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Full Length Article

Highly efficient visible light photocatalysis of CuC_2O_4/TiO_2 nanocomposite based on photoinduced interfacial charge transfer

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ABSTRACT

A series of CuC_2O_4/TiO_2 heterostructures with different mass ratio have been prepared via a simple precipitation method. Compared to bare P25 TiO_2 and pure CuC_2O_4, the as-prepared CuC_2O_4/TiO_2 exhibited superior activity and stability for the degradation of propylene under visible light. Results of X-ray photoelectron spectroscopy (XPS) and UV–vis diffuse reflectance spectroscopy (DRS) indicated that there is an intimate interaction between CuC_2O_4 and P25 TiO_2 nanoparticles by means of the coordination bond of O on the surface of TiO_2 with Cu atom in CuC_2O_4 molecular. The strong activity of CuC_2O_4/TiO_2 heterostructure is due to the interfacial charge transfer (IFCT) from the valence band of the TiO_2 to the CuC_2O_4 nanoparticles. In addition, compared to Cu (II)/TiO_2 synthesized using the same amount of $CuSO_4$ solution, CuC_2O_4/TiO_2 exhibited much higher visible light activity for the degradation of propylene because of higher atom ratio of Cu to Ti, more visible light absorption and stronger action between CuC_2O_4 and TiO_2.

1. Introduction

In the last few decades, TiO_2 has been studied extensively as an efficient photocatalyst in the fields of organics degradation, photocatalytic conversion of CO_2 and water-splitting for H_2 production. However, it can only be activated by UV light due to its wide band gap of 3.2 eV (anatase). Thus, numerous studies have been undertaken to expand its spectral absorption into visible light region. The main approaches involve cation doping [1–3], anion doping [4–6], noble metal sensitization [7–13] and combining it with narrow-bandgap semiconductors [14–18]. The visible light activity of doped TiO_2 is mainly caused by the photogenerated holes originating from the dopant metal ions or anions in the forbidden band of TiO_2, the oxidative ability of such holes decreases upon irradiation. Therefore, the holes having strong oxidative power generated in the valence band of TiO_2 cannot be utilized in these doped systems.

Recently, the novel visible-light-driven photocatalyst composites related to wide-bandgap semiconductor have been reported based on photoinduced interfacial charge transfer (IFCT). Irie and Hashimoto et al. fabricated efficient photocatalysts sensitive to visible light, Cu(II)-grafted TiO_2 (Cu(II)/TiO_2) and WO_3 (Cu(II)/WO_3), using $CuCl_2{\cdot}2H_2O$ as the source of Cu(II) [19,20]. They reported that Cu(II)/TiO_2 and Cu(II)/WO_3 photocatalysts decomposed 2-propanol under visible light with quantum efficiencies of 8.8% and 17%, respectively, by IFCT from semiconductor to adsorbed Cu(II) ions. Yu and Hashimoto et al. substituted W^{6+} and Ga^{3+} ions for Ti^{4+} sites to narrow the band gap of TiO_2 forming $Ti_{1-3x}W_xGa_{2x}O_2$ powders and demonstrated that $Ti_{1-3x}W_xGa_{2x}O_2$ can serve as an efficient visible-light-sensitive photocatalyst when its surface is grafted with Cu(II) due to IFCT and narrow band gap [21]. Zhang and Gong et al. designed a novel visible-light-driven photocatalyst CuS/ZnS porous nanosheet, which can reach a high H_2-production rate of 4147 $\mu mol\ h^{-1}\ g^{-1}$ at 420 nm based on IFCT from the valence band of ZnS to CuS [22]. Lee and Yong synthesized CuS/ZnO heterostructure nanowires through a simple two-step solution method and found that the synthesized CuS/ZnO heterostructure exhibited superior photocatalytic activity under visible light compared to bare ZnO because of IFCT from the valence band of the ZnO nanowire to the CuS nanoparticles [23]. To the best of our knowledge, however, there is no report regarding CuC_2O_4/TiO_2 nanomaterials as an efficient visible-light-responsive photocatalyst.

