



Enhanced photocatalytic activity of photocatalyst coatings by heat treatment in carbon atmosphere



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ABSTRACT

An inexpensive and effective method is used to enhance the photocatalytic activity of photocatalyst coatings by heat treatment in carbon atmosphere. Nano-bump structure with mixed crystal of titanium oxycarbide and rutile TiO₂ form on the surface of Ti coatings, during heat treatment in carbon atmosphere. In the case of heat treatment in air, micro-column structure with rutile TiO₂ form on the surface of Ti coatings. The change of surface morphologies substantially increases the accessible surface area. During heat treatment in carbon atmosphere, oxygen vacancies generated in the lattice of mixed crystal are in favor of narrowing band gap. The narrowed band gap effectively benefits the generation of more photo-induced electrons and holes to enhance the photocatalytic activity under both ultraviolet and visible-light irradiation, compared with the pristine TiO₂ coatings.

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1. Introduction

Titania (TiO₂) is well-known for its extensive applications in photocatalyst, gas sensors, and dye-sensitized solar cells, because of its favorable band-gap positions, excellent chemical stability, and low cost [1–3]. However, the photoreaction efficiency of TiO₂ is limited by its large band gap energy (> 3 eV), and fast electron-hole recombination due to a high density of trap states [4–6].

Recently, titanium oxycarbide (TiC_xO_y) is found as an intermediate product in the process of carbothermic reduction of TiO₂ [7–9], and large amount of research has been conducted on the crystal structure of TiC_xO_y system [10,11]. TiC_xO_y has been attracting much interest for their possible use in catalysis and electrocatalysis, both as catalysts and supports [12–14]. TiC_xO_y is known as kinds of solid solution of titanium carbide (TiC) and titanium monoxide (TiO), and the structure of TiC_xO_y is recognized as that Ti atoms occupy the 4a (0 0 0) sites, and C/O atoms randomly occupy the 4b (0.5 0.5 0.5) sites [15]. It is reasonable for us to believe that TiC_xO_y must contain some vacancies at both Ti and C/O sites [16]. In general, there are two approaches to prepare TiC_xO_y: one is the carbothermic reduction of TiO₂, and another involves a heat treatment of TiC and TiO under a relatively high temperature [7,8]. Both of two approaches require high vacuum

and high temperature, and the harsh conditions inevitably result in a high cost. Therefore, it is necessary to develop an alternative method to prepare TiC_xO_y with low-cost.

In this paper, an inexpensive and effective method of heat treatment in carbon atmosphere is demonstrated to enhance the photocatalytic activity of photocatalyst coatings, by controlling the surface morphologies and introducing oxygen vacancies. The relationship among the photocatalytic activity of photocatalyst coatings and the nano-bump structure as well as the narrowed band gap is discussed.

2. Experimental

2.1. Preparation of photocatalyst coatings

Titanium (Ti) powder (average diameter of 30 μm, and purity of 99.1%) was coated on alumina (Al₂O₃) balls (average diameter of 1 mm, and purity of 98.5%) by mechanical coating technique (MCT) [17], with a rotation speed of 480 rpm for 10 h, and named as "Ti coatings". The prepared Ti coatings were heat treated in carbon atmosphere (carbon powder, average diameter of 150 μm, and purity of 100%) at 1073 K for 15 h, using an electric furnace in air, then cooled to room temperature in the furnace (Supplementary Fig. S1), and named as "C-1073K15h". For comparison, the Ti coatings were also heat treated in air at 1073 K for 15 h, and named as "O-1073K15h".

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2.2. Characterization and photocatalytic activity

The crystal structure of the prepared samples was analyzed by an X-ray diffraction (XRD, JDX-3530) equipped with Cu-K α radiation at 30 kV and 20 mA. The surface morphologies were examined by scanning electron microscopy (SEM, JSM-5300). The O 1s and Ti 2p were analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi). The ultraviolet-visible (UV-vis) absorption was measured by an UV-vis spectrophotometer (UV-vis, Model MSV-370). Photocatalytic activity of photocatalyst coatings was evaluated by measuring the degradation rate of methylene blue (MB) solution under ultraviolet (UV) and visible-light irradiation at room temperature [17,18].

3. Results and discussion

3.1. Appearance and phase structure

The samples show brown (C-1073K15h) and light-white (O-1073K15h), after respectively heat treated in carbon atmosphere and air, as shown in Fig. 1. After heat treated in carbon atmosphere, the diffraction peaks at 36.1°, 42.0°, and 60.9° could be attributed to the (111), (200), and (220) crystal planes of Ti_xO_y, respectively. Whereas 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. It means C-1073K15h samples is with mixed crystal of Ti_xO_y and rutile TiO₂ forms on the surface of Ti coatings (average thickness is 50 μ m), while O-1073K15h is with only rutile TiO₂. The difference in color between C-1073K15h and O-1073K15h samples is related to the crystal structure and surface morphologies [17,18].

