



Preparation, characterization and visible-light photocatalytic activity of AgI/AgCl/TiO₂

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ABSTRACT

In this paper, a novel composite photocatalyst AgI/AgCl/TiO₂ was prepared by ion exchange method and characterized by XRD, SEM and UV–Vis spectrometry. The as-prepared AgI/AgCl/TiO₂ composites show much higher photocatalytic activity than AgCl/TiO₂ and AgI/TiO₂ under visible-light irradiation ($\lambda > 400$ nm) in the process of methyl orange (MO) degradation. When the molar percentage of AgI to initial AgCl is 20% (sample SE-20%), the maximal degradation efficiency of MO has reached 85.8% after irradiation for 120 min. The enhancement of photocatalytic activity of the composite photocatalyst AgI/AgCl/TiO₂ will be attributed to its good absorption in the visible-light region, especially low recombination rate of the electron–hole pairs based on the photoluminescence (PL) spectra investigation of AgI/AgCl/TiO₂ and the matching band structures of AgI, AgCl and TiO₂. The detection of reactive species by radical scavengers displays that $\cdot\text{O}_2^-$ and H₂O₂ are the main reactive species for the degradation of MO under visible-light irradiation. Moreover, PL analysis by using terephthalic acid (TA) as a probe molecule further reveals that $\cdot\text{OH}$ can be negligible for the degradation of MO.

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1. Introduction

In modern society, the applications on degradation of pollutants and conversion of solar energy by semiconductor photocatalysts have been received much attention. As one of the most extensively investigated photocatalysts, TiO₂ shows relatively high efficiency, low cost, non-toxicity, and high stability [1–4]. However, because of its large band gap (3.0–3.2 eV), TiO₂ is only responsive to ultraviolet irradiation, which greatly limits its practical applications. Moreover, the lack of effective surface area and low transfer rate of charge carriers also hamper the photocatalyst developments. Given the conditions above, it is desirable to develop novel photocatalysts with high photocatalytic activity under visible light.

In the most previous study, silver halides (AgX, X = Cl, Br, I) are generally employed as photosensitive materials and source materials in photographic films. As a result of their photosensitive characteristics, AgX are unstable under light irradiation and rarely used as photocatalysts. In recent years, to avoid the photodecomposition of AgX, supported-AgX composite photocatalysts have been reported for the degradation of dyes, decomposition of acetaldehyde, hydrogen generation and killing of bacteria, in which they display high efficiency and good stability in the use process [5–18]. Therefore, supported-AgX catalysts are promising for the degrada-

tion of environmental pollutants. At present, supported-AgBr and supported-AgI are investigated widely; however, little work [7,19] has been focused on the supported-AgCl catalysts due to the weak visible-light absorption of AgCl and its low photocatalytic activity under visible-light irradiation.

It is well known that the inner electric field of heterojunction catalyst can decrease the recombination of the electron–hole pairs, promote quantum efficiency, and further effectively improve the photocatalytic activity of semiconductor photocatalysts [20]. In the field of photographic films, composite particles with different AgX heterojunction have better photographic properties than single AgX, so the researches of AgX heterojunction have been extensively carried out [21]. However, few studies have been attempted to study the effect of AgX heterojunction on the photocatalytic activity of supported-AgX composite catalysts so far. In the earlier study, we have reported a preliminary study about the AgI/AgBr/TiO₂ composite photocatalyst for the degradation of methyl orange (MO) under visible light irradiation [22] and showed enhanced photocatalytic activity than single AgBr/TiO₂ and AgI/TiO₂. AgCl and AgI possess the matching energy levels, so it will be an effective way to improve the photocatalytic activity of AgCl by construction of AgI/AgCl heterojunction.

In the present work, we synthesized novel visible-light composite photocatalysts AgI/AgCl/TiO₂ with highly enhanced photocatalytic activity by a simple ion exchange method. The as-prepared AgI/AgCl/TiO₂ was characterized by XRD, SEM and UV–Vis spectrometry. The photocatalytic activity evaluation was

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carried out by the degradation of MO under visible-light irradiation ($\lambda > 400$ nm).

In addition, a number of reactive species are suspected to be involved in the photodegradation process of dyes and organic pollutants. The primary reactive species involved in the process include trapped holes (h^+), hydroxyl radicals ($\cdot\text{OH}$), hydrogen peroxide (H_2O_2) and superoxide radical anions ($\cdot\text{O}_2^-$) that are basically transformed from the initial generation of charge carriers, active holes and electrons. In order to investigate their roles, a series of quenchers were employed to scavenge the relevant reactive species by the degradation of MO under visible-light. The photocatalytic mechanism of AgI/AgCl/TiO₂ was also discussed based on the separation process of electron–hole pairs and the reactive species detection in detail.

2. Experimental

2.1. Preparation of catalyst

AgCl/TiO₂ substrate was prepared via deposition–precipitation method in advance. TiO₂ (7.5 g) was homogeneously dispersed in 300 mL of deionized water and sonicated for 30 min, then KCl (1.75 g) was added to the TiO₂ suspension and stirred for 30 min. Subsequently AgNO₃ (4.00 g) in 17.3 mL of NH₃·H₂O (25 wt% NH₃) was quickly added to the mixture. After the resulting suspension was vigorously stirred at room temperature for 10 h, the product was filtered, washed and dried at 65 °C for 24 h. Finally, white AgCl/TiO₂ substrate with theoretical Ag/Ti molar ratio of 0.25:1 was obtained.

