



High-yield water-based synthesis of truncated silver nanocubes



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ABSTRACT

A high-yield water-based hydrothermal synthesis was developed using silver nitrate, ammonia, glucose, and cetyltrimethylammonium bromide (CTAB) as precursors to synthesize truncated silver nanocubes with uniform sizes and in large quantities. With a fixed CTAB concentration, truncated silver nanocubes with sizes of 49.3 ± 4.1 nm were produced when the molar ratio of glucose/silver cation was maintained at 0.1. The sample exhibited (100), (110), and (111) planes on the facets, edges, and corners, respectively. In contrast, with a slightly larger glucose/silver cation ratio of 0.35, well-defined nanocubes with sizes of 70.9 ± 3.8 nm sizes were observed with the (100) plane on six facets. When the ratio was further increased to 1.5, excess reduction of silver cations facilitated the simultaneous formation of nanoparticles with cubic, spherical, and irregular shapes. Consistent results were obtained from transmission electron microscopy, scanning electron microscopy, X-ray diffraction, and UV–visible absorption measurements.

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1. Introduction

The synthesis of metallic nanoparticles has been an important research topic with respect to both scientific curiosity and industrial applications [1]. This interest exists because metals in the nanometer size regime not only exhibit unique physical properties due to the quantum confinement effect, but also provide enhanced activities as catalysts and biosensors because of their large surface-to-mass ratio and favorable surface morphology [2–4]. In principle, physical and chemical attributes of metallic nanoparticles are contingent on their size, shape, crystallinity, composition, and structure. Therefore, tailor-made behaviors are feasible if the synthetic steps are controlled deliberately to render nanoparticles with pre-determined specifications. To date, numerous elements, including gold, silver, platinum, and palladium have been prepared in a rich variety of sizes and shapes, and their physical and chemical characteristics have been extensively explored [5–8]. In particular, the formation of silver nanostructures in various forms is critical in applications such as electrocatalysis, water-defouling, and surface-enhanced Raman spectroscopy [9–12].

Silver is a noble metal with a relatively high redox potential. Consequently, the reduction of silver cations is readily induced by external stimuli such as a reducing agent, heat, or photons. In typical wet chemical approaches, a surfactant is usually used to distinguish the growth rate at different crystallographic planes because of its anisotropic adsorption ability. As a result, silver nanostructures in polyhedrons, spheres, cubes, wires, and rods

have been demonstrated [13–19]. Earlier, Sun and Xia employed a polyol process to prepare silver nanocubes and used them as a template to produce hollow gold nanoboxes via a displacement reaction [20]. The polyol route involved the use of ethylene glycol (EG) as a reducing agent and solvent; however, the complete removal of EG from the silver nanocubes was difficult. Recently, Yu and Yam reported a water-based hydrothermal process using glucose as a reducing agent other than EG [21]. However, their UV–visible absorption spectra showed a single broad plasma resonance peak, which implied that the resulting samples contained significant numbers of irregular or spherical nanoparticles. Although the non-water-based synthesis of monodispersed silver nanocubes in high yield has been demonstrated, the water-based synthesis of uniform truncated silver nanocubes remains a challenge, and the synthesis method requires further optimization. Moreover, to enable the practical implementation of truncated nanocubes in alkaline fuel cells, the identification of a facile synthesis scheme for their high-yield production is required.

In this work, we design a water-based formulation that enables the fabrication of uniform truncated silver nanocubes in large quantities from a simple hydrothermal process.

2. Experimental

2.1. Materials synthesis

The truncated silver nanocubes were fabricated via a hydrothermal synthetic route using silver nitrate, ammonia, glucose, and cetyltrimethylammonium bromide (CTAB) as precursors. First, 0.17 g of silver nitrate was dissolved in 20 ml of deionized water, followed by the stepwise addition of 1 M ammonia aqueous solution. After the ammonia was added, the transparent silver nitrate solution turned brown briefly, and as the amount of ammonia was increased, the mixture

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appeared transparent again. At this stage, the silver cations were present as $[\text{Ag}(\text{NH}_3)_2]^+$. Subsequently, we added extra deionized water to render a 10 mM $[\text{Ag}(\text{NH}_3)_2]^+$ solution. To form the desired silver nanoparticles, 25 ml of 10 mM $[\text{Ag}(\text{NH}_3)_2]^+$ solution was properly mixed with 15 ml of 50 mM CTAB aqueous solution and 50 ml of glucose aqueous solution. The glucose solution functioned as a reducing agent, and the sample prepared with various concentrations of glucose (i.e., 0.5, 1.75, and 7.5 mM), were designated as SA, SB, and SC, respectively. The CTAB was used as a surfactant for its anisotropic adsorption behavior on distinct crystallographic planes, which allows the silver nuclei to evolve into distinct shapes. The mixture was heated in an autoclave at 120 °C for 8 h and was allowed to cool to 25 °C afterwards. The sample was subsequently centrifuged at 6000 rpm for 20 min to retrieve the silver nanoparticles for characterization and electrochemical analysis.

2.2. Materials characterization

A Siemens D5000 X-ray diffractometer (XRD) equipped with a $\text{Cu K}\alpha$ radiation source ($\lambda = 0.154 \text{ nm}$) was used to identify relevant phases and preferred orientation. High-resolution images and selective-area electron diffraction patterns were obtained by a transmission electron microscopy (TEM; Philips TECNAI20) to determine the average size and standard deviation, the shape, and the exposed crystallographic planes. We performed UV–visible absorption measurements (JASCO) to explore characteristic plasma resonance peaks. Scanning electron microscopy (SEM; JEOL JSM-6500) was used to directly observe the silver nanoparticles in large quantities and the distribution of silver nanoparticles in working electrodes. The zeta potential of the silver nanoparticles was obtained using a Delsa™ Nano instrument (Beckman Coulter).

