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Facile Synthesis of AgCl Hollow Nanospheres for Enhanced Photocatalytic Properties

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Abstract: AgCl hollow nanospheres have been synthesized successfully via a hard-template approach using silica nanospheres as hard template for the first time. The phase, size and morphology of the as-prepared AgCl were investigated by X-Ray Diffraction (XRD), Field-Emission Scanning Electron Microscopy (FESEM); which reveals that the cubic AgCl hollow nanospheres with a cell constant a = 5.549 Å are 220 nm in diameter and 10 nm of shell-thickness. The as-prepared AgCl hollow nanospheres demonstrate enhanced photodegradation of Rhodamine (RhB) under visible light irradiation than AgCl microparticles. The AgCl hollow nanospheres are of great importance to wide application in catalysis, drug delivery and nanobiotechnology.

Keywords: Inorganic Compound, Epitaxial Growth, Crystal Growth, Nanoparticles, Photocatalysis

Introduction

Fabrication of nanomaterials with a controllable size and shape is of great interest in many current and emerging areas of technology (Xia *et al*., 2003; Lou *et al*., 2008). Hollow micro-/nanostructures have received much attention owing to their wide applications in many fields such as catalysis, drug delivery, chemical/biological separation and sensing (Davis, 2002; Qian *et al*., 2007; Zhu *et al*., 2005). Over the past decades, many efforts have been paid to the development of different methods for the design and fabrication of hollow nanospheres and nanotubes, such as chemical vapor deposition (Goldberger *et al*., 2003; Zhan *et al*., 2004) layer-by-layer technique (Caruso *et al*., 1998; Caruso, 2001), sacrificed template method (Lou and Archer, 2008; Qian *et al*., 2006; Van Bommel *et al*., 2003), microemulsion (Lin *et al*., 2008; Schacht *et al*., 1996), polymer/surfactant soft templates techniques (Li *et al*., 2003; Yu *et al*., 2006), etc. Plasmonic Ag composites are promising candidates for highly efficient, active and stable photocatalysts under visible light due to Ag strong Surface Plasmon Resonance (SPR); which has been widely applied in optical and imaging fields, photothermal cancer therapy and high electro-oxidation activity etc., (Skrabalak *et al*., 2008; Jain *et al*., 2008; Huang *et al*., 2006; Tian *et al*., 2007). Recently, sliver halides/Ag photocatalysts have been widely used to photodegradation towards organic dyes due to their stability (Yu *et al*., 2006; Jiang and Zhang, 2011; An *et al*., 2010; Cheng *et al*., 2011). However, it is still a challenge and hot topic to search for the large-scale synthesis of silver halide with well controlled size and morphology. Up to date, the plasmonic catalyst AgCl/Ag hollow nanostructures have not been achieved so far.

Herein, a facile hard template process has been developed to synthesize plasmonic photocatalyst AgCl hollow nanospheres using $[Ag(NH_3)_2]Cl$ as starting material. Epitaxial growth of AgCl layer on the surface of silica nanospheres was carried out via NH_3 volatizing to atmosphere from the mixture solution of $[Ag(NH_3)_2]Cl$ to form SiO_2@AgCl core-shell nanospheres. Finally, AgCl hollow nanospheres were achieved while the silica templates were removed using HF solution. Ag nanoparticles could be in-situ formed on the backbone of the AgCl hollow nanospheres by converting some Ag ions to Ag^0 species via visible light irradiation (Lu *et al*., 2013; An *et al*., 2012; Feng *et al*., 2012). The total synthetic process and the mechanism for the formation of the AgCl/Ag hollow nanospheres were shown in Fig. 1.

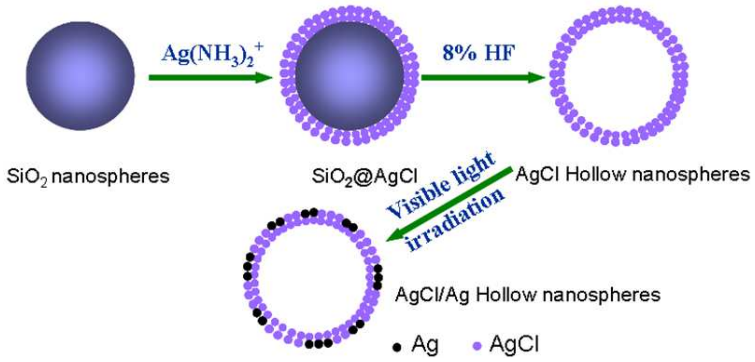

Fig. 1. Schematic illustration of formation of AgCl and the plasmonic photocatalyst AgCl/Ag hollow nanospheres

Experimental

All Chemicals are of Analytic Grade and Used as Received.

