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Preparation and characterization of nano TiO_2/micron Cr_2O_3 composite particles

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ABSTRACT

Nano-TiO_2/micro-size Cr_2O_3 composite particles were first prepared by hydrolysis of $Ti(OBu)_4$ in an abundant acidic aqueous solution without calcinations at room temperature. XPS analysis shows that the element C, O, Ti and Sn existed on the surfaces of the composite particles. Observation by field emission scanning electronic microscope shows TiO_2 particles of 10–15 nm covers on Cr_2O_3 powder surfaces to form nanometer/micron composite particles. UV–vis spectra show a red shift of the absorption edge and a significant increase of absorption intensity in the visible region. These results confirm that TiO_2 of anatase type can be synthesized on the surface of Cr_2O_3.

1. Introduction

Since Fujishima and Honda [1] discovered the photocatalytic splitting of water on TiO_2 electrodes in 1972, titanium dioxide has been the subject of research as a semiconductor photocatalyst for application in solar-energy conversion and environmental purification [2–4]. Due to its specific optical and electronic properties, low cost, chemical stability and non-toxicity, titanium dioxide is an important photocatalyst with current commercial applications. However, one obstacle toward its practical application is that photocatalytic processes can only be activated by ultraviolet light, which accounts for only about 4% of the incoming solar energy. Another shortcomings of conventional powder catalysts lay difficulty in separation of catalyst after each run [5]. These disadvantages of TiO_2 resulted in inefficient photocatalytic activity. One way to enhance the photocatalytic activity is the coating and doping of other materials, including metal ions and semiconductors, onto the surface of TiO_2 nanoparticles [6–8]. The coupling of two semiconductors provides a novel approach to achieve a more efficient charge separation, an increased lifetime of the charge carriers, and the enhancement of visible light response [9,3,10,11]. Papp et al. [12–15] investigated the TiO_2/Al_2O_3, TiO_2/ZrO_2, TiO_2/WO_3 and TiO_2/MoO_3 systems and Langlet et al. [16] have recently published results on TiO_2-coated polystyrene spheres. Much attention has been paid on the studies of TiO_2 composite nanoparticles, but little is focused on the preparation and characteristic of nano-TiO_2 coating micro-size particles. In addition, the synthesis condition of TiO_2-based catalysts is usually harsh, for example, needs high temperature or high pressure. The calcination process is usually necessary for the preparation of TiO_2.

In this study, we prepared nano-TiO_2/micro Cr_2O_3 by hydrolysis of $Ti(OBu)_4$ in an abundant acidic aqueous solution at room temperature. The as prepared samples were characterized by XPS, SEM, Raman spectrum, XRD and UV–vis. The results shows that the structure of TiO_2 loaded on the surface of Cr_2O_3 powder is mainly of anatase type which have high catalytic activity. There is a red shift of the absorption edge and a significant increase of absorption intensity in the visible region. How to load the photo-catalyst uniformly and firmly on carriers under mild conditions, keeping high catalytic activity and meeting specific physics and chemistry performance and making the catalyst easy to recycling is the difficult points of current studies.

2. Experimental

2.1. Preparation of the catalysts

Samples were prepared according to the following process. 5 g Cr_2O_3 powder was put into flask, then 0.3 g $SnCl_4 \cdot H_2O$ and 40 ml C_2H_5OH were added. 3 ml $Ti(OBu)_4$ were dissolved in 20 ml C_2H_5OH, and then 6 ml H_2O was added with vigorous stirring. Hydrochloric acid was then added in order to dissolve the precipitate forming limpid yellow sol. Poured the sol into the flask with Cr_2O_3 powders, the mixture was refluxed at 80 °C for 50 min. After that, the prepared samples were washed several times carefully with anhydrous ethanol and distilled water. The idling samples were made by refluxing directly the sol without Cr_2O_3.

