Controllable Synthesis of Ag Nanocubes via a Polyol Method

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Abstract: The controllable synthesis of uniform silver nanocubes with high purity is pivotal for the fundamental study of self-assembly and further research on the hollow nanostructures, gold nanocages for instance. Here, Ag nanocubes of different sizes were synthesized by an improved polyol method. With addition of HCl solution, Ag nanocubes with size about 100 nm were obtained under an air atmosphere. And Ag nanocubes with size around 50 nm can be produced in a short time under Argon atmosphere with the presence of NaHS instead of HCl. Meanwhile, uniform Ag nanocubes with size larger than 100 nm were also synthesized successfully via adjusting experiment parameters. Results of transmission electron microscopy (TEM) combined with selected area electron diffraction (SAED) show that the Ag nanocubes are single crystalline with six (200) surface plane. In the UV-Vis-NIR optical absorption spectrum, the diple moment resonance absorption peak is changed in the range of 420—500 nm with the increase of Ag nanocubes size.

Key words: Ag nanocubes; polyol method; UV-Vis-NIR spectrum

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0 Introduction

Noble metal (such as gold and silver) nanoparticles have been broadly studied over the past two decades because of their surface plasmon resonance (SPR) properties in the visible region which are useful for surface-enhanced Raman scattering (SERS), chemical and biological sensing [1-6]. In the fundamental study, the SPR intensity and position of silver nanostructures are highly connected with their morphology and assembly model. It is known that the SPR properties of the noble metal nanoparticles highy depend on their sizes, shapes, compositions and crystallinities. Recently, silver nanostructures have drawn an increasing interest due to their optical, electronic, and catalytic properties[7-11]. And many further studies have been carried out in a wide variety of technical fields, including optical materials, photoelectic information storages, biomedical applications and so on[12-15].

Driven by the interest in the research and applied science, noble metal nanoparticles with various shapes, like cubes[16-17], rods[18-19], prisms[20-21], wires[22-23] and polyhedrons[24] have been synthesized through different methods, such as the wet chemical methods, hydrothermal methods, modified polyol process and photo-induced methods. In these methods, modified polyol process is one of the common methods used to control morphology of nanomaterials.

Here, controllable synthesis of Ag nanocubes was introduced via a polyol method. With different addition and responsive environment, Ag nanocubes of two different sizes can be successfully obtained. The optimal synthesis condition of Ag nanocubes has been explored by adjusting the experiment parameters, such as the molar ratios (MRs) between polyvinyl pyrrolidone (PVP) and $AgNO_3$ (M_{pvp} : M_{Ag}), and the amount of additives. Meanwhile, the formation mechanism of Ag nanocubes was elucidated through analyzing

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the transmission electron microscopy (TEM) and selected area electron diffraction (SAED) patterns of the samples.

1 Experiments

1.1 Materials

PVP, MW≈40 000, sodium hydrogen sulfide anhydrous (NaHS), aqueous hydrochloric acid solution (HCl, 37%), silver nitrate ($AgNO_3$, >99.8 %) were obtained from Sinopharm Chemicals. Ethylene glycol (EG≥96%) was obtained from Nanjing Chemical Reagent Co., Ltd. All the reagents were used of analytical purity and without further purification.

1.2 Synthesis of large-sized Ag nanocubes

In a standard synthesis, 5 mL EG was added into a flask and heated under magnetic stirring in an oil bath set to 155 ℃ for 60 min. After 60 min of preheating, 1 mL hydrochloric acid solution ([HCl] = 3 mM) was quickly injected into the preheated EG solution, followed by successive injection of 3 mL PVP solution in EG ([PVP] = 150 mM) and 3 mL silver nitrate ($AgNO_3$, Aldrich) solution in EG ([$AgNO_3$] = 75 mM). After addition of $AgNO_3$, the color of the reactive system changed from golden yellow to green about 23 h late.

