



# Characterization and photostability of Cu<sub>2</sub>O–Ag–AgBr/Al<sub>2</sub>O<sub>3</sub> for the degradation of toxic pollutants with visible-light irradiation



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## ABSTRACT

A plasmonic photocatalyst Cu<sub>2</sub>O–Ag–AgBr supported on mesoporous alumina (Cu<sub>2</sub>O–Ag–AgBr/Al<sub>2</sub>O<sub>3</sub>) was prepared by deposition–precipitation methods. The samples were characterized by means of X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The results indicated that Cu<sub>2</sub>O–Ag–AgBr nanojunctions were formed by the contact of Cu<sub>2</sub>O, AgBr and Ag with each other. The catalyst showed high photocatalytic activity and stability for the degradation of toxic persistent organic pollutants under visible light irradiation. The release of metal ions from the catalyst was significantly inhibited during the photodegradation of pollutants. Four interfacial electron transfer process were verified in the photoreaction system of Cu<sub>2</sub>O–Ag–AgBr/Al<sub>2</sub>O<sub>3</sub> on the basis of electron spin resonance and cyclic voltammetry analyses under a variety of experimental conditions. The results indicated that the coupling of Cu<sub>2</sub>O with Ag NPs and AgBr not only accelerated interfacial electron transfer processes, leading to the fast photoreduction of the dissolved Ag<sup>+</sup> and the photostability of Cu<sub>2</sub>O. These findings could be useful for the practical application of plasmonic visible light photocatalyst and photovoltaic fuel cells.

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## 1. Introduction

Semiconductor–metal nanocomposites have been widely employed in photocatalysis and considered as a promising alternative to solve many environmental and energy issues [1–4]. In particular, nanoparticles (NPs) of noble metals can strongly absorb visible light because of surface plasmon resonance, which greatly enhances the overall photocatalytic efficiency at the interface between the metal and the semiconductor [5–11]. Many plasmonic photocatalysts have been developed based on this phenomenon using a combination of Ag or Au NPs and semiconductor [3,11–15]. The electron transfer was based on both photoexcitation of semiconductor and plasmon-excitations of noble metal NPs on the surface [14,16,17]. The electron injection from surface plasmon resonant noble metal NPs into semiconductor and resultant oxidation of the noble metal NPs to ions, which is released into the aqueous, has been evidenced previously [18–20]. Therefore, the corrosion and dissolution of the noble metal NPs is inevitable in the photocatalytic reaction, limiting the practical application of plasmonic photocatalysts [16,21].

It is possible that enhancing electron transfer may not only inhibit metal ion release, but also improve photocatalytic efficiency [22]. One factor that potentially influences the electronic properties of the nanocomposite is the size of the noble metal particles. For example, previous study has demonstrated the influence of gold NPs deposition on the overall energy and catalytic activity of TiO<sub>2</sub> [2]. In addition, the different surface potential in multi-metal assemblies or metal–semiconductor heterojunction may also influence interfacial electron behavior [23]. Our previous study demonstrated that the coupled Au and Ag NPs exhibited high photosensitivity and photostability in Au–Ag–AgI/Al<sub>2</sub>O<sub>3</sub> [22]. Besides, it is known that the composite of two semiconductive oxides may enhance the opto-electrical properties due to the difference in band gap structures. The matching band potentials facilitated the fast transfer and separation of the photoinduced carriers [1]. p-type cuprous oxide (Cu<sub>2</sub>O) not only make good use of visible light as photocatalyst directly, but also can be used as sensitized semiconductor for a solar cell. Cu<sub>2</sub>O with a CB level of –1.4 eV–SHE, is known to be one of the oxides with high level of conduction bands [24]. Therefore, the photogenerated electrons in Cu<sub>2</sub>O can easily transfer to other semiconductor [25] or be captured by O<sub>2</sub> and H<sub>2</sub>O [26]. It is expected that the electron transfer of plasmonic photocatalysts can be further improved by the effective modification of Cu<sub>2</sub>O.

