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Facile regeneration and photocatalytic activity of CuO-modified silver bromide photocatalyst

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ABSTRACT

CuO-modified silver bromide (AgBr/CuO) crystal was successful synthesized by a facile method at room temperature. The physical and chemical properties of AgBr/CuO crystals were carefully detected through X-ray diffraction (XRD), UV–vis diffuse reflectance spectroscopy (DRS), field emission scanning electron microscopy (FESEM), X-ray photoelectron spectroscopy (XPS), photoluminescence (PL) and Electron spin resonance (ESR) techniques. The photocatalytic activity and stability of AgBr/CuO hybrid were evaluated by photocatalytic degradation of methyl orange (MO) under visible light irradiation. The AgBr/CuO sample exhibited high photocatalytic activity, degrading 92% MO after irradiation for 40 min, which was 3.8 times higher than that of pure AgBr. Both the experimental scavenging results and characterization results revealed that O_2^- acts as the main active specie. Based on above, the high photocatalytic performance is mainly attributed to the abundant of oxygen vacancies, and which further generate lots of superoxide radicals. Moreover, the method by using bromide water to rejuvenate AgBr/CuO could well maintain the photocatalytic activity and stability without any environment pollution.

1. Introduction

To utilize solar energy, a number of researchers focus on the development of photocatalysts in a wide region of solar spectrum as photocatalysis is a great potential for the decomposition of various organic contaminates in water or air pollutants. Accordingly, a numerous of novel functional materials have been explored, such as metal surface modified catalyst [1], heterojunction type catalyst [2,3], graphene-based composite photocatalysts [4] and new monomer photocatalysts [5,6]. In recent years, the silver bromide semiconductor material as an obviously higher photocatalytic activity for the efficient removal of organic species has been studied in the field of photocatalysis research. Although silver bromide has many advantages, during the photocatalytic process, the silver ions on the surface of silver bromide will combine with photo-induced electrons and inevitably generate silver atoms (Ag^0) during the photocatalytic process, which is the light corrosive of silver bromide [7]. Recently, many composite photocalalysts (such as $AgBr/Ag_3PO_4$ [8,9], $Ag/AgBr/TiO_2$ [10,11], $AgBr/SiO_2$ [12], and Fe(III) modified AgBr [13]) have been widely developed, which solve the repeatability problem of silver bromide to some extent, but the light corrosive problem of silver bromide remains unresolved.

Nowadays, cupric oxide has been a hot topic because of its interesting property as a safety and environmental friendliness semiconductor. Especially the nonstoichiometric p-type CuO with a narrow band gap (about 1.7 eV) is easy to adsorb oxygen molecules forming oxygen vacancies, and then generate reactive oxygen species, thereby it is extensively used in various applications such as catalysis [14,15], gas sensors [16], biological applications [17] and solar energy transformation [18–20]. However, so far, the study of using copper oxide modified silver bromide has not been reported yet.

In our work, we have fabricated AgBr/CuO composites to further enhance photocatalytic performance of silver bromide. In this way, the CuO is partially embedded into the surface of AgBr and easy to absorb oxygen molecules forming oxygen vacancies, which can present strong adsorption sites for O_2 on AgBr. The O_2 adsorbed on the oxygen vacancies can capture photogenerated electrons, simultaneously producing O_2^- radical groups, which are benificial to promote the photodegradation of organic substrates. The other purpose is to solve the light corrosive problem of silver bromide. To this end, bromine water was chosen as a regenerating agent and copper oxide as modification compound to prepare a reusable and highly efficient solar photocatalyst. Furthermore, new insights in the mechanism of MO photodegradation and regeneration for AgBr/CuO composites are also discussed in this paper.

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2. Materials and methods

2.1. Preparation of photocatalysts

CuO, $AgNO_3$, KBr, ethylene glycol and bromide water were analytical reagents (A.R.) and purchased from Sinopharm used without further purification. CuO-modified silver bromide particle was prepared through a precipitation process in a dark condition at room temperature. 0.1 g of CuO was added in 20 mL ethylene glycol under ultrasonication for 30 min, and 1.5 g of silver nitrate and 1.1 g of potassium bromide were added. After stirring for 30 min vigorously, the gray green precipitate was collected by centrifugation, washed with distilled water thoroughly and dried at 60 °C for 6 h. The CuO-modified silver bromide sample was denoted as AgBr/CuO (the molar ratio of AgBr and CuO is about 6.4:1). The procedure adopted for the preparation of AgBr/CuO hybrid photocatalyst is depicted in Scheme 1. For comparation, pure AgBr was prepared with the same precipitation process without add CuO.

2.2. Regeneration of photocatalysts

After MO photodegradation in an aqueous solution under visible-light irradiation, the AgBr/CuO photocatalyst was centrifuged, washed thorough with distilled water, and dried at 60 °C for 6 h. The final sample was named as Used-AgBr/CuO. In typical regeneration reaction, the Used-AgBr/CuO photocatalyst was dispersed in 20 mL bromine water (3%) for 30 min. The regenerated product was subsequently collected by centrifugation, washed thoroughly with distilled water, and dried at 60 °C for 6 h. This sample was named as Re-AgBr/CuO. The procedure adopted for the regeneration process of AgBr/CuO hybrid photocatalyst is depicted in Scheme 2. And also we used the same method to collect Used-AgBr and Re-AgBr.