1.3 Synthesis of small-sized Ag nanocubes

The 12 mL EG was added into a three neck round-bottomed flask and heated in an oil bath at 160 ℃ under magnetic stirring. After 50 min of preheating, a flow of argon was introduced via a glass pipet at a smooth rate. After 10 min, 140 μL of a sodium hydrosulfide (NaHS, Aldrich) solution in EG ([NaHS] = 3 mM) was quickly injected into the preheated EG solution, followed by successive injection of 3 mL of PVP solution in EG ([PVP] = 180 mM) and 1 mL $AgNO_3$ solution in EG ([$AgNO_3$] = 265 mM). With argon flowing, gaseous species can be discharged from the reactive system. The color of the reactive system changed from golden yellow to deep red, reddish gray, and then green within about 2 h.

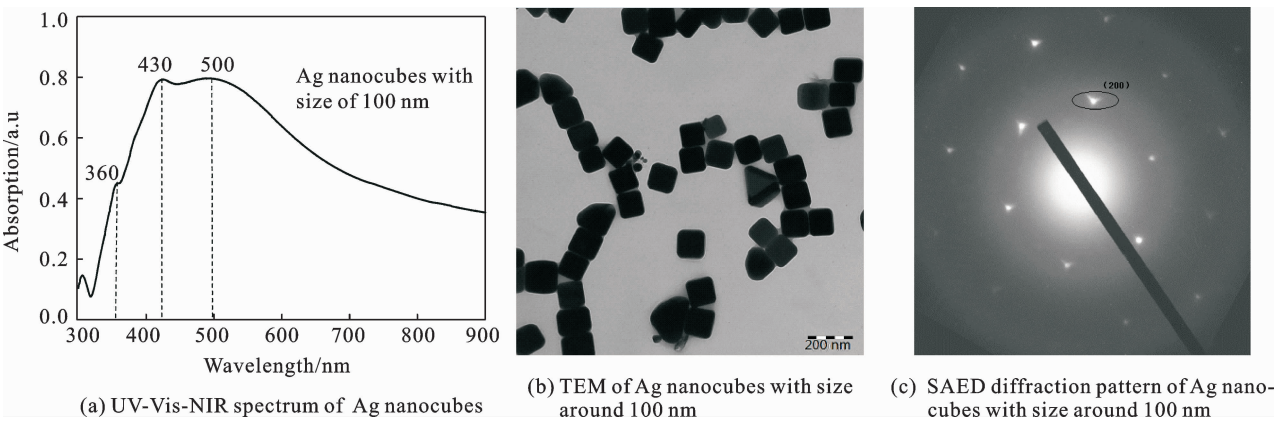
1.4 Sample preparation and characterization

For the characterizations, 4 mL of samples were centrifuged at 8 000 r/min^{-1} with acetone for 20 min, followed by twice centrifugation with deionized water at 6 500 r/min^{-1} to remove excess EG and PVP for characterization and storage. The absorption spectrum were collected on ultraviolet-visible-near infrared (UV-Vis-NIR) spectrometer (UV-6300) in the range of 200—1 100 nm. For microstructure observation, the samples were deposited on copper grids covered by an amorphous carbon film for transmission electron microscopy (TEM: JEOL-100CX) measurements.

