Fabrication of oxygen-deficient TiO₂ coatings with nano-fiber morphology for visible-light photocatalysis

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ABSTRACT

In this study, heat treatment in carbon powder is developed as a safe, simple, and effective strategy to fundamentally enhance the visible-light photocatalytic activity of titanium dioxide (TiO₂) coatings. The target TiO₂ coatings were fabricated using the prepared Ti coatings by a heat treatment process involving pretreatment in carbon powder, followed by oxidation in air, and reduction in carbon powder. The results show that Ti₂CO coatings are formed and micro-cracks appear in the surface of the coatings during pretreatment. The Ti₂CO coatings and micro-cracks are beneficial for forming rutile TiO₂ coatings with nano-fiber morphology during subsequent oxidation. During reduction, oxygen vacancies, which promote the narrowing of band gap, are generated in the lattice of rutile TiO₂. The visible-light photocatalytic activity of the target TiO₂ coatings is effectively enhanced more than 8 times, compared with the TiO₂ coatings prepared solely by oxidation of Ti coatings. The ability to fabricate highly visible-light photocatalytic TiO₂ materials by simple and safe heat treatment in carbon powder opens up new opportunities in various areas, such as the preparation of powders, nanowires, films.

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1. Introduction

Titanium dioxide (TiO₂) has been extensively investigated as a photocatalyst for environmental cleanup, sterilization, and water splitting to produce hydrogen, because of its favorable band-gap positions, excellent chemical stability, non-toxicity, and low cost [1–3]. However, the photoreaction efficiency of TiO₂ is substantially limited by its large band gap energy (Eg > 3 eV), because of which it can only absorb UV irradiation, and fast electron–hole recombination due to a high density of trap states [3–6]. Therefore, an enormous amount of research has been dedicated to enhancing the visible-light absorption for TiO₂, mainly by coupling with small band gap semiconductors, and/or narrowing the band gap via elemental doping [7–11]. However, dopant could lead to the formation of recombination centers, yield valence band holes, and/or reactive oxygen species [12–14]. On the other hand, it has been shown that manipulating the morphology and electronic structure of TiO₂ is effective approach for improving the separation and transportation of charge carriers [15,16]. In general, the nature of oxygen vacancy can be characterized by its unique electronic structure, i.e., the defect state in the band gap [17,18]. Accordingly, much effort has been devoted to the introduction of oxygen vacancies into TiO₂. Oxygen vacancies could serve as the shallow donors to form extra electron energy levels and narrow the band gap [18–20]. In addition, surface oxygen vacancies can act as the photoinduced charge traps and adsorption sites, which could effectively prevent the recombination of charge carriers [21–23]. After Chen et al. reported the preparation of “black” anatase TiO₂, many studies have successively proven that hydrogen treatment is an effective method to form surface oxygen defects and enhance the photocatalytic activity [4,9,24,25]. However, hydrogen treatment requires a high-pressure hydrogen atmosphere; therefore, simpler and safer methods are required to enhance the photocatalytic activity of TiO₂ [26,27].

In this study, the strategy of enhancing the visible-light photocatalytic activity of TiO₂ coatings is to control its morphology and introduce oxygen vacancies by heat treatment in carbon powder. The relationship among visible-light photocatalytic activity and nano-fiber morphology as well as narrowed band gap is discussed.
2. Experimental

2.1. Preparation of Ti coatings

Ti powder (Osaka titanium technologies, average diameter of 30 μm, and purity of 99.1%) and alumina (Al2O3) balls (Nikkato, average diameter of 1 mm, and purity of 98.5%) were used as the coating materials and substrates, respectively. A planetary ball mill (Type: P6, Fritsch, Germany) was used to perform mechanical coating operation. Ti coatings were fabricated by the mechanical coating technique (MCT), with a rotation speed of 480 rpm for 10 h, and named as “Ti coatings”. The detailed MCT procedure can be found in our previous work [28].

2.2. Preparation of target TiO2 coatings

The target TiO2 coatings were prepared as shown in Fig. 1a. First, the prepared Ti coatings were pretreated in carbon powder (Kanto fuel, average diameter of 150 μm, and purity of 100%) at 1073 K for 2 h. The detailed procedure of heat treatment in carbon powder has been described in detail previously [29]. The pretreated samples were then cleaned in acetone for 15 min using an ultrasonic cleaner (frequency: 40 kHz), and were named “Ti-P”. In this work, this treatment is referred to as “pretreatment”.

