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Black composites photocatalyst coatings of $K_2Ti_6O_{13}$-TiO_2/TiC with nano-sheet flower-like structure by heat treatment in molten salt

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ABSTRACT

Black photocatalyst coatings of 6-potassium titanate ($K_2Ti_6O_{13}$) and anatase TiO_2 were formed on the surface of TiC coatings by low-temperature heat treatment in molten salt of KNO_3 at 673 K for 3 h. The surface of the composite coatings of $K_2Ti_6O_{13}$-TiO_2/TiC shows the nano-sheet flower-like structure, which could substantially increase the accessible surface area, compared with that of composite coatings of $K_2Ti_6O_{13}$/Ti by the same treatment for Ti coatings. The composite coatings of $K_2Ti_6O_{13}$-TiO_2/TiC obtain high and stable adsorption, and still show photocatalytic activity. The results show that the low-temperature treatment in molten salt is a simple and effective approach to fabricate catalyst with nano-sheet $K_2Ti_6O_{13}$.

1. Introduction

For several decades, nanostructured metal oxides are the most extensively materials because of their physicochemical properties and potential applications. In particular, alkali metal incorporated titanates containing M-Ti-O (M=alkali element) bonds could be produced as nanotube, nanofiber, and nanosheets [1,2]. Among them, potassium (K)-incorporated titanates have been of particular interest due to their excellent thermal durability and specific photochemical properties [3,4]. Especially, $K_2Ti_6O_{13}$ has been reported to be adequate for degradation of toxic substances, decomposition of pure water, as so on [5–7]. Among the synthesis methods, molten salt treatment is the simplest, most versatile approaches [6–8]. However, molten salt treatment usually needs a temperature above 900 °C to obtain highly crystalline. Therefore, developing a facile and low-temperature treatment in molten salt is worth considering [8,9]. In addition, $K_2Ti_6O_{13}$ can't perform good photocatalytic activity due to its wide band gap, high recombination rate. As a result, a great effort has been devoted to enhance the photocatalytic activity [10,11].

Titania (TiO_2) is a well-known photocatalyst, because of its excellent chemical stability and photocatalytic activity. The advantage of TiO_2 powder is with a high specific surface area and hence satisfactory photocatalytic activity, while the major drawback is difficult to recycle. To solve this problem, TiO_2 film is easy to recycle and convenient for large-scale application. Therefore, many studies of TiO_2 photocatalyst are oriented toward TiO_2 film. In our early work, the composite coatings of TiO_2/Ti were fabricated by mechanical coating technique (MCT) and heat treatment process [12].

Herein, black composite photocatalyst coatings of $K_2Ti_6O_{13}$-TiO_2/TiC with nano-sheet flower-like structure was fabricated by low-temperature treatment in molten salt for TiC coatings. The formed compounds were confirmed by XRD and Raman. The surface of nano-sheet flower-like structure was investigated by SEM. The relationship between the high adsorption and photocatalytic activity, and the formed compounds as well as the surface structure was discussed.

2. Experimental

2.1. Preparation of the composite photocatalyst coatings

Firstly, TiC coatings were coated on alumina (Al_2O_3) balls (diameter: 1 mm) by MCT, with TiC powder (diameter: 2–5 μm). The detailed procedure of MCT has been described in our previous work [13]. Then, the TiC coatings were subjected to low-temperature treatment in molten salt of KNO_3 at 673 K for 3 h, and named as "TiC-K". For comparison, Ti coatings formed on Al_2O_3 balls by MCT with Ti powder (diameter: 30 μm) were treated in molten salt with same conditions, and named as "Ti-K".

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2.2. Characterization

The formed compounds were analyzed by X-ray diffraction (XRD, D8 Advance) with Cu-Kα radiation at 40 kV and 40 mA, and Raman spectroscopy (Horiba Scientific) using an Ar laser radiation (514.5 nm). The surface morphology and elemental composition analysis were examined by scanning electron microscopy (SEM, JSM-5300) equipped with an energy dispersive X-ray spectrometer (EDS, JSM-5300LV). The optical absorption was measured with a scanning UV–vis spectrophotometer (UV–vis, MSV-370). The spectra of O 1 s, K 2p and Ti 2p were analyzed by X-ray photoelectron spectroscopy (XPS, Escalab 250Xi).

2.3. Photocatalytic activity and adsorption

The photocatalytic activity and adsorption were evaluated for photodecomposition of MB solution [12]. The evaluation test was carried out under ultraviolet (UV) irradiation at room temperature, and the MB concentration (C_O: 10 μmol/L) was measured at intervals of 20–3 h. At the same time, the adsorption test in the dark was also carried out to compare with the results of the light irradiation test. The cycle tests for the adsorption stability were also conducted with fresh MB solution, according to the procedure described in a previous publication [12].