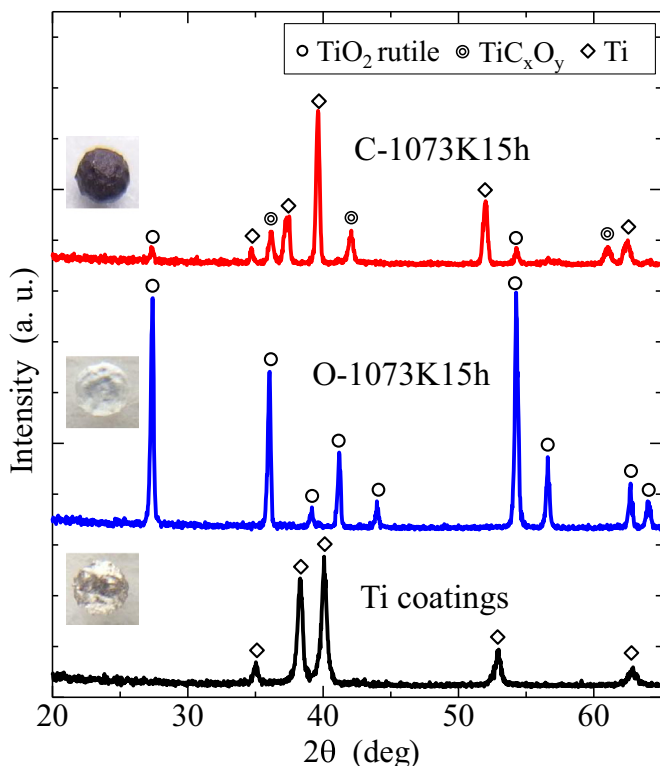


Fig. 1. Appearance and XRD patterns of samples after heat treatment in air and carbon atmosphere.

3.2. Surface morphology evolution

Fig. 2 shows the surface morphologies of O-1073K15h (average thickness is 18 μ m) and C-1073K15h (average thickness is 1.7 μ m) samples, after respectively heat treated in air and carbon atmosphere. It clearly shows the size of surface morphology substantially decreases from micro to nano, due to the change from the micro-column structure of O-1073K15h samples to the nano-bump structure of C-1073K15h samples.

It is known that Ti can easily react with oxygen to form titanium oxide, and the key oxidation process dominating the growth of titanium oxide depends on the predominant diffusion of Ti or oxygen. The predominance of Ti versus oxygen diffusion is influenced by the oxygen concentration, which would affect the structure of titanium oxide [19,20]. During the heat treatment in air, the sufficient amount of oxygen makes oxygen diffusion to be predominant, which is caused to form rutile TiO₂ with the micro-column structure [18]. In comparison, during the heat treatment in carbon atmosphere, the Ti_xO_y is formed by the reaction of Ti, oxygen and carbon, and the carbon atmosphere would cause the reaction process to occur under a relatively low oxygen concentration, which skips the reaction process of the diffusion of Ti to be predominant [19]. Therefore, the significant differences of surface morphology could be attributed to the difference in the crystal structure and the predominant diffusion of Ti and oxygen.

3.3. Photocatalytic activity and bonding environment

The photocatalytic activity of the as-prepared samples was evaluated by degradation of methylene blue (MB) solution under UV and visible-light irradiation, as shown in Fig. 3(a) and (b). It can be seen that C-1073K15h samples exhibit a substantial enhancement on the photocatalytic activity, compared with O-1073K15h samples. Fig. 3(c) and (d) show the change of surface chemical bonding of the C-1073K15h and O-1073K15h samples. The O 1s high-resolution XPS spectra show the peak located at 529.4 eV in the O-1073K15h samples, which is due to Ti–O bond. While the O 1s bonding energy of the C-1073K15h samples shows a significant shift to 529.8 eV, which could be related to the replacement of oxygen to form the oxygen vacancies [21,22]. The formed oxygen vacancies could narrow the band gap [21–23]. The Ti 2p XPS spectra are almost identical (Fig. 3(d)), which indicates that the Ti atoms have a similar bonding environment after the heat treatment in air and carbon atmosphere [21].

The higher photocatalytic activity of the C-1073K15h samples may be attributed to the following reasons. The formed nano-bump morphology with mixed crystal of Ti_xO_y and rutile TiO₂ on the surface of C-1073K15h samples significantly increases the accessible surface area (Fig. 2), which is one factor to enhance the photocatalytic activity. Moreover, the heat treatment in carbon atmosphere is main factor to enhance the photocatalytic activity, due to the dramatic change of the O 1s XPS spectra (Fig. 3(c)) and the narrowed band gap value from 2.88 eV to 1.48 eV (Fig. 3(e)). The narrowed band gap benefits the generation of more photo-induced electrons and holes to enhance the photocatalytic activity. More importantly, the capability of fabricating photocatalyst materials with highly photoactive activity by the heat treatment in carbon atmosphere opens up new opportunities in various areas. The method could be widely applied to various material shapes, powder, nanowire, film, etc.

4. Conclusions

In this paper, we report that the heat treatment in carbon atmosphere is a safe, inexpensive, and effective method to

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