Recently, we reported that Ag–AgBr/Al<sub>2</sub>O<sub>3</sub> exhibited high photocatalytic activity for the degradation and mineralization of

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pollutants, due to the Ag NPs plasmon-assisted effect on the AgBr photocatalyst [27]. However, the electron injection from Ag NPs to AgBr, resulted in the oxidation of some Ag NPs to  $\text{Ag}^+$ , which were dissolved in water and resulting in secondary water pollution [18]. In this paper,  $\text{Cu}_2\text{O}-\text{Ag}-\text{AgBr}/\text{Al}_2\text{O}_3$  composites were prepared by deposition–precipitation.  $\text{Cu}_2\text{O}-\text{Ag}-\text{AgBr}/\text{Al}_2\text{O}_3$  exhibited efficient photocatalytic activity under visible light irradiation and the release of  $\text{Ag}^+$  was successfully inhibited to low levels. A plasmon-mediated photocatalytic mechanism was verified by electron spin resonance (ESR) and cyclic voltammetry (CV) analyses under a variety of experimental conditions. A metal ion-releasing suppression mechanism was proposed.

## 2. Experimental

### 2.1. Chemicals and materials

The reagent poly(ethylene glycol)-block-poly(ethylene glycol) (P123), was purchased from Sigma Chemical Co. 5-Tert-butoxycarbonyl 5-methyl-1-pyrroline N-oxide (BMPO) was purchased from the Bioanalytical Lab (Sarasota, FL). All other chemicals used were analytical grade, purchased from Beijing Chemical Co. and used without further purification.

### 2.2. Preparation of catalysts

Mesoporous  $\gamma\text{-Al}_2\text{O}_3$  was prepared from precursors of aluminum *i*-propoxide in the presence of glucose in aqueous system as described previously [28].  $\text{Cu}_2\text{O}$  nanocubes were prepared as described previously, and stored in refrigerator before used [29]. Then,  $\text{Cu}_2\text{O}$  was deposited onto  $\text{Al}_2\text{O}_3$  during the deposition–precipitation process of Ag–AgBr as reported in our previous work [27]. Briefly, 0.08 g of  $\text{Cu}_2\text{O}$  and 0.6 g of  $\gamma\text{-Al}_2\text{O}_3$  was added to 60 mL of distilled water, and the suspension was sonicated for 30 min. Then 0.13 g of KBr was added to the suspension, and the mixture was stirred magnetically for 30 min, and then sonicated for 30 min. Subsequently, 0.6 g P123 was added to the suspension, and the mixture was stirred magnetically 30 min and then sonicated for 30 min. Then, 0.13 g of  $\text{AgNO}_3$  in 1.8 mL of  $\text{NH}_3\cdot\text{H}_2\text{O}$  (25 wt%  $\text{NH}_3$ ) was quickly added to the mixture. The resulting suspensions were stirred at room temperature for 12 h. All the above processes were carried out in a dark situation. Then, the amount of Ag and Cu ions in the supernatant was measured by inductively coupled plasma-optical-emission spectrometry (ICP-OES) on an OPTIMA 2000 (Perkin-Elmer) instrument, confirming that the Ag content of 10 wt% was incorporated in  $\text{Al}_2\text{O}_3$ . And there was not any copper was detected, confirming all the dosage of  $\text{Cu}_2\text{O}$  was deposited. So, the molar ratio of  $\text{Cu}_2\text{O}:\text{Ag}-\text{AgBr}:\text{Al}_2\text{O}_3$  is 1:1:10.59

