Hovenia Acerba Structure of Nano-Silver Materials in the Process of Synthesis of Silver Nanoparticles under Alkaline Condition

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Abstract. Silver nanoparticles (AgNPs) are attracting tremendous attention in materials, nanotechnology, biomedicine and chemical sensor fields. This paper describes the hovenia acerba structure of nano-silver materials in the process of synthesis of silver nanoparticles under alkaline condition. The analysis shows that the appearance of this structure is due to the adding of ammonium hydroxide and this structure is the intermediate state of the AgNPs.

1. Introduction
Noble metal nanomaterials (NMNs) with unique chemical and physical properties have received extensive attention and been widely applied as building blocks in engineering and technology field in recent years [1]. The functional properties of noble metal nanomaterials involved their size, shape, composition, crystallinity and surrounding medium. Numerous methods for the synthesis of NMNs (such as Au, Ag, Pd and Ru nanospheres, nanorods, nanowires, nanoclusters, nanocages, nanostars, nancubes and nanoplates) have been reported in the literature [2-4]. The early methods to produce suspensions of very small noble-metal nanoparticles were still used today. Turkevich method was the most famous to prepare Au nanoparticle suspensions which employed chloroauric acid (HAuCl4) acted as precursor and sodium citrate (Na3Cit) served as reducing agent. For silver nanoparticle (AgNPs) suspensions, AgNO3 was the most commonly used as the metal source and NaBH4 and Na3Cit were the often used reducing agent [5]. Highly monodisperse sodium citrate-coated spherical silver nanoparticles were synthesized by the combination of two chemical reducing agents: sodium citrate and tannic acid. The controllable size of AgNP in this method was from 10 to 200 nm [6]. In recent years, Schlucker and Steinigeweg reported a simple two-step seed-mediated synthesis of monodisperse quasi-spherical silver nanoparticles in glycerol–water mixtures. The size of the monodisperse silver nanospheres was in the range of 20–100 nm [7]. Meanwhile, Jia et al prepared silver nanowires by using glycerol and ethylene glycol (EG) as co-mediated solvents in the presence of poly vinyl pyrrolidine (PVP). The possible growth mechanism of the synthesis of silver nanostructures was discussed [8]. Other nanomaterials were also obtained by so-called "bottom-up" chemical reduction method. In our group, we have studied the synthesis of gold nanoparticles under the alkaline condition [9]. The structure and the formation mechanism of the gold nanoparticles were discussed in detail. In this paper, an experiment was conducted to study the synthesis of silver nanoparticles, especially explained the characteristic of hovenia acerba structure of nano-silver materials.
2. Materials and Methods

2.1. Material
Silver nitrate (AgNO₃, 99.9%), sodium citrate dihydrate (trisodium citrate or Na₃Cit, 99%), glycerol (99.0%), polyvinyl pyrrolidone (MW, 10000), ammonium hydroxide (NH₃·H₂O, 25-28%) and sodium hydroxide (NaOH, 99.9%) were purchased from Shanghai Aladdin Chemical Reagent Co., Ltd. (China). All chemicals were of analytical grade and used without any further purification. Ultrapure water (Resistivity > 18.25 MΩ·cm) was used for all solution preparation and throughout the experiments.

2.2. Instrumentation
A Shimadzu UV-2600 was used to characterize ultraviolet–visible (UV-vis) spectra of silver colloid and the localized surface plasmon resonance (LSPR) of the obtained nanomaterials. All spectra of the substrates were measured in the range from 300 to 900 nm at a resolution of 0.5 nm. Transmission electron microscopy (TEM) images were measured with a JEOL JEM-2100 electron microscope at an accelerated voltage of 200 kV.

