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Fabrication of WO_3/Ag_2CrO_4 composites with enhanced visible-light photodegradation towards methyl orange

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ABSTRACT

In this work, a novel visible-light-driven WO_3/Ag_2CrO_4 composite was successfully synthesized through a facile precipitation method and characterized by scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), UV–vis diffuse reflectance spectroscopy (UV–vis DRS) and photoluminescence (PL) spectroscopy. Compared to individual WO_3 and Ag_2CrO_4, the WO_3/Ag_2CrO_4 composite exhibited much higher photocatalytic activity for the photocatalytic degradation of methyl orange (MO) under visible light irradiation ($\lambda > 420$ nm). Importantly, it is interesting to find that the optimum photodegradation rate constant of WO_3(2.0 wt%)/Ag_2CrO_4 is 0.00487 min^{-1}, which is 14.3 and 3.1 times higher than that of individual WO_3 and Ag_2CrO_4, respectively. The enormous enhancement in photocatalytic performance could be mainly ascribed to the efficient separation of photogenerated electrons and holes through the Z-scheme electron transfer composed of WO_3, Ag and Ag_2CrO_4. Furthermore, radical trap experiments reveals that the holes and superoxide radical anions are the primary reactive species in the photocatalytic degradation of MO. Ultimately, a possible photocatalytic mechanism for the efficient WO_3/Ag_2CrO_4 composite was proposed.

1. Introduction

As a green and promising technology, semiconductor photocatalysis has attracted a great deal of attention in the last few decades because it is of great potential to solve serious challenges in the field of environmental pollution, energy shortage and global warming [1,2]. Up to now, numerous efforts have been strived to the development of high efficiency photocatalysts, such as TiO_2 [3], ZnO [4], CdS [5], C_3N_4 [6], Ta_3N_5 [7], $BiVO_4$ [8], and more. Among them, TiO_2 is considered as one of the most promising photocatalyst and has been extensively investigated owing to the non-toxicity, low cost, relatively high chemical stability and strong oxidizing power [9]. Unfortunately, TiO_2 can only be excited under ultraviolet light irradiation due to its large band gap (3.2 eV for anatase TiO_2 and 3.0 eV for rutile TiO_2) [10,11]. Additionally, it is well known that the ultraviolet region occupies only approximately 4% of the entire solar spectrum, while about 43% of the energy belongs to the visible light [12]. Consequently, in order to utilize solar energy more efficiently in the photocatalytic processes, there is an urgent need to develop highly efficient and stable visible light driven photocatalysts for practical applications.

To date, many visible light driven photocatalysts, such as Bi-containing compounds [8,13], W-containing compounds [14,15], Ag-containing compounds [16,17], and so forth, have been created and applied to degrade organic pollutants and produce hydrogen from splitting water through utilizing abundant sunlight. Among them, silver chromate (Ag_2CrO_4), as a novel high-efficiency visible light driven photocatalyst with a narrow band gap (~1.8 eV), has intrigued significant research interest and has been recognized as one of the most promising photocatalysts for the degradation of organic pollutants under visible light irradiation due to its strong absorption in visible-light region, unique electronic structure and crystal structure [18–20]. Unfortunately, the practical application of Ag_2CrO_4 is currently limited due to it usually undergo photocorrosion and fast recombination ratios of photogenerated charge carriers during the photocatalytic reactions, and it is slightly soluble in aqueous solution [21], resulting in low photocatalytic activity. Excitingly, coupling a wide band gap semiconductor with a narrow

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band gap semiconductor to form heterojunction composites by well-matched energy bands has been considered as an efficient strategy toward extending visible light spectral responsive range, improving the separation efficiency of photogenerated charge carriers, and enhancing the photocatalytic activity and stability [22]. Up to now, some coupling systems of Ag_2CrO_4-based composites, including of $AgBr/Ag_2CrO_4$ [21], $ZnO/AgBr/Ag_2CrO_4$ [23], ZnO/Ag_2CrO_4 [20], GO/Ag_2CrO_4 [19], $ZnO/AgI/Ag_2CrO_4$ [24], $ZnO/Ag_3VO_4/Ag_2CrO_4$ [25], $g\text{-}C_3N_4/Fe_3O_4/Ag_2CrO_4$ [26], and so forth, have been reported to be enhanced photocatalytic activity of Ag_2CrO_4 for the degradation of organic contaminants under visible light irradiation. Furthermore, tungsten trioxide (WO_3), as a transition metal oxide semiconductor and a promising visible light driven photocatalyst, has been considered as an effective candidate for pollutant degradation due to its narrow band gap (2.6–2.8 eV), nontoxicity, resilience to photocorrosion and good electron transport properties [27–29]. Fortunately, it has been found that the conduction band (E_{CB}) and valence band (E_{VB}) edge potential positions of Ag_2CrO_4 (E_{CB} = 0.50 eV and E_{VB} = 2.22 eV) are both more negative than that of WO_3 (E_{CB} = 0.79 eV and E_{VB} = 3.39 eV) [18,29]. It implies that under visible light irradiation the photogenerated electrons can move from the conduction band of Ag_2CrO_4 to that of WO_3, meanwhile, the photogenerated holes in the valence band of WO_3 can migrate to that of Ag_2CrO_4, which avoid the recombination of the electron-hole pairs and accumulation of photogenerated electrons on the conduction band of Ag_2CrO_4, and thus improve the stability of Ag_2CrO_4. Therefore, WO_3 emerges as a promising combinational candidate. Nonetheless, to the best of our knowledge, there is no report on the preparation and photocatalytic activity of WO_3 modified Ag_2CrO_4 photocatalyst.

