Enhanced photocatalytic activity of wool-ball-like TiO₂ microspheres on carbon fabric and FTO substrates

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Abstract: The wool-ball-like TiO₂ microspheres on carbon fabric (TiO₂-CF) and FTO substrates (TiO₂-FTO) have been synthesized by a facile hydrothermal method in alkali environment, using commercial TiO₂ (P25) as precursors. The XRD results indicate that the as-prepared TiO₂ have good crystallinity. And the SEM images show that the wool-ball-like TiO₂ microspheres with a diameter of 2-3 μm are composed of TiO₂ nanowires, which have a diameter of ~50 nm. The photocatalytic behavior of the wool-ball-like TiO₂ microspheres, TiO₂-CF and TiO₂-FTO under ultraviolet light was investigated by a pseudo first-order kinetic model, using methyl orange (MO) as pollutant. The wool-ball-like TiO₂ microspheres obtained a degradation rate constant (Kap) of 6.91×10⁻³ min⁻¹. The Kap values of TiO₂-FTO and TiO₂-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 TiO₂ microspheres due to the “sum effect” between TiO₂ and substrates. This study offers a facile hydrothermal method to prepare wool-ball-like TiO₂ microspheres on CF and FTO substrates, which will improve the recyclability of photocatalysts 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 (TiO₂), 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 TiO₂ 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 TiO₂ nanomaterials, one-dimensional TiO₂ nanomaterials have higher photocatalytic activity due to reduced agglomeration and increased surface area.[11] Moreover, the unique structure of one-dimensional TiO₂ 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 TiO₂ nanomaterials, including sol-gel method [13], hydrothermal method [14] and electrochemical anodic oxidation.[15] In order to obtain one-dimensional TiO₂ nanomaterials, various templates are developed [15-17]. Template-free synthesis of one-dimensional TiO₂ nanomaterials also gained great attention [18, 19]. In addition, these traditional methods of synthesizing one-dimensional TiO₂ nanomaterials often used titanium compounds (titanium alkoxide, titanium halide, et.al) as Ti precursors. Recently, TiO₂ as a starting material to prepare nanostructured TiO₂ 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 TiO₂ nanowires after 24h hydrothermal treatment at 269°C in a Teflon-lined stainless steel autoclave.[11]

However, recycling these one-dimensional TiO₂ 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 TiO₂ nanomaterials on certain substrates is an ideal way.[25] In this work, we demonstrated a facile synthesis of wool-ball-like TiO₂ microspheres composed of one-dimensional TiO₂ nanowires on fluorine doped SnO₂ (FTO) and carbon fabric using P25 as precursor by a modified hydrothermal method. With the “sum effect” between TiO₂ and substrates on decomposition of methylene
orange (MO), TiO2 growing on substrates exhibits better photocatalytic efficiency than that of wool-ball-like TiO2 microspheres.

2 Experimental Procedures

2.1 Material preparation

In a typical synthesis process of wool-ball-like TiO2 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 °C for 24 h. Finally, the product was obtained after being washed by MilliQ water (resistivity: 18 MΩ·cm) for several times and dried in an oven at 80 °C overnight. To get Anatase TiO2, the dried product was calcined at 550 °C 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 Kα 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 shows the X-ray diffraction (XRD) patterns of as-prepared wool-ball-like TiO2 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 (10 1), (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 m²,[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 TiO2 microspheres. (a) The wool-ball-like TiO2 microspheres; (b) the magnification image of specific area in (a); (c) the magnification image of specific area in (b), the wool-ball-like TiO2 microspheres are composed of TiO2 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](image1.png)

**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](image2.png)

**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](image3.png)

**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 photocatalysts[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).

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These results indicate that the photocatalytic activity of TiO\(_2\) nanowire microspheres grown on FTO and CF substrates significantly enhanced compared to that of TiO\(_2\). The degradation of MO using TiO\(_2\) nanowire microspheres on FTO and CF shows that the apparent reaction rate constant (K\(\text{app}\)) from these curves are presented in the time of (FTO and CF) were also estimated by a first-order equation ln\(\frac{C}{C_0}\) = -K\(\text{app}\)t, where K\(\text{app}\) is the apparent reaction rate constant, C\(_0\) is the initial concentration of MO, C is the concentration of MO after t seconds, K\(\text{app}\) is the apparent reaction rate constant, t is the time, and C\(_0\) is the initial concentration of MO.

Due to the enhanced photocatalytic activity, the value of TiO\(_2\) under a facile hydrothermal synthesis is 1.7 times higher than that of TiO\(_2\) nanowire microspheres. The pseudo-first-order kinetic model is described by: ln\(\frac{C}{C_0}\) = -K\(\text{app}\)t, where K\(\text{app}\) is the apparent reaction rate constant, C\(_0\) is the initial concentration of MO, C is the concentration of MO after t seconds, K\(\text{app}\) is the apparent reaction rate constant, t is the time, and C\(_0\) is the initial concentration of MO. This work was financially supported in part by the Fundamental Research Funds for the Doctoral Scientific Development of Hubei University of Science and Technology (BK201503), the National Natural Science Foundation of China (21503892), the Project of the Hubei Provincial Department of Science and Technology (2017CFB74051701092), and the National High-tech Research and Development Program (2014CFB63151701092). The authors gratefully acknowledge financial supported by the Hubei Innovation Research Team Program in Higher Education (T201706) and the Young Scholars Fund of Hubei University of Science and Technology (2017CFB49851701092). The University of Science and Technology (2017CFB49851701092). The University of Science and Technology (2017CFB49851701092).

In order to get a better understanding of the enhanced photocatalytic activity, the coefficient (R\(^2\)) of linear regression of ln\(\frac{C}{C_0}\) vs. t is also almost the same to that of the linear regression of ln\(\frac{C}{C_0}\) vs. 1/t, which shows that pseudo-first-order kinetic model is the reaction order kinetic model of TiO\(_2\). The apparent reaction rate constant (K\(\text{app}\)) is described by K\(\text{app}\) = R\(^2\) - 1, which is the concentration of MO.

The results show that the photocatalytic activity of TiO\(_2\) nanowire microspheres was significantly enhanced compared to that of TiO\(_2\) nanowire microspheres grown on FTO and CF substrates. The degradation of MO using TiO\(_2\) nanowire microspheres on FTO and CF shows that the apparent reaction rate constant (K\(\text{app}\)) from these curves are presented in the time of (FTO and CF) were also estimated by a first-order equation ln\(\frac{C}{C_0}\) = -K\(\text{app}\)t.