2.2. Characterization

The phases presented in the as-prepared particles, its chemical composition, and morphology were determined by X-ray diffraction (XRD; Rigaku RAD-C; Cu-Ka, 40 kV, 30 mA), X-ray photoelectron spectroscopy (XPS; ESCA System; PHI1600X), along with field emission scanning electron microscopy (FE-SEM; XL30S-FEG),

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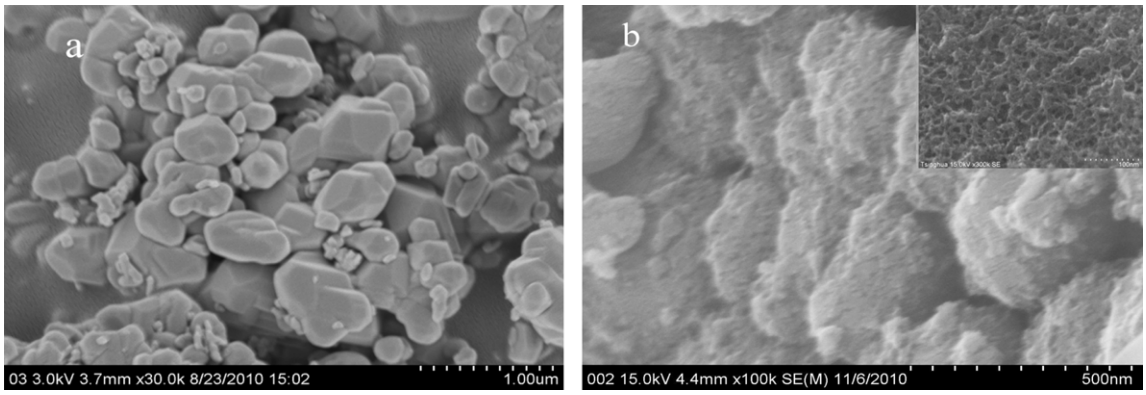

Fig. 1. SEM micrographs of (a) naked chromic oxide and (b) titania-coated chromic oxide.

respectively. The absorption edge of the samples was measured using a UV–vis spectrophotometer (Perkin Elmer-Lambda 35 UV–vis Spectrometer), and $BaSO_4$ was used as the reflectance standard in a UV–vis diffuse reflectance experiment.

3. Results and discussion

3.1. Morphology of TiO_2 – mounted chromic oxide

Fig. 1 illustrates the SEM micrographs of TiO_2/Cr_2O_3 composite particles and naked Cr_2O_3. The results show that the naked Cr_2O_3 particles are smooth and irregularly shaped with the sizes below 1 μm. After coating process, TiO_2 nanoparticles were formed on the surfaces of chromic oxide, as shown in Fig. 1b. The inserted image in Fig. 1b shows that TiO_2 particles are evenly distributed on the surfaces without aggregation, and the size of the TiO_2 is about 10–15 nm. It is proved from the results that nano TiO_2/micro Cr_2O_3 composite particles have been prepared.

3.2. XPS analysis

Fig. 2 shows the XPS results of the particles. The peaks of C1s, O1s, Ti2p, Sn3d and Cr2p appeared on the surface of the composite particles, showing that the surface mainly contained elements of C, O, Ti, Sn and Cr. Among them, the element of C was the residuum created by organic rough material. The results show that the binding energy of Ti2p, Sn3d and Cr2p peaks were 459 eV, 486 eV and 580 eV, separately.

Due to the spinning-rail coupling of the electron, the energy level of Ti2p was broken to two levels marked as $Ti2p_{1/2}$ and $Ti2p_{3/2}$, $Ti2p_{3/2}$ and $Ti2p_{1/2}$ located at 458.7 and 464.5 eV (Fig. 3a), respectively. The proportion of the two peaks zone was about 0.5 and

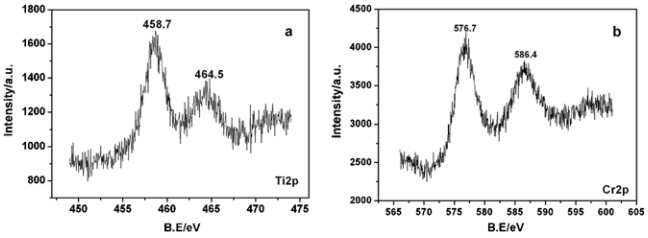

Fig. 3. Spectra of Ti element and Cr element on sample.