3. Results and discussions

3.1. Appearance and catalyst characterization

Fig. 1a shows the appearance and XRD patterns of the Ti-K and TiC-K samples. The appearance of the TiC-K sample is black. From Fig. 1a, the diffraction peaks at 24.4° could be attributed to the (101) crystal plane of anatase TiO_2, 28.9° could be attributed to the (310) crystal plane of $K_2Ti_6O_{13}$, and 35.9°, 41.7° and 60.5° could be attributed to the (111), (200) and (220) crystal planes of TiC, respectively. Also, XRD results show the strong peaks of the substrate of Al_2O_3. It hints that the TiC coatings formed on Al_2O_3 ball are very thin. While the appearance of the Ti-K sample is light-gold, XRD results reveal that only $K_2Ti_6O_{13}$ formed on Ti coatings, and it does not show the peak of Al_2O_3, due to the thickness of Ti coatings is about 18 µm [13]. In order to study the generated chemical bond in more detail, Raman results are presented in Fig. 1b. The Raman spectra of the Ti-K sample is similar to that of Ti [4]. For comparison of the Ti-K sample, the Raman peaks of the TiC-K sample at 200 and 280 cm^{-1} can be observed, which are agree with the Ti-O-K bonding of $K_2Ti_6O_{13}$ [7,14]. Also, the peaks at 155, 399 and 620 cm^{-1} can be agree with the Ti-O bonding of anatase TiO_2 [4,15]. Notably, the compounds with $K_2Ti_6O_{13}$ inserting anatase TiO_2 is formed on TiC coatings.

3.2. Surface morphology

Fig. 2 shows the surface morphology of the Ti-K and TiC-K samples. It is difficult to find any compound formed on the surface of Ti coatings from the Ti-K sample. While from the TiC-K sample, the flower-like structure with nano-sheet is formed. The thickness of nano-sheet is about 20 nm, which could substantially increase the accessible surface area, compared with that of the Ti-K sample. Table 1 shows the composition analysis by EDS of the Ti-K and TiC-K samples. The potassium (K) content increases from 0.74 of Ti-K to 11.47 of TiC-K, and the O content increases from 7.99 of Ti-K to 32.33 of TiC-K. The results hint that TiC is easier to be reacted than that of Ti, and the nano-sheet structure could be considered to be $K_2Ti_6O_{13}$ and TiO_2.

3.3. Bonding environment

The UV–vis absorption spectra is used to investigate the electronic states of the Ti-K and TiC-K samples, as shown in Fig. 3a. The Ti-K sample shows that the absorbance edge is about 430 nm. Whereas in the TiC-K sample, it shows absorption in almost entire region. It may be attributed to the formed compounds, and the appearance. The XPS survey spectra confirms the existence of O, K, Ti and C elements (Fig. S1). Compared with the Ti-K sample, the K 2p peaks of the TiC-K sample are more obvious (Fig. 3b). This result also confirms the formation of the Ti-O-K bonding on the surface. The O 1s XPS spectra of the Ti-K and TiC-K samples show dramatic differences (Fig. 3c). For the Ti-K sample, the O 1s peak at 528.88 eV could be attributed to the formed $K_2Ti_6O_{13}$ [16]. Whereas in the TiC-K sample, this peak shows a significant shift to 530.08 eV. This shift is related to the mixed compounds of $K_2Ti_6O_{13}$ and anatase TiO_2 [17].

3.4. Photocatalytic activity

Fig. 3d and e show the relationship between MB solution concentration and irradiation time of the Ti-C and TiC-K samples. After UV irradiation test for 3 h, the MB solution concentration decreases by about 6% for the Ti-K sample, and about 16% for the TiC-K sample,

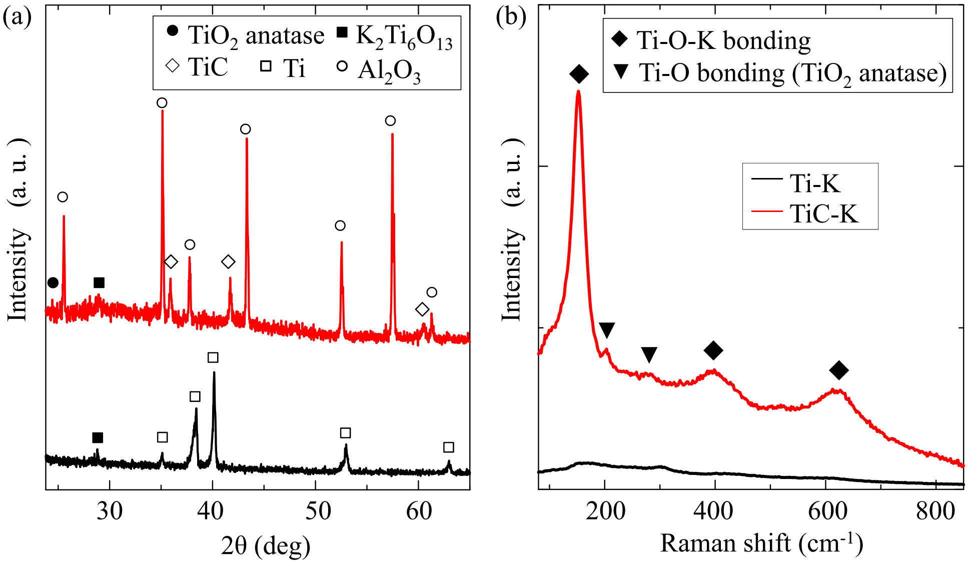

Fig. 1. XRD patterns (a) and Raman spectra (b) of the Ti-K and TiC-K samples.