In this work, for the first time we prepared visible-light-activated CuC_2O_4/TiO_2 series with different ratio via a chemical precipitation (CP) method. Many methods such as successive ion layer adsorption and reaction (SILAR), chemical bath deposition (CBD), microwave

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(MW) and hydrothermal (HT) have been reported to synthesize nanocomposites [24–26]. Chemical precipitation (CP) method was used in this work because it is a simple, low temperature, and inexpensive technique. Moreover, the photocatalytic properties of CuC_2O_4/TiO_2 nanocomposites were investigated under visible light irradiation, and they exhibited high activities and stabilities for the photodegradation of propylene gas. Especially for CuC_2O_4/TiO_2 (0.25:1), with a mass ratio of 0.25:1 of CuC_2O_4 to TiO_2, the highest propylene degradation of 46% in online system was found and the activity was stable in three successive cycling experiments. This strong photocatalytic activity under visible light was attributed to the interfacial charge transfer (IFCT) from the valence band (VB) of the TiO_2 to the CuC_2O_4 nanoparticles. The holes produced in the VB of TiO_2 are then capable of decomposing organic substances. By comparison with Cu (II)-grafted TiO_2 (denoted as Cu(II)/TiO_2) synthesized using the same amount of $CuSO_4$ solution as precursor, CuC_2O_4/TiO_2 nanocomposites displayed superior activity for higher atom ratio of Cu to Ti, more visible light absorption and stronger action between CuC_2O_4 and TiO_2. CuC_2O_4/TiO_2 photocatalyst is composed of environmental friendly Cu and Ti and without involvement of noble metals [27]. So, it will be utilized extensively in practice application for its nontoxic, cheap and strong oxidative ability.

2. Experimental

P25-TiO_2 crystals were produced from Guangzhou Hualisen Trade Co., Ltd. Other used reagents were of analytical reagent grade and used without further purification.

2.1. Preparation of pure CuC_2O_4, Cu (II)/TiO_2 and CuC_2O_4/TiO_2 composite

The nanocrystalline CuC_2O_4/TiO_2 heterostructures with different mass ratio were synthesized via a chemical precipitation method. In brief, 1.0 g of P25-TiO_2 was ultrasonic dispersed into 20 mL of distilled water, then a certain volume of $Na_2C_2O_4$ (0.1 M) aqueous solution was slowly added drop-wise to the above suspension mixture with constant stirring. After 20 min of stirring, a certain volume of $CuSO_4$ solution (0.1 M) was dripped into above suspension to yield CuC_2O_4/TiO_2 precipitate. In the above procedure, the volume of $Na_2C_2O_4$ was larger than that of $CuSO_4$ to ensure the complete precipitation of Cu^{2+}. Finally, the precipitate was collected, washed with distilled water for several times, and then dried at 60 °C in vacuum oven to get the nanocrystalline CuC_2O_4/TiO_2 hybrid photocatalyst. By changing the volume of $Na_2C_2O_4$ and $CuSO_4$ solution added, CuC_2O_4/TiO_2 composites with different mass ratio (0.05:1, 0.1:1, 0.15:1, 0.25:1, 0.3:1) have been prepared and labeled as CuC_2O_4/TiO_2 (X:Y), where X:Y means the theoretical mass ratio of CuC_2O_4 to TiO_2 in the composite. To make a comparison, pure CuC_2O_4 and Cu (II)-grafted TiO_2 (Cu (II)/TiO_2) were also synthesized. The former was prepared with $CuSO_4$ and $Na_2C_2O_4$ and the latter was synthesized using $CuSO_4$ and P25-TiO_2 without addition of $Na_2C_2O_4$. For Cu (II)/TiO_2, briefly, 1.0 g of P25-TiO_2 and certain volume of $CuSO_4$ solution (0.1 M) were ultrasonic mixed into a beaker, and then were stirring for 20 min. The volume of $CuSO_4$ solution is 3.3, 6.6, 10, 16.5 and 20 mL, respectively, which is identical to that for preparing CuC_2O_4/TiO_2 (X:Y). The suspension was filtered and dried at 60 °C in vacuum oven to get Cu (II)/TiO_2 series and labeled as Cu (II)/TiO_2-I, Cu (II)/TiO_2-II, Cu (II)/TiO_2-III, Cu (II)/TiO_2-IV and Cu (II)/TiO_2-V, respectively.