the *D*-value was about 5.8, which was coincident with the reference [17]. The $Ti2p_{3/2}$ binding energy exceeds that of Ti metal (454.0 eV), TiO (455.0 eV), and Ti_2O_3 (456.7 eV), but is similar to that of TiO_2 (458.4–458.7 eV), which suggests that Ti is in the +4 oxidation state and directly bonded to oxygen. At the same time, for the as-deposited composite particles, Fig. 3b shows the existence of chromic oxide: the binding energy of Cr_{2p} located at 576.7 and 586.4 eV corresponding to that of $Cr_{2p3/2}$, the possible reason for which is that the thickness of TiO_2 film is very thin, so chromic oxide under it can be detected.

3.3. X-ray diffraction

The XRD patterns of nano TiO_2/Cr_2O_3 are shown in Fig. 4. By careful observation, it can be found that peaks emerge at $2\theta = 24.5$, 33.6, 36.2, 41.5, 44.1 and 54.3, which indicates that the structure of Cr_2O_3 was mainly green chrome ore. The analysis of the diffraction peaks of composite particles reveals the presence of Cr_2O_3, while no obvious peaks indicating the existence of TiO_2. The rea-

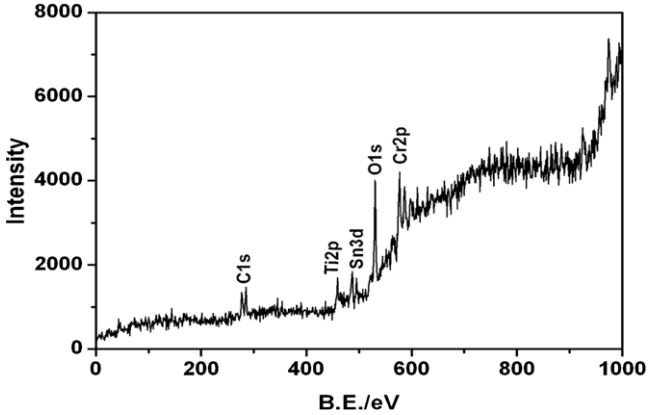

Fig. 2. XPS of the compound powders.

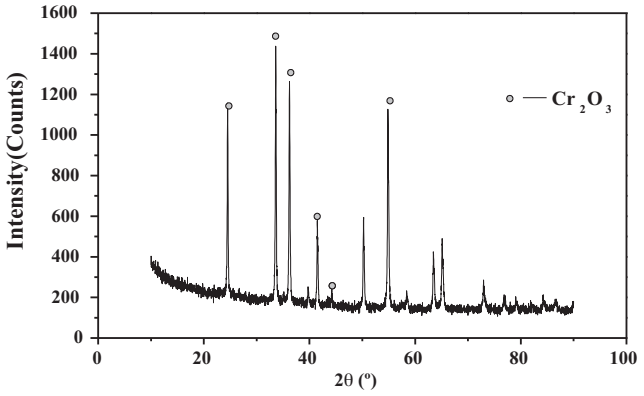

Fig. 4. XRD of the TiO_2/Cr_2O_3 compound powders.

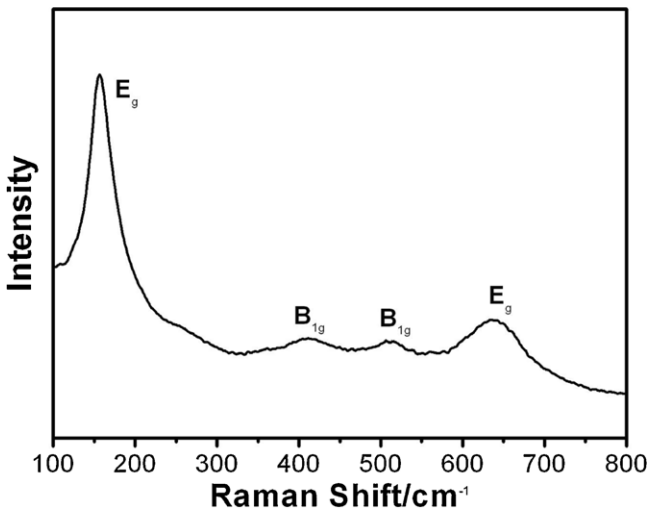

Fig. 5. Raman spectra of idling samples.