2 Results and Discussion

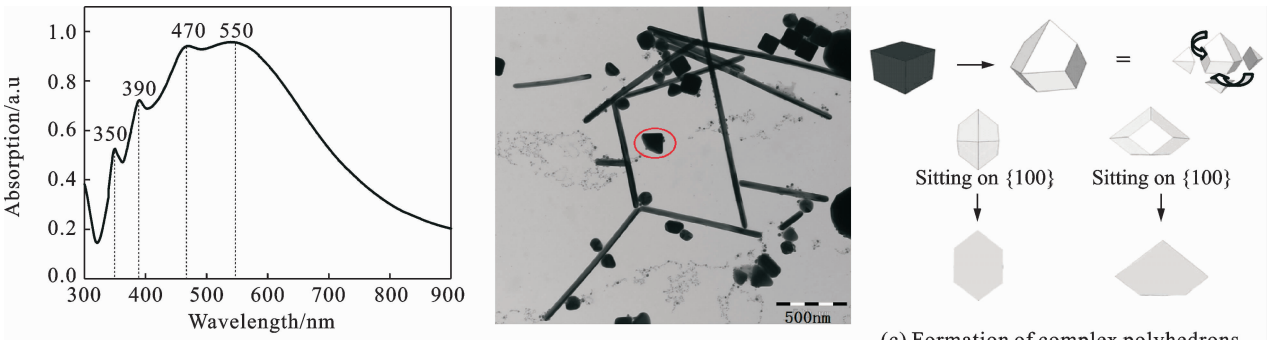
In the process of synthesis, it is found that the M_{pvp} : M_{Ag}, as well as reaction temperatures are vital to the morphology and size of final products. Although the slight change of the experimental conditions, the yield and uniformity of the Ag nanocubes will be greatly reduced. Take Ag nanocube with size around 100 nm as an example, we found that Ag nanocubes can be obtained when the M_{pvp} : M_{Ag} is 2 and the reaction temperature is 155 ℃. In the UV-Vis-NIR spectrum of Ag nanocubes (see Fig. 1(a)), it can be seen that three resonance absorption peaks located at 360, 430, and 500 nm, corresponding to the quadrupole and multipolar moment resonance, quadrupole moment resonance, and dipole moment resonance, respectively. From the TEM of Ag nanocubes (Figs. 1 (b, c)), the size of Ag nanocubes was about 100 nm with snippings. During the synthesis of Ag nanocubes, EG generated reducing aldehyde groups through heated, Cl^- (HCl) etched the crystal nucleus and PVP adsorbed selectively on the (200) crystal plane. Because of the lowest surface energy of (111) crystal plane, they were easier to form snippings of (111) plane on the Ag nanocubes. Fig. 1(c) is the SAED diffraction pattern of a single Ag nanocube. From the SAED, Ag nanocubes have anisotropic crystalline nanostructures made up of six (200) surfaces.

In the chemical methods, the growths of nanostructures were controlled by nucleation and dynamics factors rather than thermodynamic factors. In the open synthetic system, single crystal and multiple twinned seeds were sensitive to the conditions for the face-centered cubic (FCC) metal nanostructures. When the initial products of $AgNO_3$ were single crystal seeds, monodisperse Ag nanocubes dominated the products. While multiple twinned seeds were formed in the initial stage, then Ag nanowires and nanorods with the pentagon sections were the main products. Usually, in the open synthetic system, single crystalline and multiple twinned seeds coexist in the system, resulting in the formation of nanocubes and nanowires. Fig. 2(a) shows the UV-Vis-NIR spectrum of Ag nano-cubes during the synthesis process, in which the SPR resonance absorption peaks located at 350 and 390 nm corresponding to the peaks of Ag nanowires or long Ag nanorods, and the SPR resonance absorption peaks located at 470 and 548 nm corresponding to the peaks of Ag nanocubes. The TEM image of products was demonstrated in Fig. 2(b). It can be seen that the products were consisted of Ag nanowires, naorods, nanocubes and other several polyhedrons. Corresponding to solid circle line in Fig. 2(b), it was understood that several polyhedrons were evolved from nanocubes and the polyhedrons with cutting angles formed from nanocubes were reported previously by Ding's work[25] as indicated by Fig. 2(c). This method was relatively harsh for synthesizing perfect Ag nanocubes in a short time.