In a typical synthetic process, 2 mL Tetraethyl Orthosilicate (TEOS) and 1 mL distilled water were added into 20 mL absolute ethanol to form clear solution in a bottle; and then 2 mL ammonium hydroxide was dropwise added into the former solution and stirred vigorously for 24 h. Subsequently, the product in white was collected by centrifugation and washed three times with absolute alcohol and distilled water; respectively. Finally, it was dried at 60°C for 6 h.

About 0.5 g amorphous silica nanospheres were dispersed with 10 mL water and stirred vigorously in a 50 mL wide-necked bottle; and then 1 mmol of $AgNO_3$ and 1 mmol of NaCl were added into the above dispersed silica solution. Subsequently, 3 mL of ammonia solution (25-28%, wt%) was added into the previous mixed solution; and the total mixture solution was sonicated for 10 min and kept stirring vigorously for 6 h. The product was collected by centrifugation and washed three times with double distilled water. Finally, 0.2 g of the product was dispersed with 5 mL distilled water and 2 mL of 8% HF solution was added into the solution and kept at room temperature for 6 h to remove the silica templates. The final product was collected by centrifugation and washed with water for three times and then dried at 60°C for 6 h.

The morphology and size of the samples were investigated by Field-Emission Scanning Electron Microscopy (FESEM, JEOL-6700F); and UV-vis spectroscopy was recorded on Shimadzu spectrophotometer (2501 PC model, Kyoto, Japan), respectively. The phase of the as-prepared product was characterized by X-Ray power Diffraction (XRD) analyses, which was carried out on a Philips X'Pert PRO SUPER X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation and the operation voltage and current were maintained at 40 kV and 40 mA, respectively. The photocatalytic activity of the as-prepared samples was evaluated by the degradation of RhB under visible light irradiation of 250 w Xe lamp with Uv cut off filter. The degradation of Rhodamine (RhB) was carried out in a 100 mL beaker containing 50 mL RhB with a concentration of 1×10^{-5} mol L^{-1} (4.8 mg L^{-1}) and 40 mg of the as-prepared AgCl hollow nanospheres with vigorous magnetic stirring at room temperature under visible light irradiation for given time interval. The concentration of RhB was measured by UV-vis spectrophotometer at given interval during the degradation process of RhB.

Results and Discussion

The first step of the synthesis of AgCl hollow nanospheres involved the production of uniform silica nanospheres according to the modified protocol (Stöber *et al*., 1968). Figure 2a and b show typical FESEM images of the as-prepared silica nanospheres with 220 nm in diameter. The phase of the as-prepared product was investigated by X-Ray Diffraction (XRD) analyses.

Figure 3 displays the XRD patterns of the as-prepared samples obtained from 1 mmol of $AgNO_3$ and 1 mmol of NaCl and 3 mL of ammonia solution (25-28%, wt%) in presence of 0.5 g silica nanospheres at room temperature for 6 h according to schematic illustration shown in Fig. 1; in which all the diffraction peaks can be identified to cubic AgCl (JCPDS no. 31-1238) with a cell constant a = 5.549 Å and the broad peak around 23° corresponding to amorphous silica.

Figure 4a and b show the FESEM images of the as-prepared SiO_2@AgCl core-shell nanospheres; which are consisted of uniform nanospheres with similar size and rougher surface than the SiO_2 nanospheres. AgCl hollow nanospheres could be obtained by removal the hard template using 8% HF solution. As shown in Fig. 4c-d, uniform nanospheres with 220 nm in diameter and shell-thickness of *ca.* 10 nm were obtained and no free nanoparticles could be found elsewhere.

