like TiO_2 microspheres were grew on FTO and CF substrates, respectively. Fig. 5 shows the photocatalytic kinetics of TiO_2, TiO_2-FTO, TiO_2-CF, FTO and CF. As shown in Fig. 5a, 42.2%, 57.0%, 53.4%, 50.0% and 40.8% of MO are decomposed by TiO_2, TiO_2-FTO, TiO_2-CF, FTO and CF after irradiation for 60 min, respectively. Compared with TiO_2, TiO_2-FTO and TiO_2-CF exhibit better degrading efficiency. The apparent reaction rate constant (K_{ap}) is applied to quantitatively evaluate the photocatalytic activity of these photocatalyts[11]. The apparent reaction rate constant is described by the apparent pseudo-first-order equation $\ln(C_0/C)=K_{ap}t$, where K_{ap} is the apparent rate constant, C_0 is the concentration of MO after darkness adsorption for 1 h and C is the concentration of MO after irradiation. Fig. 5b shows the linear relation of $\ln(C_0/C)$ versus irradiation time for degradation of MO using different photocatalysts. The determined rate constants (K_{ap}) and linear regression coefficient (R^2) from these curves are presented in Fig. 5b. All the kinetic data agrees well with the pseudo-first-order model because the R^2 values are higher than 0.95. The K_{ap} values of TiO_2-FTO and TiO_2-CF for the photodegradation of MO reaches 13.97×10^{-3} min^{-1} and 11.80×10^{-3} min^{-1}, which are 2.0 and 1.7 times higher than that of TiO_2, respectively. This result indicates that growing TiO_2 on FTO and CF can enhance photocatalytic activity. In order to get a better understanding of the enhanced photocatalytic activity, the photocatalytic behavior of (FTO and CF) were also quantitatively estimated by the apparent reaction rate constant (as shown in Fig. 5b). It is observed that the K_{ap} value of TiO_2-FTO is almost the sum of that of TiO_2 and FTO. This "sum effect" is also occurred for TiO_2-CF. These results indicate that the "sum effect" between TiO_2 and substrates can improve the photocatalytic activity.

4 Conclusions

The wool-ball-like TiO_2 microspheres on carbon fabric (TiO_2-CF) and FTO substrates (TiO_2-FTO) were successfully synthesized by a facile hydrothermal method. These obtained 3D hierarchical microspheres have a diameter of 2-3 μm, which are composed of TiO_2 nanowires with a diameter of ~50 nm. The photocatalytic behavior of the wool-ball-like TiO_2 microspheres, TiO_2-CF and TiO_2-FTO were estimated by a pseudo first-order kinetic model. Due to the "sum effect" between TiO_2 and substrates, the photocatalytic activity of TiO_2-CF and TiO_2-FTO was significantly enhanced. The K_{ap} value of TiO_2-CF and TiO_2-FTO were 2.0 and 1.7 times higher than that of the wool-ball-like TiO_2 microspheres. This work not only offers a facile hydrothermal method to prepare wool-ball-like TiO_2 microspheres on CF and FTO substrates, but also provides an 3D hierarchical structure based on TiO_2, which can be extended to other fields (hydrogen evolution, energy storage, et.al).

Acknowledgements

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