2.3. Characterization of photocatalysts

The physical property of AgBr/CuO, Re-AgBr/CuO, AgBr and Re-AgBr were systematically investigated. Powder X-ray diffraction (XRD) measurements were performed on the D/max-2500 instrument using Cu Kα radiation (λ=0.15406 nm) at a scanning rate of 0.02°/s. The morphologies (FESEM) of samples were observed with a field-emission scanning electron microscopy (JSM-7001F), and the energy-dispersive spectroscope (EDS) was investigated using a QX200 detector. Diffuse reflectance spectra (DRS) of the samples were evaluated by a Cary 3000 spectrophotometer. X-ray photoelectron spectroscopy (XPS) measurements were detected on an ESCAL-AB 250Xi spectrometer, and the spectra were calibrated to the C 1s peak at 284.8 eV. Fluorescence emission spectra (PL) were carried on an FLsp920 fluorescence spectrophotometer. Room temperature electron spin resonant (ESR) was recorded on a Bruker model JES FA200 spectroscopy at room temperature with the signals of radicals trapped by 5, 5-dimethyl-1-pyrroline N-oxide (DMPO). The setting is as followed: center field is 323.734 mT, microwave freguency is 9055.173 MHz and the power is 0.99800 mW.

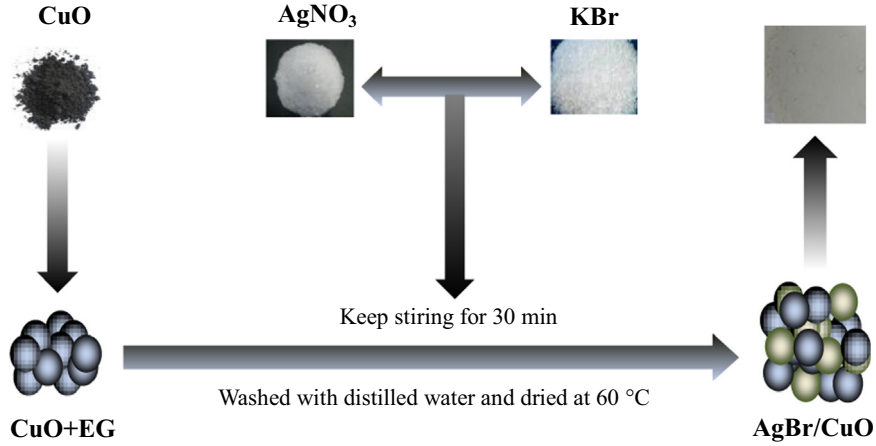
2.4. Photocatalytic activity

The photocatalytic activities of the samples were evaluated by photocatalytic degradation of MO in an aqueous solution under visible-light irradiation. The visible light was obtained from a 500 W Xe lamp with a 420 nm cut off filter produced by Shanghai Lansheng Electronics Company Limited. In each experiment, 0.1 g of as-prepared sample was dispersed in 100 mL of 15 mg L^{-1} MO solution. Prior to illumination, the suspension was stirred for 20 min to reach the absorbance equilibrium. During photocatalysis, 4 mL of the suspension was periodically sampled every 10 min and centrifuged to remove the photocatalyst particles. The upper clear liquid was analyzed using a Varian Cary 50 UV–vis spectrophotometer, and the characteristic absorption of MO at 464 nm was determined to monitor photocatalytic degradation rate.

3. Results and discussion

3.1. XRD analysis

Fig. 1 displays the XRD patterns of pure AgBr, AgBr/CuO, Re-AgBr/CuO and Used-AgBr/CuO hybrid photocatalysts. It is observed that CuO is monoclinic phase (JCPDS no.65-2309) [21], while AgBr is cubic phase (JCPDS no. 06-0438) [22]. As shown in the pattern Fig. 1(b) and (c), AgBr/CuO and Re-AgBr/CuO hybrids exhibit co-existence of both AgBr and CuO phases. Furthermore, as shown in Fig. 1(b) and (d), compared with AgBr/CuO, the diffraction peak at 38.15° (JCPDS no. 02-0931) [9] assigned to Ag^0 was found in Used-AgBr/CuO after three recycling run, indicating that serious photocorrosion of AgBr occurred in the process of photocatalysis. However, the diffraction peak of Ag^0 in the XRD patterns of the Re-AgBr/CuO (Fig. 1(c)) is apparently disappeared, suggesting that Ag^0 originated from light corrosion process transformed to Ag^+ after regeneration. In addition, the diffraction peaks of Re-AgBr/CuO have no obvious difference from that of AgBr/CuO except that the



Scheme 1. Preparing procedure of AgBr/CuO hybrid photocatalysts.