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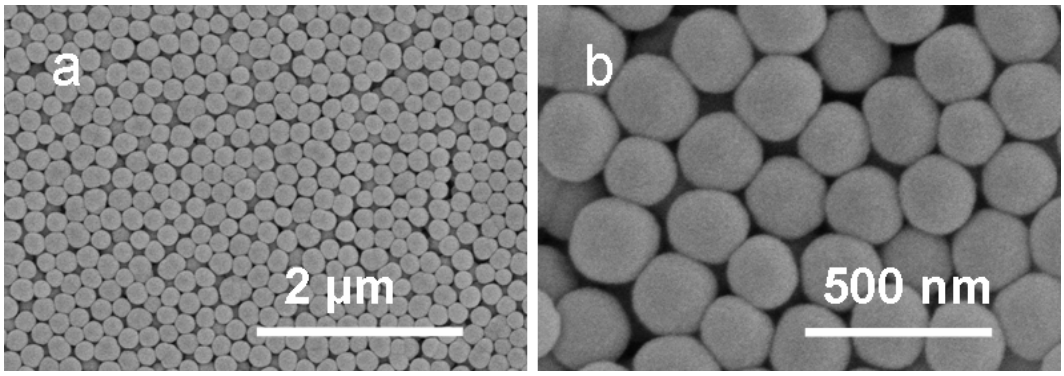

Fig. 2. FESEM images of silica amorphous nanospheres (a-b)

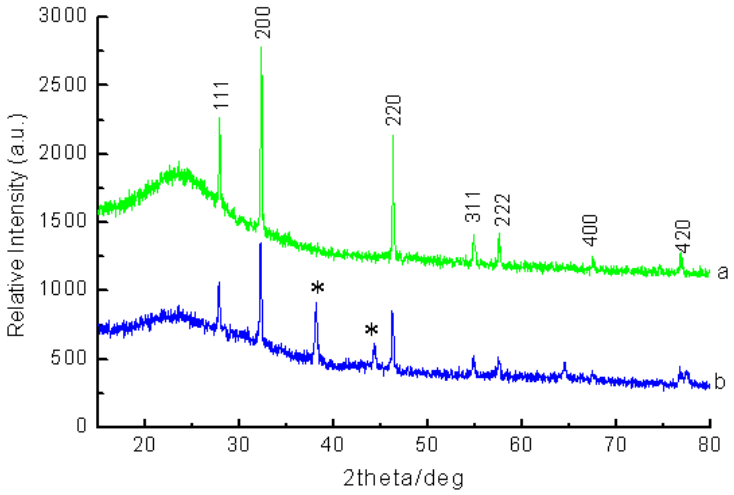

Fig. 3. XRD patterns of the as-prepared samples obtained from 1 mmol of $AgNO_3$ and 1 mmol of NaCl and 3 mL of ammonia solution in presence of 0.5 g silica nanospheres at room temperature for 6 h (a); and the as-prepared photocatalysts after irradiation by Xe lamp

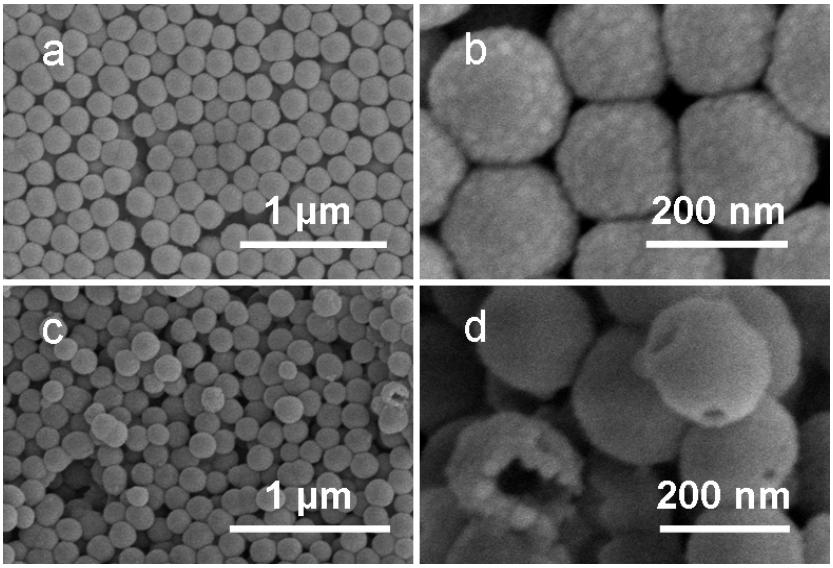

Fig. 4. (a and b) FESEM images of the SiO_2@AgCl core-shell nanospheres (c and d) FESEM images of the AgCl hollow nanospheres

