Colloids and Surfaces A 540 (2018) 136–142

Contents lists available at ScienceDirect

Colloids and Surfaces A

journal homepage: www.elsevier.com/locate/colsurfa

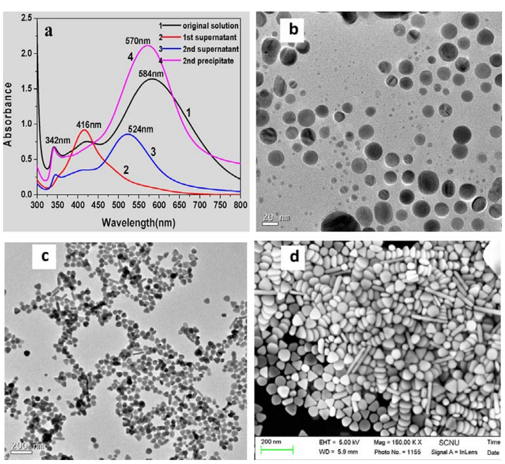
Surfactant-assisted shape separation from silver nanoparticles prepared by a seed-mediated method

Guansong Hu[a,1], Wenxiu Jin[a,1], Wen Zhang[b], Kai Wu[c], Jiahui He[a], Yan Zhang[a], Qingyuan Chen[a], Wanzhong Zhang[a,*]

[a] Guangdong Provincial Key Laboratory of New Drug Screening, School of Pharmaceutical Sciences, Southern Medical University, Guangzhou 510515, PR China
[b] School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, PR China
[c] School of Public Health and Tropical Medicine, Southern Medical University, Guangzhou 510515, PR China

GRAPHICAL ABSTRACT

Silver nanospheres, small nanotriangles and big nanotriangles can be separated successfully from their associated nanoparticles by the improved surfactant-assisted shape separation method and the separated nanotriangles have a relatively high regularity and uniform size.



ARTICLE INFO

Keywords:
Silver nanoparticles
Nanotriangles
Cetyltrimethylammonium bromide
Surfactant-assisted separation
A seed-mediated method

ABSTRACT

So far from the suggestion of a seed-mediated method, there has been considerable development in the controllable synthesis of anisotropic nanoparticles. However, the formed nanoparticles often exhibit considerable polydispersity in their size or shape. In this work, we improved the surfactant-assisted shape separation method that were different from gold nanorods reported previously to purify silver nanotriangles and investigated the important parameters systematically. The results showed that relative amount of CTAB to AgNPs (which was determined by the concentration and volume of CTAB) and the temperature of CTAB were the critical roles in the separation of silver nanotriangles. Silver nanospheres, small nanotriangles and big nanotriangles were separated successfully from their associated nanoparticles by the surfactant-assisted shape separation in twice. The se-

* Corresponding author.
E-mail address: zhangwz6@smu.edu.cn (W. Zhang).
[1] These authors contributed equally to this work.

https://doi.org/10.1016/j.colsurfa.2017.12.071
Received 23 October 2017; Received in revised form 31 December 2017; Accepted 31 December 2017
Available online 02 January 2018

parated nanoparticles have higher regularity and more uniform size, which is important to enlarge the application scope of silver nanomaterials. This improved method allows us to purify silver or other metal nanoparticles prepared by a facile seed-mediated method in high efficiency and yield.

1. Introduction

Anisotropic noble nanoparticles, e.g., nanorods, nanotriangles (triangular nanoplates or triangular nanoparticles) and nanocubes, are of great interest in recent decades due to their excellent optical behavior [1], electrical property [2] and catalytic property [3,4]. As a result, they have been used in the field of analysis and determination [5–7], biomedicine [8] and nanodevices, antibiotics bacteriostasis [9], cancer therapy [10,11], sensing application [12], and so on. The properties of anisotropic nanomaterials are strongly dependent on their morphology and particle size [13,14]. Therefore, how to obtain silver nanoparticles with uniform size and morphology is a key problem for their applications.

It is well-known that silver nanoparticles are commonly obtained by chemical reduction of silver salt precursor under the protection of organic or inorganic stabilizers [15–17]. Hard templates are usually used for fabrication of silver nanowires [18]. The synthesis routes of silver nanotriangles includes photoinduced conversion [19–21], template method [22] and solution phase method [12,23]. Xia et al. used polyvinyl pyrrolidone (PVP) as coating material and reduction agent to prepare triangular nanoparticles. Truncated triangular silver nanoplates were synthesized in solution with the presence of cetyltrimethylammonium bromide (CTAB) micelles [23].

However, it is relatively difficult to obtain the uniform nanoparticles by a seed-mediated method (surfactant-directed synthesis, soft-template technique). For example, while silver nanorods with controllable aspect ratio have formed, the associated nanoparticles (such as nanospheres and nanoplates) are also produced due to the unbalance between nucleation and growth [24]. Consequently, the resulting nanorods are not the same in the aspect ratio. That is to say, the resulting nanoparticles prepared by a typical seed-mediated method are commonly a mixture of the nanorods, nanospheres and triangular nanoplates [25,26]. As a result, efficient and robust separation methods are important and necessary to obtain uniform nanoparticles from the mixture.