Subsequently, the Ti-P samples were oxidized at 1073 K for 15 h in air using an electric furnace, and were named “P-TiO2”. For comparison, the Ti coatings were also oxidized under the same conditions and were named “TiO2”.

Finally, the P-TiO2 and TiO2 samples were both treated in carbon powder again at 973 K for 30 min, and were named “P-TiO2-R” and “TiO2-R”, respectively. In this work, the treatment after oxidation is referred to as “reduction”.

2.3. Characterization

The crystal structure of the prepared samples was analyzed using an X-ray diffraction (XRD, JDX-3530, Jeol, Japan) equipped with Cu-Kα radiation at 30 kV and 20 mA, at a scanning rate of 0.02° s⁻¹ in the 2θ range of 23°–65°. The surface morphologies were observed by scanning electron microscopy (SEM, JSM-5300, Jeol, Japan). The O 1s and Ti 2p were analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB 250XI, Thermo, US). The ultraviolet-visible absorption spectra of the prepared samples were measured by an ultraviolet-visible spectrophotometer (UV-vis, Model MSV-370, Jasco, Japan) with a wavelength range of 370–800 nm.

2.4. Photocatalytic activity

Photocatalytic activity was evaluated by measuring the degradation rate of methylene blue (MB) solution (C0: 10 μmol/L, 35 mL) under visible-light irradiation at room temperature. The photocatalytic reactor system schematically is shown in Fig. 1. The prepared samples were dried under UV light (FL20S BLB, Toshiba) for 24 h, and adsorption of MB solution (20 μmol/L, 35 mL) was carried out in the dark for 18 h. Two 20 W fluorescent lamps (NEC FL20SWW/18) were used as the irradiation source (irradiance of 5000 lx), and a UV cut-off filter (L42, Hoya) was used to ensure that only visible light (λ > 420 nm) could reach the samples. To clearly show the photocatalytic activity of the samples, the difference (Δk) between the degradation rate constants k_{sample} and k_{MB solution} was used. To establish the stability of the photocatalytic activity, cycling tests were carried out, according to the procedure described in a previous publication [24]. Once a testing cycle was completed, the next cycle began after fresh MB solution was adsorbed to ensure an initial concentration of ~10 μmol/L.

3. Results and discussion

3.1. Appearance and phase structure

The samples show color changes during the heat treatment process (pretreatment–oxidation–reduction), as shown in Fig. 2a. The color changes from silvery (Ti coatings) to brown (Ti-P), after pretreatment in carbon powder. After subsequent oxidation of Ti coatings and Ti-P in air, the color changes to light-white (TiO2) and dark-white with slight yellow (P-TiO2), respectively [30,31]. Then, the color becomes light-gray (TiO2-R) and gray (P-TiO2-R), after reduction in carbon powder. Fig. 2b shows the XRD patterns of the samples during heat treatment. For Ti-P sample, the diffraction peaks at 36.1°, 42.0°, and 60.9° could be attributed to the (111), (200), and (220) crystal planes of Ti2CO, respectively. After oxidation in air, the diffraction peaks at 27.4°, 36.1°, 41.2°, and 54.3° could be well indexed to the (110), (101), (111), and (211) crystal planes of rutile TiO2, respectively, indicating that only rutile TiO2 is formed. During subsequent reduction in carbon powder, there is no evident change in the formed phases. Considering the appearance and XRD patterns, the color becomes brown (Ti-P) after pretreatment is related to the formation of new phases on the surface (Fig. 2b). The difference in color between TiO2 and P-TiO2 is related to surface structure and thickness of the crystal coatings [28]. The color change after reduction in carbon powder indicates that reduction affects the formation of oxygen vacancies, which produce the color centers of Ti3+ in the TiO2 [32,33], and this is similar to these results obtained by hydrogen treatment [4,25].