2.3. Synthesis of Silver Nanoparticles
In a typical experiment, 250 μL of 1mM AgNO₃ solution was added into a 25 mL of glycerol–water mixtures (2:3, v:v) in a 50 mL of round-bottomed flask. Then, 5 mL of ammonia hydroxide was quickly added into the mixture and the solution was heated to boiling. Finally, 750 μL of 4% Na₃Cit was added into the round bottomed flask at one time. The whole reaction is performed about 90 min. The control group of silver nanoparticles was prepared by varying addition amount of ammonium hydroxide and glycerol.

3. Discussion
It is well known that the localized surface plasmon resonance (LSPR) absorption peak of AgNPs indicates the formation of AgNPs. Additionally, a color change to yellow of the reaction solution can be observed with the naked eye. The UV–vis spectra show an UV absorption maximum at 420 nm (Fig.1 A). The corresponding TEM micrograph of the nano-silver structure was shown in Fig.1 B. The important observations from the TEM images were the structure of the nano-silver with hovenia acerba structure. In general, the spectra of the silver nanoparticles with the shape of sphere will be shown a single peak of absorption. This phenomenon agreed with Mie’s theory and many experimental results. However, the TEM observations showed that the nano-silver with hovenia acerba structure. The hovenia acerba structure of nano-silver can save in the room temperature for a longer period of time. This structure hasn’t been reported so far. We speculate that the structure appeared to be the adding of ammonium hydroxide and the hovenia acerba structure was the intermediate state of the AgNPs. Next, we analyzed the cause of hovenia acerba structure.

![Figure 1](image)

**Figure 1.** Optical characterization and structural of hovenia acerba structure of nano-silver. A) UV-vis spectra. B) TEM image. Scale bar: 200 nm
Fig. 2 showed the UV-vis spectra of AgNPs prepared under different reaction condition. Curve a represented the synthesis of AgNPs without ammonium hydroxide. The peak of absorption was blue-shift compared to the hovenia acerba structure of nano-silver (curve b). Curve c showed that the AgNPs synthesized without ammonium hydroxide and glycerol, and adding a certain amount of PVP. The absorption curve had a significant red shift suggesting the different size and shape of AgNPs. After the hovenia acerba structure of nano-silver kept for about 6 months. The UV-vis spectra showed a wide-band absorption peak. The results indicated that the hovenia acerba structure was undergoing continuous changes.

![UV-vis spectra of AgNPs](image)

**Figure 2.** Normalized UV-vis spectra of AgNPs prepared under different reaction condition: (a) without ammonium hydroxide, (b) the reaction conditions described in 2.3, (c) without ammonium hydroxide and glycerol, adding 100 μL of 0.1M PVP, (d) keep for 6 months.

TEM images can explain directly and clearly about the change of size and shape of AgNPs. Fig. 3A showed that the preparation of AgNPs without ammonium hydroxide. The nanoparticles were almost the spherical structure. As adding ammonium hydroxide in the reaction solution, the hovenia acerba structure was appeared (Fig. 3B). Fig. 3C showed that the prepared various shape and size of AgNPs with adding a certain amount of PVP. The result suggested that the hovenia acerba structure cannot form at the condition of neutral molecule of PVP. After six months of storage, the shape of the nano-silver was changed to Quasi-spherical structure (Fig. 3D). These analyses indicated that hovenia acerba structure of nano-silver materials are the intermediate state in the process of synthesis of AgNPs under alkaline condition.
Figure 3. TEM images of AgNPs prepared under different reaction condition: (a) without ammonium hydroxide, (b) the reaction conditions described in 2.3, (c) without ammonium hydroxide and glycerol, adding 100 μL of 0.1M PVP, (d) keep for 6 months. Scale bars: 200 nm

4. Conclusions
In this work, we have studied the hovenia acerba structure of nano-silver materials in the process of synthesis of silver nanoparticles. It is found that, the hovenia acerba structure of nano-silver was the intermediate state of the AgNPs. This structure can keep a longer time. We expect that the hovenia acerba structure of nano-silver will be applied in the field of nanotechnology and nanoengineering.

5. Acknowledgments
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6. References
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