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Self-organized formation of silver nanowires, nanocubes and bipyramids via a solvothermal method

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Abstract

Three kinds of silver nanostructures – nanowires, nanocubes and bipyramids – were synthesized via a simple solvothermal method by reducing silver nitrate with ethylene glycol using poly(vinylpyrrolidone) as an adsorption agent and adding different concentrations of sodium chloride (NaCl) into the solution. When a low-concentration NaCl solution is used, trace amounts of silver chloride (AgCl) appear and act as the seeds to facilitate the formation of the silver nanowires. However, when a high-concentration NaCl solution is used, large amounts of AgCl appear and mainly act as the controlling agent leading to the formation of silver nanocubes and bipyramids. Electron microscopy, X-ray diffraction and absorption spectra have been used to investigate the products, and a mechanism is proposed to interpret the morphological control of these structures. Our work provides a strategy to fabricate silver nanostructures with different shapes.

Keywords: Solvothermal method; Silver nanostructures

1. Introduction

In recent years, silver nanostructures have drawn much attention due to their unique electrical, optical and thermal properties, as well as their potential applications in microelectronics, optoelectronic devices and surface-enhanced Raman scattering (SERS) [1–7]. Many methods have been developed to produce silver nanostructures with various morphologies [8–10]. In particular, a polyol process was proposed to prepare various silver nanostructures such as nanowires [11], nanobelts [12], nanocubes [13] and bipyramids [14]. In general, in order to obtain morphologically controlled silver nanostructures, especially nanowires, researchers usually introduce special seeds or use shielding gases in the synthesis process to obtain the desired morphologies [15–17]. Based on this strategy, single-crystal cubes or truncated cubes have been prepared in high yields by introducing trace amounts of chloride ions and oxygen (from air) in the polyol process [18,19]. Silver nanocubes have also been fabricated by adding a trace amount of Na_2S during the polyol synthesis [20]. Furthermore, Chen et al. [21] have reported that the silver products can be changed from nanocubes to nanowires by increasing the concentration of Na_2S in the conventional polyol process.

A simple and convenient hydrothermal/solvothermal method is commonly utilized to obtain morphologically different nanostructures of many materials [22–25]. Wang et al. [26] prepared silver nanowires with a uniform diameter by reducing freshly prepared silver chloride with glucose in the absence of surfactants or polymers. Wei et al. [27,28] synthesized chainlike and dendritic silver nanostructures by means of a soft template with poly(vinylpyrrolidone) (PVP) as an adsorption agent. However, there have been few reports to date on the synthesis of morphologically controlled silver nanostructures by adding exotic agents to

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the mixing solution in a hydrothermal/solvothermal method. In this article, we report the fabrication of silver nanostructures via a simple solvothermal method by reducing silver nitrate ($AgNO_3$) with ethylene glycol (EG) and using PVP as an adsorption agent. An interesting morphology evolution was observed by simply changing the concentration of sodium choride (NaCl). Our experiments suggest that the concentration ratio of the silver chloride (AgCl) colloids formed in the initial stage to free silver ions in the solution determines the final morphology of the products. The AgCl colloids act as seeds or controlling agents in the reaction. It is found that more silver nanocubes and bipyramids than nanowires are formed by increasing the NaCl concentration, whereas the reaction time has little influence on the morphology. A mechanism interpreting these morphologically controlling structures has been proposed. Our results indicate that this simple method provides an idea of how to grow silver nanostructures with different shapes.

2. Experimental section

All of the chemical reagents used in our experiments were analytical grade. A 40 ml EG solution of NaCl with different concentrations (0.2 and 20 mM) was vigorously stirred after the addition of 1.776 g of PVP. The mixed solution was injected drop by drop using a syringe into 40 ml of a magnetically stirred EG solution of $AgNO_3$ (0.1 M) for 5 min. The solution became milky white at a low NaCl concentration but cloudy at a high NaCl concentration. Afterwards, the solution was put into four separate 25 ml Teflon-lined autoclave tubes. The tubes were sealed and maintained at 160 °C for different periods of time, followed by natural cooling to room temperature. Finally, the products were washed with acetone and deionized water and centrifuged at 8000 rpm for 20 min. A syringe was used to remove the supernatants containing redundant EG and PVP, and the samples were retrieved from the bottom of the tubes. This process was repeated three times in order to improve the purity of the products. The final samples were preserved in deionized water prior to microstructural and spectroscopic characterization.

The morphologies and chemical compositions of the samples were determined by scanning electron microscopy (SEM) using an FEG JSM 6335 field-emission microscope (JEOL Company, Tokyo) equipped with an EDAX PV7715/89ME energy dispersive X-ray (EDX) spectrometer. Powder X-ray diffraction (XRD) measurements were carried out on a Rigaku 3015 type single-crystal diffractometer using Cu K_α radiation to determine the crystal structures. The samples for XRD and SEM measurements were prepared by dropping the solutions onto polished silicon substrates and drying these at 60 °C. Images were taken by TEM on a JEOL JSM-2010 microscope from specimens prepared by dripping the solution onto a copper grid covered with a carbon film. The ultraviolet–visible (UV–vis) absorption spectra were taken on a Lambda35 spectrometer. All the measurements were performed at room temperature.

3. Results and discussion

The solutions prepared with different reaction times have different colors. When the reaction time is 40 min, the solution is red; after 1 h the solution is ash black. With increasing reaction time, some precipitates appear gradually on the bottom of the vessel and the solution becomes silver gray. In this process, the concentration of NaCl is fixed at 0.2 mM. When the NaCl concentration is increased to 20 mM, the solution becomes pink after 30 min, salmon pink after 1 h, and ocher after 90 min. According to the colors of the samples, four typical powder products representing different reaction times were sampled to examine their crystal structures. Fig. 1 shows the XRD patterns of the samples synthesized with different NaCl concentrations. In the sample synthesized with 0.2 mM NaCl (see Fig. 1a), three weak diffraction peaks appear after reaction for 1 h. Two of the weak peaks are related to silver nanocrystals and the third one (marked with an asterisk) is associated with AgCl. The coexistence of the three peaks suggests that the sample consists of a mixture of AgCl and silver. The crystal structures of the samples remain almost unchanged after reaction for 2 h. Five diffraction peaks can be observed and indexed to the (111), (200), (220), (311) and (222) planes

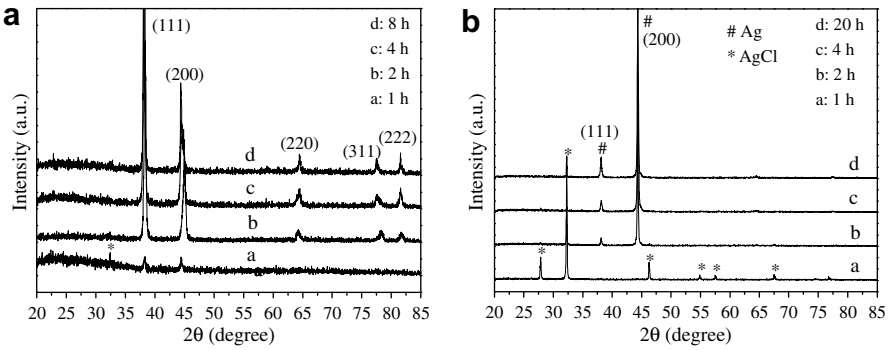

Fig. 1. XRD pattern of silver nanostructures synthesized using different NaCl concentrations: (a) 0.2 mM, (b) 20 mM.