2.2. Characterization

The morphology of as-prepared photocatalysts was studied using a JEOL JSM-7610F scanning electron microscope (SEM) and a JEOL JEM-2010 transmission electron microscope (TEM). The crystal phase of the obtained samples was measured with a Bruker D8 X-ray diffractometer (XRD) with Cu Kα radiation at an accelerating voltage of 40 kV. The ultraviolet–visible light diffusion reflectance spectra (DRS) of the photocatalysts were recorded with a CARY5000 spectrometer ($BaSO_4$ was used as a reference). X-ray photoelectron spectroscopy (XPS) data were obtained using a Thermo Fisher Scientific Escalab 250Xi X-ray photoelectron spectrometer using monochromatized Al-*Kα* ($h\nu$ = 1486.6 eV) radiation as excitation source. The binding energies were calibrated with reference to adventitious C 1s line at 284.8 eV.

The photocurrent measurements were examined by electrochemical station (CHI 650E Chenhua Instrument Company) in a three-electrode quartz cell with 0.1 M Na_2SO_4 electrolyte solution. The as prepared samples electrode with an active area of 1.5 cm^2 were used as the working electrode. The working electrode was prepared by dip-coating method as follows: 2 mg of sample, 30 μL of water and 5 μL of Nafion were mixed to form homogeneous slurry, and then was dropped onto the precleaned ITO glass and dried at room temperature for 12 h. A platinum wire and Ag/AgCl were used as counter electrode and reference electrode, respectively. A xenon lamp equipped with an ultraviolet cutoff filter ($\lambda > 420$ nm) was served as the visible light source and was positioned 10 cm away from the photoelectrochemical cell.

2.3. Evaluation of visible light photocatalytic activity

The visible light photocatalytic activity of P25, $Cu_2C_2O_4$, Cu (II)/TiO_2 and $Cu_2C_2O_4/TiO_2$ (X:Y) was evaluated by monitoring the oxidation of propylene in an on-line analysis system equipped with a gas chromatograph (GC7900) to monitor the concentration change of C_3H_6 (C). The photocalyst (ca. 25 mg) was coated on one side of a roughened glass plate (ca. 10 cm^2), which was put in a quartz tube reactor surrounded with a cycling water channel to keep the reaction temperature unchanged. The feed gas was mixed of propylene and dry air, and flowed through the reactor at a flow rate of 200 mL/h. A 500 W xenon lamp was used as the visible light source and an ultraviolet (UV) cut 420 filter was inserted between the xenon lamp and reactor to eliminate UV light. Prior to irradiation, the feed gas was allowed to flow through the reactor continuously until the adsorption/desorption equilibrium was established. The concentrations of C_3H_6 and CO_2 production were measured by GC equipped with a flame ionization detector (FID), a GDX-502 column, and a reactor loaded with Ni catalyst for methanization of CO_2. The removal rate of C_3H_6 is calculated as $(C_0 - C)/C_0 \times 100\%$, where C_0 refers to the initial C_3H_6 concentration with a value of about 500 ppm V.

3. Results and discussion

3.1. Characterization of catalysts

Fig. 1 displays the powder XRD patterns of pure CuC_2O_4 and CuC_2O_4/TiO_2 heterostructures with different mass ratio. All characteristic peaks of pure CuC_2O_4 coincide well with the standard data of orthorhombic CuC_2O_4 (JCPDS 21-0297) [28,29]. The strong diffraction peaks of CuC_2O_4 at 2θ angles of 22.902°, 36.251°, 36.946°, 38.835°, 39.063°, 42.443°, 46.865°, 51.469°, and 52.036° are corresponded to the (1 1 0), (1 2 0), (2 1 0), (0 1 1), (1 0 1), (1 1 1), (2 2 0), (1 2 1), and (1 3 0) planes respectively. As for all CuC_2O_4/TiO_2 composites, the major peak of orthorhombic CuC_2O_4 at $2\theta = 22.902°$ is clearly observed and its intensity increases with increasing the mass ratio of CuC_2O_4. Moreover, after coupling with CuC_2O_4, all of the diffraction peaks of anatase (A) and rutile (R) phase still exist without change, suggesting that the heterogeneous process doesn't affect the crystal structure of TiO_2.

Fig. 2 shows SEM images of CuC_2O_4 synthesized with $CuSO_4$ and $Na_2C_2O_4$ at different temperature including 30 °C, 60 °C and 90 °C. It can be seen that all samples contain two shapes of copper oxalate: spherical and fusiform. Fig. S1 shows the proportion of two different shapes in CuC_2O_4 sample prepared at different temperature. Apparently, the fusiform shape is the main component of CuC_2O_4 produced at