Usually, high-speed centrifugation is used in separation of the mixture to obtain the uniform nanoparticles, e.g., silver nanotriangles or nanorods. This separation method requires that the prepared nanoparticles have a good monodispersity, or the separating effect is very low so as to not obtain the uniform nanoparticles. That is to say, the centrifugation method is not suitable for the separation of the nanoparticles with polydispersity. Jana et al. prepared gold nanorods in CTAB solution and separated the nanorods by adding CTAB solution into the precipitate for several times [25]. They obtained the highly monodisperse gold nanorods from the associated nanoparticles by this surfactant-assisted separation method and thought it was attributed to CTAB-assisted self-assembly of the nanorods. We noticed that they isolated the small nanospheres from the 1.0 L solution by centrifugation and all the precipitates were collected and then dissolved in 10 mL of 0.1 M hot CTAB solution. The same dissolved process of the precipitate needed repeating 4–5 times. Obviously, the separation process will be a very tedious work to consume time and energy, which does not facilitate the shape separation on a large scale. In addition, the main nanoparticles are gold rod-like nanoparticles rather than silver triangular nanoplates.

In general, a seed-mediated method is used to prepare nanorods and nanowires [14,27]. In this paper, we first prepared high concentration of silver nanotriangles by the improved seed-mediated method. Only 10 mL instead of 1 L of the colloidal solution is needed in the separation of silver nanotriangles from the associated nanoparticles, which make it easy and efficient to separate the uniform nanotriangles. However, there are few literatures published to study the separation of silver nanotriangles from the mixture of the nanoparticles by the surfactant-assisted inducement. Although the shape separation of gold nanorods was reported by a short communication [25], no other detailed studies on the shape separation of gold or other nanoparticles were published.

Here, we attempt to isolate the silver nanotriangles from the as-synthesized nanoparticles by adding different concentrations, volumes or temperatures of CTAB solution into the precipitate. Some crucial parameters were obtained in the separation of silver nanotriangles from the mixed nanoparticles with different morphologies. Silver nanospheres, small nanotriangles and big nanotriangles were separated respectively only by double separation. As a result, silver nanoparticles with different morphologies, i.e., silver nanospheres and nanotriangles, can be separated perfectly by the surfactant-assisted shape separation. The efficiency is superior to that of centrifugation in the separation of nanospheres and nanotriangles. The nanoparticles with different shapes, especially the nanotriangles with different side lengths can also be separated efficiently, even though the CTAB solution at room temperature is employed to replace 50 °C CTAB solution. Obviously, the separation of the different morphologies of silver nanoparticles and different side lengths of silver nanotriangles from the mixture is an effective separation method and can facilitate a large-scale production.

2. Materials and methods

2.1. Preparation of silver nanoparticles

First, silver seed colloid was prepared by the following method, which is different for 10 times equivalent of reducing agent than one in traditional seed prepared method: 0.6 mL of KBH_4 (100 mM) was added into 20 mL solution contained 0.25 mM $AgNO_3$ and 0.25 mM sodium citrate and then vigorously stirring the mixed solution for 30s. The formed sol turned to stable pale yellow and was preserved as seed sol to prepare silver nanotriangles. Under stirring, silver nanotriangles were prepared by mixing 0.5 mL of 0.01 M silver nitrate ($AgNO_3$), 1.0 mL of 0.1 M ascorbic acid (V_c), 16 mL of 0.1 M CTAB aqueous solution, 0.25 mL of the seed sol and 1.0 mL of 0.2 M NaOH in order. After NaOH was added, the conical flask was gently shaken for 30 s and then put into 25 °C water-bath to maintain the reaction for about 10 min. The colloidal solution changed in color rapidly from colorless to blue-black and then unchanged obviously after 10 min, implying that the reaction for the formation of silver nanotriangles had finished.

2.2. Surfactant-assisted shape separation for the prepared nanoparticles

Typical separation process is as follows: 10.0 mL above prepared colloidal solution was centrifuged at 10,000 rpm for 10 min. The supernatant mainly containing CTAB was discarded and the precipitate containing main silver nanotriangles, some silver nanospheres and few silver nanorods was dissolved in 0.4 to 1.5 mL of 0.2 to 0.5 M hot CTAB solution (25 to 80 °C). The dissolved solution was aged for 5 h or 12 h to get the first supernatant and precipitate. The first supernatant presented in bright yellow, implying that silver nanospheres with a small particle size were separated out from the precipitate. The precipitate separated from the first supernatant dissolved in 0.2 to 1.6 mL of 0.1 to 0.4 M hot and fresh CTAB solution. With the same depositing time or centrifugation at 400 g for 16 min, the secondary supernatant and precipitate were obtained by this simple separation for the next studies.