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Short Communication

Synthesis of cube-like Ag/AgCl plasmonic photocatalyst with enhanced visible light photocatalytic activity

Xiaxi Yao [a], Xiaoheng Liu [a,*], Dan Zhu [a], Chunbao Zhao [b], Lude Lu [a]

[a] Key Laboratory for Soft Chemistry and Functional Materials of Ministry Education, Nanjing University of Science and Technology, Nanjing 210094, China
[b] Faculty of Microelectric Engineering, Nanjing College of Information and Technology, Nanjing 210046, China

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ABSTRACT

Cube-like Ag/AgCl plasmonic photocatalyst was successfully synthesized through a one-pot precipitation method by simply adding an aqueous solution of $AgNO_3$ into the natural hot spring, wherein the hot spring acted as the chlorine source. The cube-like Ag/AgCl with a size of 0.5–0.9 μm exhibited enhanced visible light photocatalytic performance for the degradation of organic MO dye due to the localized surface plasmon resonance (LSPR) of the photoexcited Ag species. The trapping experiments confirmed that $\bullet O_2^-$ and h^+ were the main active species during the photocatalytic process.

1. Introduction

Heterogeneous photocatalysis is a significantly efficient way for the elimination of environmental pollutants [1–3]. Semiconductor-based photocatalysts have been widely investigated for the application in the photocatalytic field [4,5]. Unfortunately, most of the semiconductors, for example, TiO_2, can only be photoexcited by UV light (a small fraction of solar spectrum, ca 5%) owing to their large band gap. As a result, a tremendous effort has been made to explore visible light-driven photocatalysts. Recently, nano-scale noble metals have received intense attention because of their localized surface plasmon resonance (LSPR) [6–9]. This is much favorable for the full use of sunlight and this kind of material is named as plasmonic photocatalyst. Among the various plasmonic photocatalysts, Ag/AgX (X = Cl, Br) composites become the concerned focus owing to the outstanding photocatalytic performance and excellent stability [10–12]. Surfactant-assistant or template-direction is the conventional technique to synthesize Ag/AgCl structure with special cubic shapes [11,13,14]. However, much work remains to be done to form the metallic Ag^0 species by chemical reduction or photoreduction and remove the residual surfactants or templates. It is of much importance to explore a facile way to synthesize visible light-driven Ag/AgCl photocatalyst with cube-like morphology.

Geothermal energy is the natural heat energy contained in the depths of the earth, primarily attributed to the magma and the decay of the radioactive isotopes [15]. Geothermal resource is a kind of renewable energy, which can provide clean and green energy. The formation of hot spring originates from the ground water heated by geothermal energy and hot magma. Then the heated water gushes out of the surface cracks owing to the existence of hydrostatic pressure gradient. Hot spring is widely distributed in the world and has been used in many fields as diverse as heat supply, generation of electric power, physical therapy and crop irrigation [16]. In general, hot spring contains Cl^-, HCO_3^-, SO_4^{2-}, Na^+, Mg^{2+} and so on. In this work, we highlight the synthesis of cube-like Ag/AgCl through a one-pot precipitation reaction, wherein no surfactant, template or other additives were required. The as-synthesized Ag/AgCl sample exhibited a superior photocatalytic activity for the photodegradation of organic pollutants under visible light irradiation. This new work might extend the potential application of cheap hot spring in environment purification.

2. Experimental section

2.1. Synthesis of cube-like Ag/AgCl plasmonic photocatalyst

The hot spring in this work was taken from Tengchong County, Yunnan Province, China. In a typical process, 5 mL of 0.01 M $AgNO_3$ aqueous solution was dropwise added into 20 mL of diluted hot spring at room temperature under vigorous magnetic stirring. The color of the suspension turned from white to dark gray quickly about 30 min later owing to the partial decomposition of AgCl under sunlight. The resultant product was washed with deionized water and collected by centrifugation. The Cl^- concentration in the raw hot spring is 1131.1 mg/L, which has been reported in our previous literature [17]. The Cl^-

* Corresponding author. Tel.: +86 25 84315943; fax: +86 25 84315054.
E-mail address: xhliu@mail.njust.edu.cn (X. Liu).

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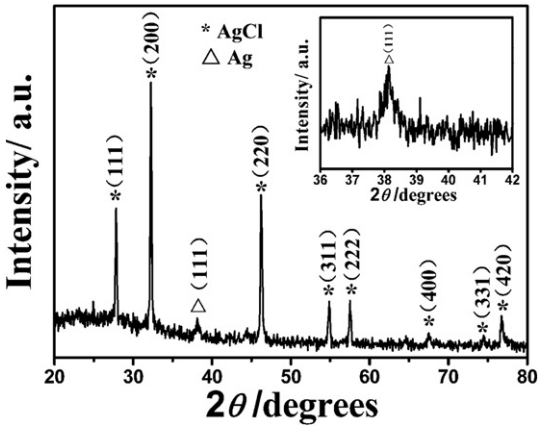

Fig. 1. The XRD pattern of as-synthesized Ag/AgCl photocatalyst. Inset: slow sweep XRD pattern from 36° to 42°.

concentration used in this work is about 141.4 mg/L by diluting the raw hot spring. White AgCl sample was prepared in a similar way in a dark room. Yellowish N-doped TiO_2 product was obtained according to the reported literature [18].

2.2. Characterization

The phase structure and morphology were investigated by powder X-ray diffraction (XRD, Bruker D8 advance) with Cu K_α radiation, scanning electron microscopy (SEM, JEOL JSM-6380 LV) and transmission electron microscopy (TEM, JEOL JEM2100). The surface elemental components were analyzed by X-ray photoelectron spectra (XPS, Phi Quantera II SXM) using a monochromatic Al K_α radiation ($\lambda = 8.4$ Å) as the exciting source. UV–vis diffuse reflectance spectra (UV–vis DRS) were conducted on a UV–vis spectrophotometer (Shimadzu UV-2500).

