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Hydrothermal synthesis of silver crystals via a sodium chloride assisted route

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ABSTRACT

Novel silver crystals with three ditches on one of the facets have been synthesized via a simple hydrothermal method using poly(vinylpyrrolidone) (PVP) as mild reductant and capping agent. Sodium chloride (NaCl) served as aCl^- source, and the formation of AgCl compound could greatly reduce the amount of free Ag^+ in solution and therefore can control the reaction rate. The factors including ratio of Ag^+:Cl^- and temperature on the shape as well as size of the silver product were investigated in detail, and higher concentration of NaCl was helpful in the formation of one-dimensional (1D) silver nanorods. This work provides a new way to fabricate silver crystals from insoluble salts, and it can be extended to synthesize other nanomaterials.

1. Introduction

Noble metal micro/nanomaterials have received increasing attention due to their fascinating properties and potential applications in many fields, such as sensing, biomedicine, catalysis, and electronic devices [1,2]. It is widely accepted that the intrinsic properties of nanomaterials are highly dependent on their size, shape, composition, and crystallinity. To date, many approaches have been developed to prepare metal micro/nanostructures in different shapes, including wires, belts, ribbons, prisms, sheets, cubes, and so on [3–5]. Among these noble metals, silver nanostructures have received intensive interest because silver possesses the highest electrical and thermal conductivity. Hence, it has found many applications as a photonic crystal, an optical polarizer, and a catalyst, as well as in biomedical and chemical sensing via surface-enhanced Raman scattering (SERS) or surface-enhanced fluorescence (SEF) [6,7].

Silver nanostructures with various morphologies have been successfully prepared via different methods [8–12]. For example, Coskun successfully prepared silver nanowires using ethylene glycol as both solvent and reducing agent [8]. Personick and coworkers reported the plasmon-mediated synthesis of silver cubes with unusual twinning structures using short wavelength excitation [10]. Most of the above work needed special instruments or toxic reagents, and this would hinder the large scale production for practical applications. The polyol process seems to be a promising method for the synthesis of silver nanostructures in terms of cost, yield, and simplicity. Xia's group developed this route to prepare silver nanowires on a large scale with the assistance of PVP molecules [13]. PVP is a type of polymer with a hydroxyl end group, and it can serve as a mild reducing agent for the fabrication of noble metal nanostructures.

In this work, we demonstrate a simple Cl^--assisted hydrothermal route to synthesize silver microcrystals with ditches on one of the facets, and such silver microstructures were seldom reported previously. PVP served as a very mild reductant, and different mole ratios of Ag^+:Cl^- as well as temperature effect were investigated in details for the formation of silver crystals. The results revealed that higher concentration of NaCl was helpful to produce 1D silver nanorods.

2. Experimental procedure

Materials and method: All reagents were of analytical grade and were used without further purification. In a typical procedure, 0.34 g of $AgNO_3$ and 1.5 g of PVP (K-30) were dissolved in 20 mL of deionized water with magnetic stirring, and followed by introduction of 20 mL of NaCl aqueous solution (Ag^+:Cl^-=2:1). A milky hydrosol was produced, indicating the formation of colloidal AgCl. After that, the mixture was transferred to a Teflon-lined stainless steel autoclave with 50 mL of capacity, sealed, and maintained at 190 °C for 10 h. After reaction, the product was washed and dried for characterization.

Characterizations: The XRD pattern was recorded on a Bruker D8 focus diffractometer with Cu Kα radiation. FESEM images were

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taken on a JEOL JSM6300F scanning electron microscope equipped with an EDS attachment. An HRTEM image and a SAED pattern were obtained by a JEOL JEM2100F transmission electron microscope with an accelerating voltage of 200 kV.

3. Results and discussion

Fig. 1 shows the typical XRD patterns of the samples obtained at various temperatures, and all the five diffraction peaks can be assigned to the (111), (200), (220), (311), and (222) planes of face-centered cubic (fcc) silver, in good agreement with the reported literature (JCPDS card no. 87-0720). No other peaks of impurities are detected, indicating that metallic silver with high purity can be obtained through the current method.

Fig. 2a shows the EDS spectrum and indicates the fact that the peak for Si originated from silicon wafer. All other peaks could all be ascribed to silver, demonstrating the high purity. Fig. 2b displays the SEM image of the silver sample with a panoramic view, and the size of the particles ranges from 3 to 4 μm. It seems that several ditches exist on the surface of each crystal. The magnified view in Fig. 2c gives more detailed information. The overall silver crystal is of tetrahedral shape, and one of the facets is separated into three smaller ones by ditches. The three ditches with one shared center radiate outside, and the neighboring ditches possess nearly 120° angle. It is probably that triplet crystals grow together and share some facets. As per the HRTEM image shown in Fig. 2d, the clearly observed lattice spacing was calculated to be 0.236 nm, consistent with the interplanar distance between the (111) planes of fcc silver. The SAED pattern in the inset demonstrated the single crystalline nature.

