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One pot controllable synthesis of AgCl nanocrystals with different morphology and their photocatalytic activity

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ABSTRACT

AgCl nanocrystals with cubic, spherical and octahedral morphology, and tunable size of 0.3– 2 μm have been successfully prepared by a one pot hydrothermal method using cetyltrimethyl ammonium chloride (CTAC) as Cl^- source and stabilizer. Besides, the unconventional plate-like AgCl particles can be obtained by the addition of polyvinyl pyrrolidone (PVP). Photocatalytic tests show that the as-prepared AgCl photocatalysts with cubic, octahedral and plate morphology all exhibit stable photocatalytic efficiency, and the plate AgCl nanocrystals exhibits higher photocatalytic activity than cubic and octahedral AgCl nanocrystals owing to its high-index facets, stacking faults and twin defects, making it a promising photocatalyst applied in environmental management.

1. Introduction

Semiconductor photocatalysts have attracted increasing attention in many areas, such as water splitting [1,2], water disinfection [3], and organic pollution control [4]. In general, most research focused on transient metal oxide semiconductors, such as the TiO_2 photocatalyst [5–7], but this kind of photocatalyst could only make use of ultraviolet (UV) light to ensure their photocatalytic activity [8], which limits their application driven by visible light. Although modified measures such as doping [9], sensitization [10] and coupling [11] have been taken to increase the absorption coefficient of TiO_2, the limited improvement and the complex preparation method limit their application in large scale. Thus, fabricating efficient photocatalysts sensitive to visible light with facile and simple synthesis process is still a promising issue.

Silver halides (AgX, X═ Cl, Br, I) are one of the most promising photocatalysts that have found to exhibit high photocatalytic activity under illumination of visible light [12–16]. Previous researches have shown that photocatalysts with different shape and particle size often exhibit different photocatalytic activity [17,18], thus making the controllable preparation of photocatalysts with different shape and size by a simple approach extremely important. To date, most synthesis utilize EG (ethylene glycol) as solvent, and the ionic liquid as Cl^- source [12,19,20], the research on the synthesis of AgCl particles in aqueous solution (with relatively lower preparation cost) is relatively less. In addition, although AgCl particles with several morphologies have been successfully synthesized by different synthetic method [21–24], the diversity of AgCl morphology is still not high, and there are few reports on the controllable preparation of AgCl with different morphology and size by simply changing the reaction parameters.

Herein, a simple one pot process for the synthesis of AgCl with tunable morphology and size was reported. The cetyltrimethyl ammonium chloride (CTAC), a common surfactant, was used as both the Cl^- source and stabilizer. The AgCl particles with cubic, spherical and octahedral morphology with different particle size (0.3– 2 μm) were obtained by simply changing the reaction conditions. Besides, the plate AgCl particles could be prepared with the assistance of PVP, which have not been reported for the AgCl photocatalysts. The cubic, octahedral and plate AgCl were chosen to evaluate their photocatalytic activity, and they all exhibit stable photocatalytic efficiency. The plate AgCl exhibits higher photocatalytic activity compared with octahedral and cubic AgCl in the photodegradation of methyl orange (MO), attribute to its high-index facets, stacking faults and the twin defects.

2. Experimental section

2.1. Materials

Analytical reagents of silver nitrate ($AgNO_3$, 99.99%) and cetyltrimethyl ammonium chloride (CTAC) were purchased from Aladdin Chemical Reagent Co. Ltd. Analytical reagents of aqueous ammonia ($NH_3 \cdot H_2O$), absolute ethanol, methyl orange (MO) and polyvinyl pyrrolidone-K30 (PVP-K30) were purchased from Sinopharm Chemical Reagent Co. Ltd. All reagents were used without further purification.

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2.2. Synthesis of AgCl nanocrystals

The AgCl nanocrystals were prepared with CTAC as both the Cl^- source and protective agent. In a typical experiment, 5 mL silver ammonia with concentration of 30 mM was added to 20 mL water with magnetic stirring. The silver ammonia was prepared by adding aqueous ammonia dropwise into the $AgNO_3$ solution until the solution turned clear. After 1–2 min, 5 mL CTAC solution ($AgNO_3$/CTAC molar ratio $=$ 1/2) was introduced and the mixture was stirred at room temperature for 30 min. The resulting mixture was transferred into a 50 mL teflon autoclave, then heated at 120 °C for 15 min. The as-prepared AgCl were separated by centrifugation and washed with water and ethanol for two times, respectively, and then were dispersed in ethanol for further characterization.

2.3. Study of photocatalytic activity

The photocatalytic activity of AgCl particles were measured by the photodegradation of methyl orange (MO). Typically, 40 mg AgCl photocatalysts were dispersed in 100 mL MO aqueous solution (20 mg/L). Before light irradiation, the suspension was firstly sonicated for 5 min and then kept stirring in the dark for 30 min until the dye absorption equilibrium reached. The suspension was then exposed to visible light emitted by a 500 W Xe arc lamp. 3 mL of the sample was taken out at every 10 min and centrifuged at 12000 rpm for 5 min. The top solution was analyzed by a UV–Vis spectrophotometer.

2.4. Characterization

The morphology and size of the resulted AgCl were investigated by scanning electron microscopy (SEM) with a JSM-6360LV instrument. The structure of the samples was determined by X-ray diffraction (XRD) using a Rigaku-TTR III diffractometer with the Cu K_α wavelength (1.5406 Å). The UV–vis absorption spectra were measured by a Hitachi U-4100 UV–vis spectrophotometer. The elemental components were analyzed by an ESCALAB 250Xi X-ray photoelecton spectra (XPS) using a monochromatic Al K_α radiation ($\lambda = 8.4$ Å) as the exciting source.