(a) UV-Vis-NIR spectrum of Ag nanocubes (b) TEM of Ag nanocubes with size around 100 nm (c) SAED diffraction pattern of Ag nanocubes with size around 100 nm

Fig. 1 UV-Vis-NIR spectrum of Ag nanocubes and TEM and SAED diffraction pattern of Ag nanocubes with size around 100 nm



(a) UV-Vis-NIR spectrum of Ag nanocubes during the synthesis process when parts of $AgNO_3$ were firstly reduced into multiple twinned (b) TEM images corresponding to Fig.2(a) (c) Formation of complex polyhedrons marked with red solid line in Fig.2(b)

Fig. 2 2UV-Vis-NIR spectrum, TEM image and views in different directions of the product

With the presence of NaHS instead of HCl, Ag nanocubes with size around 50 nm were produced in a short time under Argon atmosphere. Experimentally, it could be observed that vast Ag nanocubes formed within 60 min. According to Xia's work, the mechanism is based on the formation of highly insoluble Ag_2S crystallites, as indicated by a fleeting purple color when $AgNO_3$

was introduced[17,26]. Ag_2S is a catalyst for Ag reduction, which can remarkably shorten the time for the reduction of $AgNO_3$. It made the thermodynamically less favorable, and single-crystal, cuboctahedral seeds formed thro-ugh a heterogeneous nucleation process. During this synthesis process, the colors of the solutions changed from golden yellow to deep red, reddish gray, and finally green as the reactions proceeded within 60 min. Fig. 3 is the UV-Vis-NIR spectrum of Ag nanocubes with size around 50 nm corresponding to the four color change stages. The spectral curve that measured at 15 min with a SPR absorption peak around 410 nm represented large amounts of Ag nanoparticles existing in reaction solution. With reaction time of 30 min, another SPR peak had a tiny red shift and a new peak occurred at about 340 nm. And for the last sample measured at 60 min, three resonance absorption peaks located at 340, 390, and 480 nm, respectively. This phenomena indicated the morphological changes from nanoparticle to anistropic nanostructure. Fig. 4 is the TEM of Ag nanocubes corresponding to the four samples of Fig 3. It can be found that Ag nanocubes grow perfectly step by step with the increase of the reaction time from TEM images in Figs. 4(a)—(d).

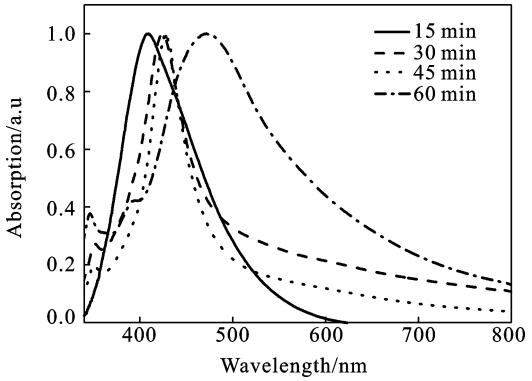


Fig. 3 UV-Vis-NIR spectrum of Ag nanocubes with size around 50 nm corresponding to four color change stages

3 Conclusions

We have successfully synthesized Ag nanocubes with size about 100 nm with addition of HCl solution. Ag nanocubes with size around 50 nm can be produced in a short time under Argon atmosphere with the presence of NaHS instead of HCl. The controllable synthesis of uniform silver nanocubes with high purity is essential for the fundamental study of self-assembly and further research on the hollow nanostructures.

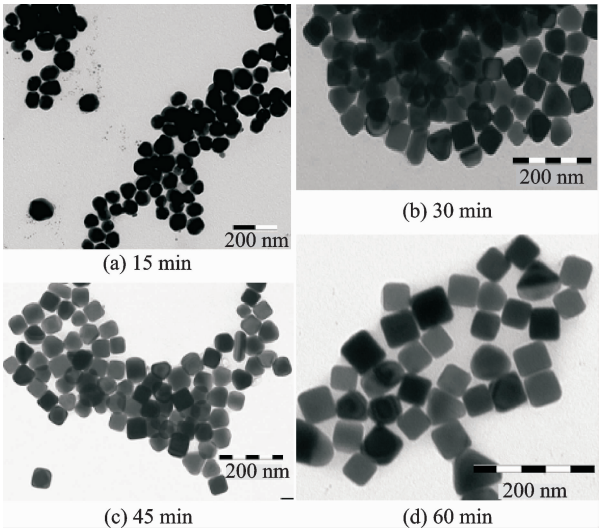


Fig. 4 TEMs of Ag nanocubes corresponding to the spectral curves measured at different mintues

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