3.2. Morphology evolution

After subsequent oxidation in air, the effect of pretreatment on the morphology of the P-TiO2 sample is shown in Fig. 3. Micro-cracks are clearly observed on the surface of P-TiO2 sample (Fig. 3b) but not on the surface of TiO2 sample (Fig. 3a). Compared with TiO2 sample, the crystal size of P-TiO2 is smaller and the crystal morphology changes from columnar for TiO2 sample (Fig. 3c) to the nano-fiber for P-TiO2 sample, especially along micro-cracks (Fig. 3b and d). Moreover, the effect of pretreatment on the morphology was determined by SEM analysis of the Ti-P and P-TiO2 samples, as shown in Fig. 4. The micro-cracks formed during pretreatment (Fig. 4a) may be related to thermal stress and heat treatment in carbon powder [34]. After subsequent oxidation, the nano-fiber morphology grows along the micro-cracks, and the width is ~40 times than that of micro-crack itself. Therefore, the
micro-crack in the Ti coatings is one of the factors promoting the formation of the nano-fiber morphology.

Morphology change of TiO₂ and P-TiO₂ samples shows that the Ti₂CO coatings and micro-cracks formed during pretreatment have a remarkable effect on the oxidation process of Ti. It is known that Ti can easily react with oxygen to form titanium oxide (TiOₓ). However, the reaction sites of oxidation affect the growth of titanium oxide. Oxidation processes distinguished by the reaction sites could occur on the surface of Ti, the interface of Ti and TiO₂, or inside the TiO₂ [35,36]. It is believed that the key oxidation process dominating the growth of TiO₂ depends on the predominant diffusion of Ti or oxygen [37,38]. The predominance of Ti versus oxygen diffusion is influenced by the oxygen concentration, oxidation temperature, and thickness of the TiO₂ films [36,38].

**Fig. 2.** (a) Appearance and (b) XRD patterns of the samples after heat treatment process. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

**Fig. 3.** Comparison of morphology of samples (a) and (c) TiO₂; (b) and (d) P-TiO₂.
Titanium oxide could be formed with various morphologies, e.g. pin-shaped, lamellar and needle, or nanofiber, during different oxidation processes [36,39,40]. The $\text{Ti}_2\text{CO}$ coatings formed on the surface of Ti coatings during pretreatment cause the oxidation process to occur under a relatively low oxygen concentration, which skips the oxidation process involving the predominant diffusion of oxygen and Ti diffusion predominantly occurs. Compared with the TiO$_2$ sample, the formation of nano-fiber morphology on the P-TiO$_2$ sample is due to the change from predominantly oxygen diffusion to predominantly Ti diffusion [36,37]. Similarly, the formed micro-cracks could also contribute to predominantly Ti diffusion, leading to the formation of the nano-fiber morphology along the micro-cracks.

3.3. Bonding environment and optical properties

XPS is used to investigate the photocatalyst coatings of TiO$_2$ and P-TiO$_2$–R, as shown in Fig. 5. For the O 1s high-resolution XPS
environment in the TiO2 and P-TiO2-R samples [24]. The replacement of oxygen to form the oxygen vacancies [24, 41].

enhancement on the photocatalytic activity, with a degradation rate constant that is more than 8 times, compared with TiO2 sample. To interpret the references to color in this figure, the reader is referred to the web version of this article.

In summary, we have demonstrated that the heat treatment in carbon powder narrows the band gap of the TiO2 coatings, and micro-cracks form in the surface of the Ti coatings during the pretreatment in carbon powder. The micro-cracks promote the formation of nanofiber morphology TiO2 during subsequent oxidation in air. Oxygen vacancies generated in the oxide layer during the reduction in carbon powder is in favor of narrowing the band gap, which effectively enhances the visible-light photocatalytic activity by more than 8 times. The nanofiber morphology further enhances the reduction effect, which is in agreement with the photocatalytic activity and the narrowed band gap. More importantly, the ability of fabricating highly visible-light photoactive TiO2 materials by heat treatment in carbon powder opens up new opportunities in various areas.

4. Conclusions

In summary, we have demonstrated that the heat treatment in carbon powder is a safe, simple, and effective strategy to fundamentally enhance the visible-light photocatalytic activity of oxygen-deficient TiO2 materials. Ti2CO coatings and micro-cracks form in the surface of the TiO2 coatings during the pretreatment in carbon powder. The micro-cracks promote the formation of nanofiber morphology TiO2 during subsequent oxidation in air. Oxygen vacancies generated in the oxide layer during the reduction in carbon powder is in favor of narrowing the band gap, which effectively enhances the visible-light photocatalytic activity by more than 8 times. The nanofiber morphology further enhances the reduction effect, which is in agreement with the photocatalytic activity and the narrowed band gap. More importantly, the ability of fabricating highly visible-light photoactive TiO2 materials by heat treatment in carbon powder opens up new opportunities in various areas.

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