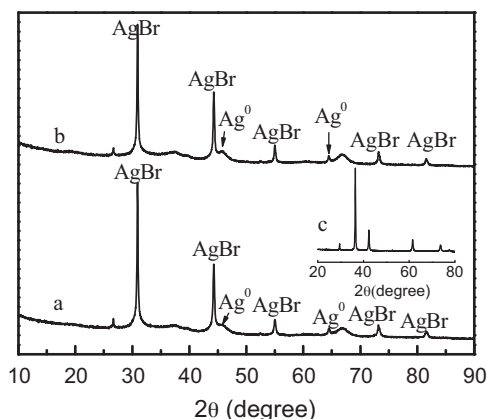


Fig. 1. XRD patterns of (a) Ag–AgBr/ $\text{Al}_2\text{O}_3$ , (b)  $\text{Cu}_2\text{O}-\text{Ag}-\text{AgBr}/\text{Al}_2\text{O}_3$ , (c)  $\text{Cu}_2\text{O}$ .

in  $\text{Cu}_2\text{O}-\text{Ag}-\text{AgBr}/\text{Al}_2\text{O}_3$ . The product was filtered, washed with water, and dried at  $70^\circ\text{C}$ . Finally, the powder was calcined in air at  $500^\circ\text{C}$  for 3 h.

### 2.3. Characterization

The samples were examined by obtaining XRD patterns (XDS-2000 diffractometer; Scintag, Inc., Sunnyvale, CA) and UV–vis diffuse reflectance spectra (Hitachi UV-3100). The high-resolution transmission electron microscopy (HRTEM) images were obtained by using a JEOL-2010 TEM with an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) data were taken on an AXIS-Ultra instrument from Kratos using monochromatic Al  $K\alpha$  radiation and low-energy electron-flooding for charge compensation. All binding energies were calibrated by the C 1s hydrocarbon peak at 284.80 eV. ESR spectra were obtained using a Bruker model A300-10/12 electron paramagnetic resonance spectrometer. The photocurrent from the various samples was measured in a basic electrochemical system (AMETEK Princeton Applied Research, Oak Ridge, TN) with a two-compartment, three-electrode electrochemical cell equipped with

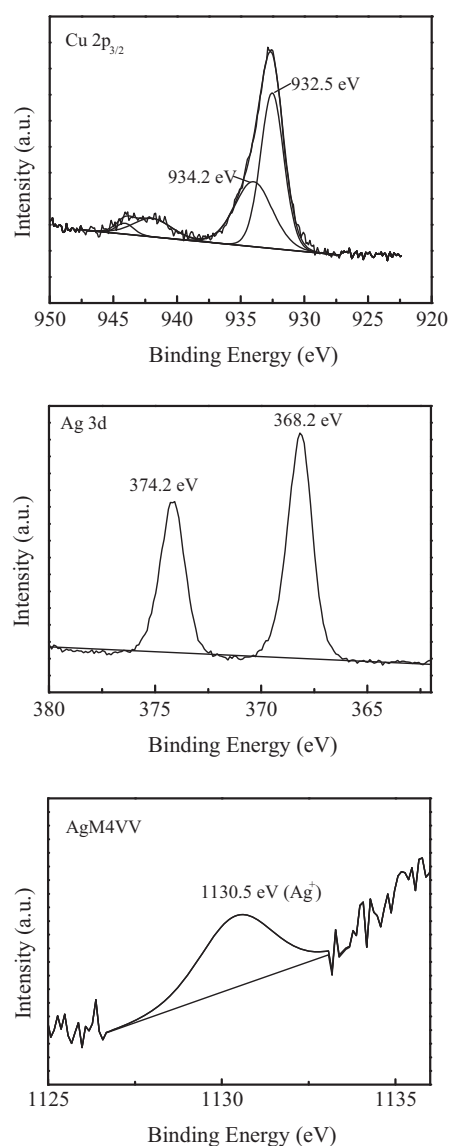


Fig. 2. Cu 2p XPS, Ag 3d XPS and Ag AES spectra for the as prepared  $\text{Cu}_2\text{O}-\text{Ag}-\text{AgBr}/\text{Al}_2\text{O}_3$  sample.

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