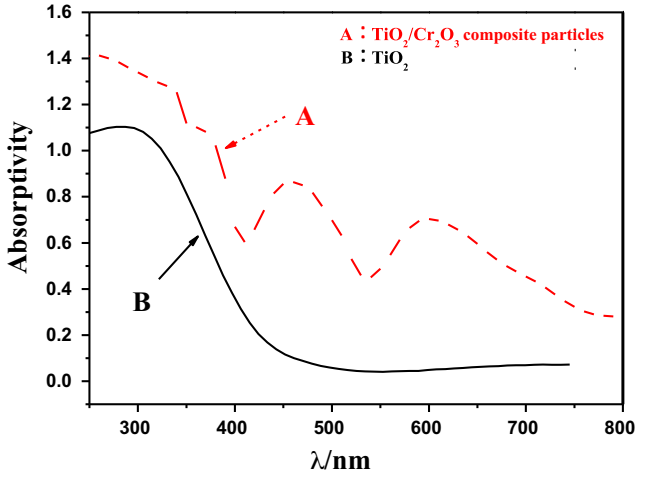

Fig. 6. UV–vis spectrum of the TiO_2/Cr_2O_3 composite particles (A) and naked TiO_2 particles (B).

son is that the concentration of the loaded TiO_2 particles is very low (less than 5%). XRD cannot detect components with such low contents [18].

3.4. Raman analysis of idling samples

In order to confirm the crystal structure of TiO_2, we carry on Raman spectrum for the idling samples. The results were showed in Fig. 5. The characteristic peaks appeared at 143, 392, 510 and 633 cm^{-1} stand for Raman oscillating mode E_g(143, 633 cm^{-1}), B_{1g}(392 cm^{-1}) and B_{2g}(510 cm^{-1}) separately, which can confirm that the structure of TiO_2 loaded on the surface of Cr_2O_3 powder is mainly of anatase type [19]. The result shows that the Raman signal of the nano TiO_2 particle is a little weak and obviously broadened compared with the bulk TiO_2, which is possibly due to the effects of long-range coulomb force on the phonon spectrum [20].

3.5. UV–vis diffuse reflectance spectra of the composite particles

Fig. 6 shows the UV–vis diffuse reflectance spectra of the TiO_2/Cr_2O_3 composite particles and TiO_2. Three absorption peaks appear at 370 nm, 460 nm and 600 nm. The absorption is extended to the wavelength of 750 nm. An obvious red shift of UV–vis reflectance spectra of TiO_2/Cr_2O_3 composite nanoparticles was observed when compared with the spectrum of neat anatase TiO_2 nanoparticles. This suggests that the TiO_2/Cr_2O_3 composite particles have a lower band gap than the neat anatase TiO_2 nanoparticles. It has been reported that the band-gap energy of Cr_2O_3 and that of TiO_2 were of 3.5 eV and 3.2 eV, and the wavelength of the absorption edge of Cr_2O_3 and TiO_2 was 357 nm and 365 nm, respectively. Therefore, the red shift of TiO_2/Cr_2O_3 composite nanoparticles could be attributed to the contribution of each of the oxide component Cr_2O_3 and TiO_2 [21]. So the Cr_2O_3 as the carrier for TiO_2 extends the photo response range of composite semiconductor.

4. Conclusions

Nano-TiO_2/micro size Cr_2O_3 composite particles was successfully synthesized without calcination by hydrolysis of $Ti(OBu)_4$ in an abundant acidic aqueous solution. The particle size of TiO_2 in the composites is less than 15 nm and the TiO_2 loaded on the surface of Cr_2O_3 powder is mainly of anatase type. The UV absorption edge of the composites shows a red-shift as compared to that of TiO_2 particles. The prepared samples show a high absorption intensity, which could be attributed to the combination effect Cr_2O_3 and TiO_2.

Acknowledgements

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