2.3. Evaluation of photocatalytic activity

The photocatalytic performance was estimated by the photodegradation of methyl orange (MO) or 4-chlorophenol (4-CP) aqueous solution under visible light irradiation. Typically, 10 mg photocatalysts were dispersed in a 20 mL MO aqueous solution (10 mg/L) or 18 mg photocatalysts were dispersed in a 20 mL 4-CP aqueous solution (10 mg/L). The suspension was stirred in the dark for 30 min to reach an adsorption–desorption equilibrium. Then the suspension was irradiated using a 300 W xenon lamp equipped with a 400 nm cut-off filter. The photodegradation process of MO and 4-CP was monitored by measuring the UV–vis absorption on a UV–vis spectrophotometer (UV-1201).

3. Results and discussion

3.1. Crystal structure and morphology

Fig. 1 shows the XRD pattern of the as-obtained Ag/AgCl photocatalyst. The diffraction peaks at 27.8°, 32.2°, 46.2°, 54.8°, 57.4°, 67.4°, 74.4° and 76.7° can be ascribed to (111), (200), (220), (311), (222), (400), (331) and (420) planes of cubic phase AgCl (JCPDS No 31-1238), respectively [19,20]. Fig. 1 inset presents the slow sweep XRD pattern from 36° to 42°. The weak diffraction peak at 38.1° is indexed to (111) plane of the face-centered cubic phase Ag (JCPDS No. 65-2871) [21–23]. As a result, Ag/AgCl photocatalyst was successfully synthesized via a one-pot precipitation method in hot spring.

The morphology of the resultant products was observed by SEM and TEM. As shown in Fig. 2(a,b), the Ag/AgCl sample shows a cube-like morphology with a size of 0.5–0.9 μm. Fig. 2(c) displays the TEM image of an individual Ag/AgCl cube with a side length of 0.6 μm. The Ag/AgCl photocatalyst exhibited the square shape, which is consistent with the cubic morphology in SEM images. The nanoparticles on the surface may be metallic Ag particles, which are formed by the decomposition of AgCl under the high-energy electron beam [24]. Fig. 2(c) inset demonstrated the further decomposition of AgCl after long-time focusing and many small particles produced all around.

The chlorine anion is indispensable for the precipitation of AgCl sample, and the other species in the hot spring are helpful for the formation of cube-like Ag/AgCl photocatalyst. In order to verify the particularity of the hot spring, a controllable experiment was conducted to synthesize Ag/AgCl photocatalyst in the sodium chloride (NaCl) solution. The chlorine anion concentration was kept the same as that used for the synthesis of cube-like Ag/AgCl in hot spring. Fig. S1 shows the typical SEM images of Ag/AgCl photocatalyst prepared in NaCl solution. It was found that the obtained Ag/AgCl were irregular particles with a wider size distribution from 0.5 to 2 μm. Therefore, the hot spring is helpful for the synthesis of uniform and highly-dispersed cube-like Ag/AgCl although the function of other species in the hot spring has not been clearly understood.

3.2. XPS and UV–vis DRS analyses

Fig. 3(a) depicts the wide XPS spectrum of cube-like Ag/AgCl and it is composed of Ag, Cl, Si, O and C elements. The little amount of Si arises from the silica in hot spring [25–27]. The C 1s and O 1s are attributed to the adventitious contaminants and adsorbed hydroxyl groups (or water) [28]. The spectrum of Cl 2p gives two isolated peaks at 197.8 and 199.4 eV, which can be ascribed to Cl $2p_{3/2}$ and Cl $2p_{1/2}$, respectively [29]. The Ag 3d region in Fig. 3(c) displays two peaks at 376.7 and 373.7 eV, corresponding to Ag $3d_{5/2}$ and Ag $3d_{3/2}$, respectively. The XPS peaks for Ag $3d_{5/2}$ and Ag $3d_{3/2}$ can be further deconvoluted into two distinct peaks. Those at 367.6 and 373.6 eV belong to Ag^+ of AgCl, while those at 368.1 and 374.1 eV belong to Ag^0 species. The molar

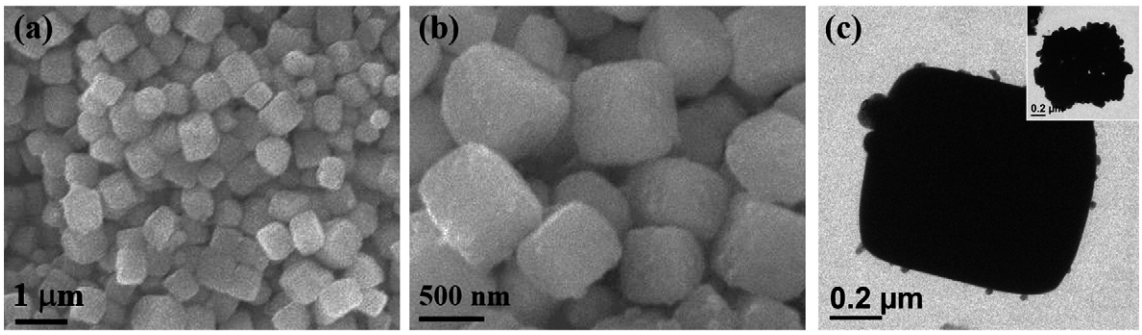

Fig. 2. (a,b) SEM images of cube-like Ag/AgCl, and (c) TEM image of an individual Ag/AgCl cube. (c) Inset: the TEM image captured after further focusing.