3. Results and discussion

Glucose is a known reducing agent with a relatively mild reducing power, and the addition of OH^- is often used to accelerate the reduction reaction [22]. In our case, the reduction of silver ions is further facilitated by an autoclave process at 120 °C for 8 h. The chemical reduction of silver ions by glucose proceeds according to the following equation:

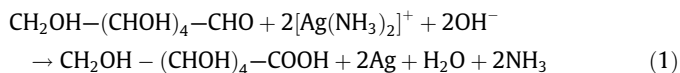


Fig. 1 provides TEM images of the silver nanoparticles prepared under different synthesis conditions. As shown in Fig. 1a, sample SA consisted of nanoparticles with cubic shapes whose average edge length was $49.3 \pm 4.1 \text{ nm}$. In particular, these silver nanocubes also revealed truncated corners and rounded edges. In contrast, in sample SB, as shown in Fig. 1b, the silver nanoparticles exhibited an ideal cubic form with well-defined sharp edges. Their average size, however, was increased to $70.9 \pm 3.8 \text{ nm}$. In the case of sample SC, as shown in Fig. 1c, the morphology was notably altered, and cubic, spherical, and irregular-shaped nanoparticles were simultaneously present; the size distribution became slightly wider than those in the other two samples. On average, the particles exhibited a length of $43.8 \pm 6.6 \text{ nm}$. Although these samples exhibited distinct sizes and shapes, impressive packing behaviors were observed in that two-dimensional arrays were easily observed by TEM. Interestingly, individual silver nanoparticles were not in direct contact with each other because residual CTAB adsorbed on the surface provided steric hindrance, which prevented their coalescence or aggregation during their formation stage in solution. As a result, after the nanoparticles were retrieved and dried, their relatively uniform size distribution enabled an orderly-packed arrangement because of the weak van der Waals attraction among them. In addition, every particle can be reasonably concluded to have existed as a single crystal. Moreover, the notable color contrast among them was caused by uneven TEM grid that led to minute misalignment of incident electron beam along crystallographic planes of selective nanoparticles.

The morphology of the silver nanoparticles is determined by the relative concentrations of the ingredients involved because nucleation and growth are the primary formation steps. Literature reports have established that the separation of nucleation and growth is critical for the fabrication of monodispersed

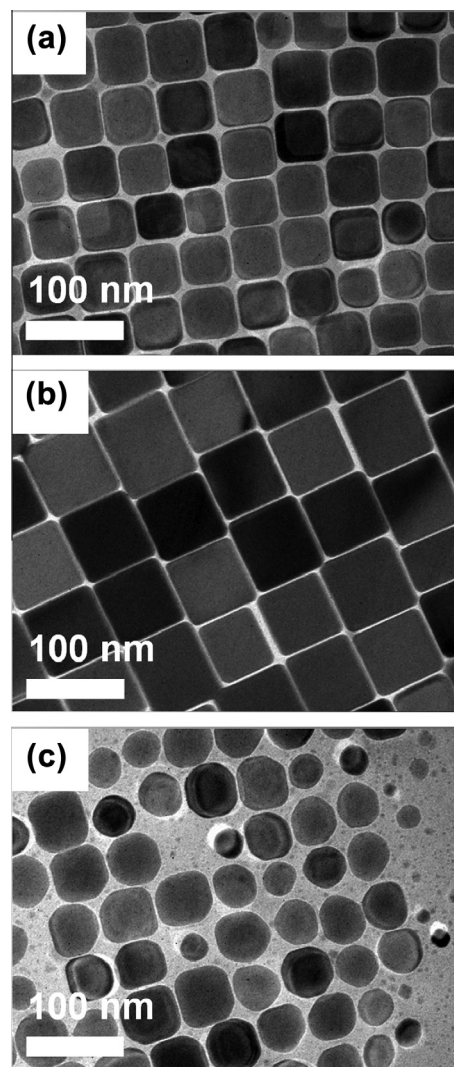


Fig. 1. TEM images of samples (a) SA, (b) SB, and (c) SC, respectively.

nanoparticles [23–25]. The separation of nucleation and growth can be realized by LaMer’s concept of “burst nucleation”, where numerous nuclei are produced simultaneously followed by diffusional control of growth without further nucleation [26]. To synthesize silver nanoparticles, a large molar ratio (CTAB/silver cations > 2.5) is essential in directing the reaction toward the formation of cubic nanoparticles rather than spherical nanoparticles [27]. In our samples, we fixed the ratio at 3 so that the formation of nanocubes was expected. Qualitative understanding of size variation among these samples can be rationalized by the molar ratio between glucose and silver cations (glucose was used as a reducing agent). At a ratio of 1.5 (sample SC), the silver cations were readily reduced to reach a supersaturation state for numerous nuclei to form and compete for growth. As a result, the silver nanoparticles appeared in both cubic and spherical forms with a slightly broader size distribution. In contrast, when a subdued ratio of 0.1 was used (sample SA), inadequate glucose inhibited the reduction of silver ions; hence only a limited number of nuclei became available. This limited number of nuclei allowed the CTAB to affect the growth rate via its anisotropic adsorption behavior. Therefore, the resulting silver nanocubes exhibited truncated edges and rounded corners with a relatively narrower size distribution. For sample SB, which was prepared at a ratio of 0.35, the concentration of glucose was sufficiently high to initiate the “burst nucleation”, but the

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