As a consequence, in this work, a novel composite photocatalyst WO_3/Ag_2CrO_4 has been fabricated by a facile chemical precipitation method at room temperature without using any surfactants. The photocatalytic activity and stability of the as-prepared samples were evaluated in the photocatalytic degradation of methyl orange (MO) organic dye in an aqueous solution under visible light irradiation ($\lambda > 420$ nm). The results indicated that WO_3 nanoparticles can significantly improve the photocatalytic activity of Ag_2CrO_4 due to the formation of Z-scheme system composed of WO_3, Ag and Ag_2CrO_4, which effectively facilitated the separation of hole-electron pairs. Furthermore, a possible photocatalytic mechanism of WO_3/Ag_2CrO_4 composite related to the band positions of the two semiconductors was discussed in detail.

2. Experimental

2.1. Materials

All reagents were of analytical grade and used without further purifications. Deionized water was used throughout this study.

2.2. Catalysts preparation

WO_3 nanoparticles were prepared by a solid-state decomposition reaction of $(NH_4)_{10}W_{12}O_{41}{\cdot}xH_2O$ at 500 °C in a muffle furnace for 4 h in a semiclosed system at a heating rate of 20 °C min^{-1} under air condition. The product was washed several times with distilled water and absolute ethanol and dried at 80 °C for 12 h.

WO_3/Ag_2CrO_4 composites were fabricated by a facile in situ chemical precipitation method under the dark condition. Typically, first of all, a certain amount of the as-prepared WO_3 samples (6.7 mg, 13.5 mg and 27.6 mg) were sonicated thoroughly into 30 mL distilled water for 30 min. Then, 4 mmol $AgNO_3$ was added into the dispersion of WO_3 under the vigorous stirring. After stirring for 30 min, 2 mmol K_2CrO_4 dissolved in 20 mL distilled water was added dropwise into the dispersion with constant stirring, and the mixture was further vigorously stirred at room temperature for 4 h. Finally, the precipitate was collected by centrifugation, washed several times with distilled water and absolute ethanol, and dried at 55 °C in a vacuum oven for 24 h. The obtained products were denoted as $WO_3(x)/Ag_2CrO_4$, where x% stands for the theoretical mass percent of WO_3 in the WO_3/Ag_2CrO_4 composites. That is to say, the as-prepared samples were also accordingly denoted as WO_3(1.0 wt%)/Ag_2CrO_4, WO_3(2.0 wt%)/Ag_2CrO_4 and WO_3(4.0 wt%)/Ag_2CrO_4. Moreover, for comparison, pure Ag_2CrO_4 nanoparticles were prepared following the similar procedure mentioned above in the absence of WO_3.

2.3. Catalysts characterization

X-ray diffraction (XRD) patterns of the as-prepared samples were recorded on an X-ray diffractometer (D/max-IIIA, Japan) using Cu K_α radiation. The surface morphology of the as-prepared samples was examined by a scanning electron microscopy (SEM) (LEO1530VP, LEO Company) and a high-resolution transmission electron microscope (HRTEM, JEOL, JEM2100). The UV–Vis light absorption spectra of the as-prepared samples were obtained from a Hitachi UV-3010 spectrophotometer equipped with an integrating sphere assembly and using the diffuse reflection method and $BaSO_4$ as a reference to measure all the samples. X-ray photoelectron spectroscopy (XPS) analysis was performed with a Krato Axis ultra DLD spectrometer equipped with an AlKα X-ray source, the binding energy was referenced to C 1s peak at 284.6 eV for calibration. Photoluminescence (PL) spectra were measured on an F-7000 Fluorescence spectrophotometer (Hitachi, Japan).

2.4. Photocatalytic tests of photocatalysts

The photocatalytic performance of the as-prepared samples was evaluated through the photodegradation of MO under visible light. A 300 W Xe-arc lamp equipped with a 420 nm cutoff filter was used as a visible light source. In a typical photocatalytic measurement, suspension including the photocatalyst (50 mg) and MO solution (150 mL, 10 mg L^{-1}) was laid in a 250 mL cylindrical quartz reactor equipped with a water circulation facility. Before irradiation, the reaction suspension was sonicated for 5 min and stirred in the dark for 60 min to ensure the equilibrium of adsorption and desorption. During the photocatalytic tests, 5 mL of the suspension was obtained at a given time intervals, followed by centrifugation at 10,000 rpm for 10 min to remove the photocatalyst. The concentration of the remaining MO was measured by its absorbance (A) at 465 nm with a Hitachi UV-3010 spectrophotometer. The degradation ratio of MO can be calculated by $X = (A_0\text{-}A_t)/A0 \times 100\%$, where A_0 and A_t are the concentration of MO before illumination and after illumination time t.

Moreover, the tests of active species trapping were carried out under the identical procedure mentioned above except for adding 2 mmol tert-butyl alcohol (t-BuOH, a quencher of $\cdot OH$), 1 mmol triethanolamine (TEOA, a quencher of h^+) and 0.1 mmol 1,4-benzoquinone (BQ, a quencher of $\cdot O_2^-$), respectively.

3. Results and discussion

3.1. Characterization of the samples

The crystalline structure and purity of the as-prepared samples were investigated by X-ray powder diffraction (XRD). Fig. 1 displays XRD patterns of the pure Ag_2CrO_4, WO_3 and WO_3/Ag_2CrO_4 composites with different weight percents of WO_3. It can be clearly seen that all the samples were well crystallized. For the pure

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