AgI/AgCl/TiO₂ photocatalyst was synthesized by ion exchange method. In a typical synthetic route, AgCl/TiO₂ (1.0 g) was homogeneously dispersed in 100 mL of deionized water and sonicated for 5 min. Then a stoichiometric amount of KI solution was dropped into the AgCl/TiO₂ suspension and stirred magnetically for 20 min. After that, the product was filtered, washed and dried at 65 °C for 24 h. AgI/AgCl/TiO₂ photocatalysts with different molar percentage of AgI to initial AgCl were respectively obtained by changing the dosage of KI solution. The corresponding AgI/AgCl/TiO₂ samples were defined as SA-2.5%, SB-5.0%, SC-10%, SD-15%, SE-20% and SF-25%, respectively. All the reagents are of analytical purity from Sinopharm Chemical Reagent Co., Ltd. and used for the experiment without further purification. Deionized water was used throughout this study.

2.2. Characterization of catalyst

X-ray diffraction (XRD) measurement was carried out at room temperature using a BRUKER D8 ADVANCE X-ray powder diffractometer with Cu K α radiation ($\lambda = 1.5406$ Å) and a scanning speed of 10°/min. The accelerating voltage and emission current were 40 kV and 40 mA, respectively. JEOL JSM-6610LV scanning electron microscopy (SEM) with 30 kV scanning voltages was employed to observe the morphologies of as prepared catalysts. UV–Vis diffuse reflectance spectroscopy measurements were carried out using a TU-1901 UV–VIS spectrophotometer (Beijing Purkinje General Instrument Co., Ltd.) equipped with an integrating sphere attachment. Fluorescence emission spectra were recorded on a JASCO FP-6500 type fluorescence spectrophotometer with 260 nm excited source over a wavelength range of 350–600 nm.

2.3. Evaluation of photocatalytic activities under visible light

The photocatalytic activity of AgI/AgCl/TiO₂ was evaluated by degradation of MO under irradiation of visible light ($\lambda > 400$ nm). The light source was a 500 W Xe lamp (Institute of Electric Light Source, Beijing). Light passed through a water filter, a beam turner

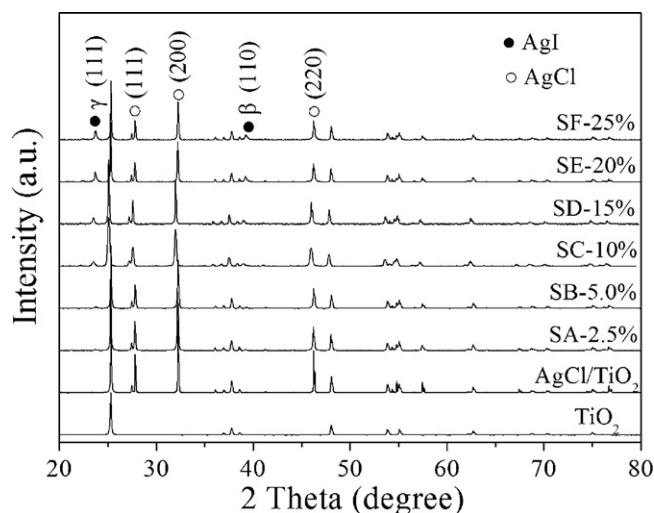


Fig. 1. XRD patterns of TiO₂, AgCl/TiO₂, SA-2.5%, SB-5.0%, SC-10%, SD-15%, SE-20% and SF-25%.

and a 400 nm filter (Instrument Company of Nantong, China) before entering the reactor. In a typical experiment, 50 mL of the reaction suspension containing 0.10 g catalyst and MO (10 mg/L) was transferred to the reactor. Prior to illumination, the suspension was magnetically stirred in the dark for 20 min to establish an adsorption–desorption equilibrium between the photocatalyst and MO. Then it was illuminated for a certain period of time with constant stirring. About 5 mL of the suspension was collected at each specific irradiation time interval, filtrated and then analyzed using 722 s spectrophotometer. The MO concentration was determined from the absorbance at a wavelength of 464 nm, with deionized water as a reference sample.

The examination experiment process of reactive species is similar to the photodegradation experiment. A quantity of scavengers was introduced into the MO solution prior to addition of the catalyst. Terephthalic acid photoluminescence probing technique (TA-PL) is used in the detection of $\cdot\text{OH}$ radicals. In the detection experiment, a basic TA solution was added to the reactor instead of MO and the concentration of TA was set at 5×10^{-4} M in 2×10^{-3} M NaOH solution. The sample collected every 30 min was measured on a JASCO FP-6500 type fluorescence spectrophotometer after centrifugation. The excitation wavelength used was 315 nm.

3. Results and discussion

3.1. Characterization of AgI/AgCl/TiO₂

3.1.1. XRD analysis

Powder XRD study was carried out to confirm the crystalline structures of prepared catalysts. Fig. 1 shows the XRD patterns of as-synthesized AgI/AgCl/TiO₂ with different AgI contents, AgCl/TiO₂ and TiO₂. It can be observed that TiO₂ is anatase phase (JCPDS 21-1272) while AgCl (JCPDS 31-1238) is cubic structure. AgI supported on AgCl/TiO₂ is a mixture of β -AgI (JCPDS 85-0801) and γ -AgI (JCPDS 09-0399), assigned to β -(1 1 0) and γ -(1 1 1) diffraction peak, respectively. The intensities of diffraction peaks of AgI increase with increasing the AgI contents in AgI/AgCl/TiO₂, whereas those of AgCl decrease simultaneously due to its consumption.

3.1.2. UV–Vis analysis

The UV–Vis diffuse reflectance spectra (DRS) of the samples are represented in Fig. 2. It is shown that TiO₂ is only responsive to ultraviolet irradiation ($\lambda < 400$ nm) whereas AgCl, AgI, AgCl/TiO₂ and AgI/AgCl/TiO₂ with different AgI contents all exhibit absorption

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