3. Results and discussion

3.1. Morphology and crystal structure of the typical cubic AgCl

Fig. 1 shows SEM images and the histogram of particle size distribution of the as-prepared typical cubic AgCl particles when $AgNO_3$ concentration $=$ 30 mM and $AgNO_3$/CTAC molar ratio $=$ 1/2. As shown in Fig. 1, the AgCl particles have a cubic shape, with a narrow size distribution and an average particle size of 307.2 nm (Fig. 1c). Fig. 2 shows the XRD pattern of the cubic AgCl particles, and all the diffraction peaks observed in the spectra can be indexed to (111), (200), (220), (311), (222), (400), (331) and (420) crystal planes of AgCl with a cubic phase structure (JCPDS file: 31–1238), demonstrating that the samples are pure AgCl crystals, and no metallic Ag was generated in this process.

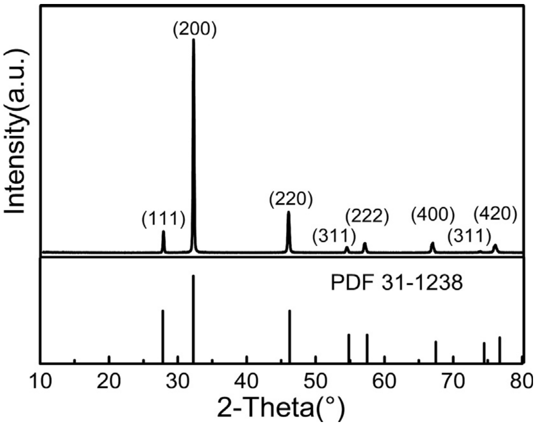

Fig. 2. XRD pattern of cubic AgCl particles.

Fig. 3 (a) presents the XPS spectra of cubic AgCl particles. It is composed of Ag, Cl, C and O elements. The C 1s and O 1s may be due to the residual CTAC additive and adsorbed water. The Cl 2p region in Fig. 3(c) displays two peaks at 197.8 and 199.4 eV, corresponding to Cl $2d_{3/2}$ and Cl $2d_{1/2}$, respectively. The spectrum of Ag 3d gives two isolated peaks at 367.6 and 373.6 eV, which can be ascribed to Ag $3d_{5/2}$ and Ag $3d_{3/2}$, respectively. These two peaks at 367.6 and 373.6 eV are belong to Ag^+ of AgCl [8,22], indicating that no metallic Ag was generated, which was accorded with the XRD analysis.

3.2. Shape control of AgCl particles

The effect of reaction time was studied to investigate the growth development of cubic AgCl particles, the results are shown as Fig. 4. From Fig. 4, quasi-spherical AgCl particles with size of 200– 400 nm are observed when reaction mixture is hearted up to 120 °C without duration (0 min, Fig. 4a). The cubic particles with a size of ~300 nm are formed when heated at 120 °C for 15 min (Fig. 4b). As time prolonged, the particle size increases and the number of small cubic AgCl particles decreases (Fig. 4c and d), and the AgCl particles grow into cubic morphology with a size of ~2 μm in 8 h (Fig. 4e). As the reaction time further prolonged to 16 h, the size of micron-cubic AgCl further increased and the cubic morphology transformed to quasi-spherical.

(a) $t = 0$ min, (b) $t = 15$ min, (c) $t = 1$ h, (d) $t = 4$ h, (e) $t = 8$ h and (f) $t = 16$ h.

Fig. 5 shows the SEM images of the products prepared at different temperature with reaction time of 8 h. The quasi-spherical AgCl particles are formed at 100 °C(Fig. 5a). When the temperature is 120 °C, cubic AgCl particles with a size of ~2 μm are obtained (Fig. 5b). With further increasing of the reaction temperature, the AgCl particles become more and more irregularly, and some agglomerated particles are formed, as shown in the red square of Fig. 5d. When the reaction

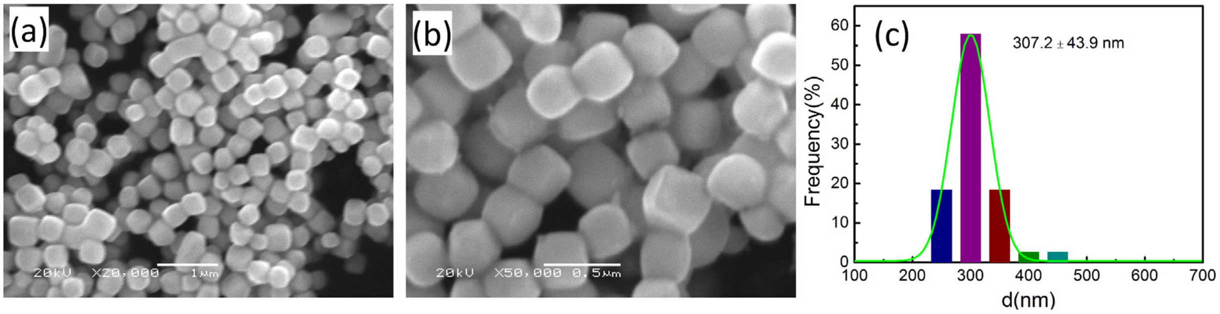

Fig. 1. (a,b) SEM images of cubic AgCl particles. (c) Size distribution of the cubic AgCl particles.