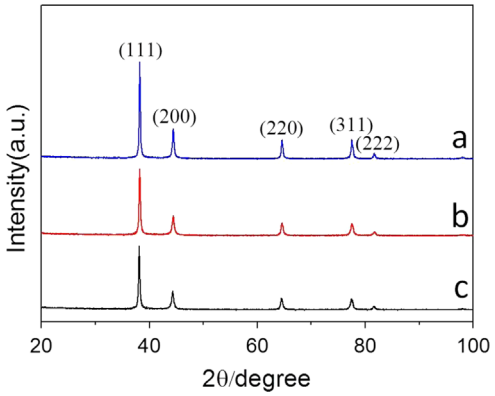

Fig. 1. XRD patterns of silver crystals obtained at (a) 220 °C, (b) 190 °C, and (c) 160 °C.

The molecule of PVP not only acted as a capping agent to protect the product from aggregation, but it also served as a mild reductant to reduce AgCl to metallic silver. It is widely accepted that the reducing ability of alcohol becomes weaker with the increase in the alkyl chains . So a polymer composed of hydroxyl end groups might be an ideal reductant for the synthesis of metal micro/nanostructures because it could kinetically control the nucleation and crystal growth. Only AgCl particles with broad size distribution were produced when no PVP was employed, as shown in Fig. 3a. The inset of the Fig. 3a shows the XRD pattern, where all the diffraction peaks can be indexed to a cubic phase of AgCl (JCPDS no. 31-1238). The maximum size of such particle can be about 40 μm, and AgCl was directly generated when the solution of sodium chloride was introduced into $AgNO_3$ solution. The formation process of compound crystals was so rapid that the nucleation step was hardly separated from the crystal growth step, resulting in the irregular particles with different sizes. On the other hand, AgCl emerged as the final product suggested the role of PVP as reducing agent.

The concentration of NaCl was found to play an important role for the shape control of the silver product. When a minute amount of NaCl (Ag^+:Cl^-=4:1) was added, the product was composed of silver microparticles in large quantities (Fig. 3b). The size ranged from 10 to 20 μm, and it can be clearly observed that a larger microparticle contains several smaller particles grown together. The intermediate compound AgCl has very low solubility in water,

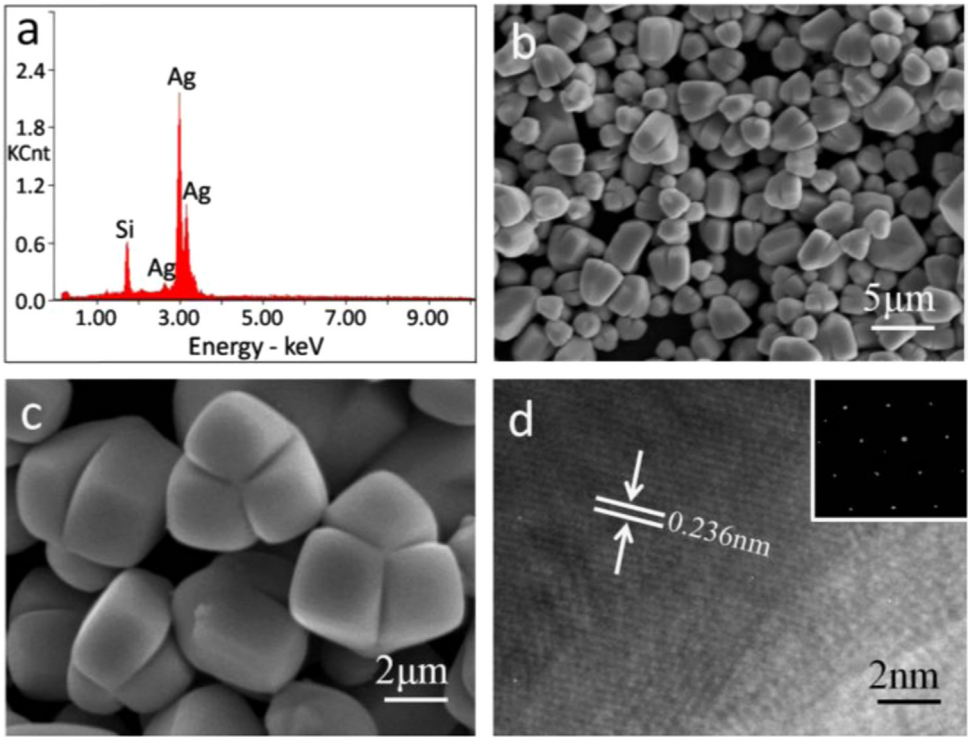

Fig. 2. (a) EDS spectrum, (b, c) SEM images, and (d) HRTEM image of silver particles. The inset of (d) is the SAED pattern.