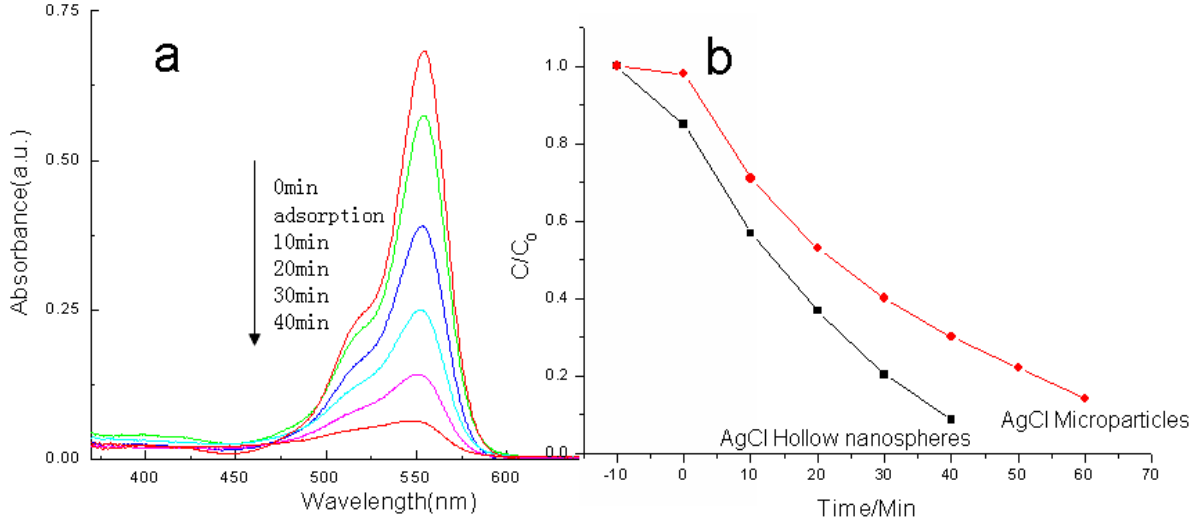

Fig. 5. UV-vis spectra showing photodecomposition of RhB dye in solution over the as-prepared AgCl hollow nanospheres (40 mg) under visible light irradiation and the relationship of degradation rate of RhB with the irradiation time

Figure 5 displayed the photodegradation behaviors of RhB solution (4.8 mg L^{-1}, 50 mL) over the AgCl hollow nanospheres under visible light irradiation of 250 w Xe lamp. The characterized peak located at 553 nm for RhB dye in UV-vis spectra was used to evaluate their photodegradation at given time interval. The complete photodegradation of RhB solution (4.8 mg L^{-1}, 50 mL) only requires 40 min over the as-prepared AgCl hollow nanospheres, suggesting the as-prepared AgCl photocatalyst has more excellent catalytic performance toward the RhB solution than our previous Ag_2WO_4/AgCl photocatalyst (Liu *et al*., 2013). For comparison, the complete photodegradation of RhB solution (4.8 mg L^{-1}, 50 mL) requires more than 60 min for the AgCl microparticles as revealed by our previous study. The as-prepared AgCl photocatalyst has remarkable photocatalytic activity because Ag nanoparticles can trap electrons; and then facilitate the separation of photo-generated electron-hole pairs and enhance photocatalytic efficiency by converting some Ag ions to Ag^0 species via visible light irradiation (Feng *et al*., 2012; Darroudi *et al*., 2012). As shown in Fig. 2b, the peaks located at 38.2, 44.3, 64.3° could be indexed to the cubic Ag (JCPDS no. 87-0597) with a cell constant a = 4.086 Å, which revealed that Ag phase has been observed and formed after visible light irradiation.

Conclusion

In summary, plasmonic photocatalyst AgCl hollow nanospheres have been fabricated successfully via a hard template process. The results reveal that the AgCl hollow nanospheres are with 220 nm in diameter and 10 nm in shell-thickness. The as-prepared AgCl hollow nanospheres exhibit enhanced photodegradation of RhB dye under visible light irradiation due to the Surface Plasmon Resonance (SPR) absorption and remarkable photocatalytic activity of the new Ag phase derived from photodecomposition of AgCl by photoirradiation. The AgCl hollow nanospheres will be of great importance due to potential applications in optical and imaging field, photothermal cancer therapy.

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Author's Contributions

Jing Chen: Synthesized the AgCl hollow nanospheres.

Yuling Zhao: Synthesized silica nanospheres.

Xinhui Liu: Operated the SEM images for the products.

Fang Li: Performed the photocatalytic experiments.

Haisheng Qian: Conceived the research and designed the experiments and wrote the paper.

Ethics

This article is original and contains unpublished material. The corresponding author confirms that all of the other authors have read and approved the manuscript and no ethical issues involved.

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