Journal of
Nanoscience and Nanotechnology
Vol. 12, 7280–7283, 2012

One-Pot Low Temperature Synthesis of Monodisperse Silver Nanoparticles

Renchun Yang[1,*], Dingxing Tang[1], Fengyun Ma[2], Ting Xian Tao[1], Yiming Ren[1], Zhiming Chen[1], Cuige Zhang[1], and Fang Li[1]

[1] School of Biological and Chemical Engineering, Anhui Polytechnic University, Wuhu 241000, China
[2] Key Laboratory of Oil and Gas Fine Chemicals, Ministry of Education and Xinjiang Uyghur Autonomous Region, Xinjiang University, Urumqi, Xinjiang 830046, China

A facile one-pot route for the synthesis of monodisperse Ag nanocrystals with a narrow size distribution is described. Uniform Ag nanoparticles with the size of around 12 nm were obtained by reduction of $AgNO_3$ in the presence of oleylamine and polymer polyvinylpyrrolidone (PVP) at low temperature. It is found that temperature has a significant effect on the sizes and the size distributions of the nanoparticles. Because irregular Ag nanoparticles are produced easily due to Ostwald ripening or kinetic control at both high temperature and low temperature, respectively, uniform nanocrystals can be obtained at an appropriate temperature (70 °C).

Keywords: Ag Nanocrystals, Low Temperature, Monodisperse.

1. INTRODUCTION

Over the past decade, Ag nanostructures have attracted considerable attention owing to their intriguing properties in biological, optical and catalytic fields. To enhance their potential properties, great efforts have been devoted to the preparation of Ag nanoparticles with various structures.[1] Among various Ag nanoparticles, monodispersion nanocrystals with small size may be one of the most important categories due to the fact that such structure is not only helpful to their function[2,3] but also beneficial for increasing the specific surface area and widen the industrial application.[4]

To date, several synthetic routes of monodispersion Ag nanocrystals have been developed, such as thermolysis, chemical reduction and two-phase approach. A review of recent literatures[2,3,5–14] about various preparation methods and experimental conditions for synthesizing the monodispersion Ag nanocrystals is given in Table I. As can be seen: (i) for thermolysis method, the high reaction temperature (>150 °C) and the high cost organic Ag precursor seems to be needed synchronously;[2,5–8] (ii) for chemical reduction method, though monodispersion Ag nanocrystals can be obtained at relatively low temperature (55~130 °C), some complex organic Ag precursors (silver carboxylate, silver myristate and $C_2F_3O_2Ag$) are indispensable;[3,11–13] compared with the high cost organic Ag precursor, the low cost Ag precursor ($AgNO_3$) will be required to operate at high temperature (180 °C) to achieving the monodispersion and the small size structure;[9,10] (iii) for two-phase method, many-step procedure is needed to be carried out.[14]

From the above analysis, it is still a challenge to overcome the relative rigorous conditions (high temperature, high cost Ag precursor and complex process) for preparing uniform Ag nanocrystals with small size. Herein, we report a facile one-pot low temperature method to obtain monodispersion Ag nanocrystals by using the facile $AgNO_3$ as Ag precursor.

2. EXPERIMENTAL DETAILS

All chemicals (from Aladdin) used were of analytical grade. In a typical procedure, 34.0 mg silver nitrate, 66.0 mg PVP ($K = 30$, $M_W = 58000$), 0.1 mL oleylamine and 20.0 mL ethanol were added to a 50.0 mL autoclave and then the mixture was stirred for 20 min at room temperature. After that, the autoclave was sealed and then heated at a certain temperature (30, 60, 70, 80 or 90 °C) and reaction time. The solutions all were changed its color from colorless before heating to red–brown after the end of the experiment. After centrifugation (10000 rpm, 10 min) and washed with ethanol three times, the product was collected and re-dispersed in hexane. The morphology and the structure of the samples were studied by Field-Emission

*Author to whom correspondence should be addressed.

 1533-4880/2012/12/7280/004 doi:10.1166/jnn.2012.6564

Table I. Results of preparing monodispersion Ag nanocrystals known in the literature.

Method	Temperature (°C)	Ag precursor	Ambience	Size (nm)	Ref.
Thermolysis	250	Silver-fatty acids	N_2	5.0	[5]
Thermolysis	200	$Ag(CH_3COO)$	Air	4.4±0.4	[6]
Thermolysis	180	Ag-oleate	Air	<4.0	[2]
Thermolysis	160	$C_2F_3O_2Ag$	Ar	7.0~11.0	[7]
Thermolysis	150	$C_2F_3O_2Ag$	Ar	14.0	[8]
Reduction	180	$AgNO_3$	Air	11.0±1.1	[9]
Reduction	180	$AgNO_3$	Air	6.8	[10]
Reduction	130	Silver carboxylate	Air	10.0	[11]
Reduction	80	Silver carboxylate	Air	5.0	[12]
Reduction	80	Silver myristate	N_2	2.8±0.3	[13]
Reduction	55	$C_2F_3O_2Ag$	Air	5.5	[3]
Two-phase	150	Metal salt	Air	6.2±1.6	[14]

Scanning Electron Microscopy (FE-SEM, S-4800), High Resolution Transmission Electron Microscopy (HR-TEM, JEM-2010) and Ultraviolet-Visible Absorption Spectroscopic (UV-Vis, Hitachi-UV 3600).

3. RESULTS AND DISCUSSION

Temperature is known, as a key factor, with significant impact not only on the size but also on the size distribution of the nanocrystals. Thus, to obtain monodispersion Ag nanoparticles with small size, the impact of temperature is investigated in detail by SEM, TEM and UV-vis absorption spectra. Figure 1 shows SEM images of the obtained Ag nanoparticles which are synthesized at different temperatures. As shown in Figure 1(B), the nearly monodisperse nanoparticles with a narrow size distribution can be obtained at 70 °C. As the reaction temperature was raised from 70 °C to 80 °C while all other reaction conditions were kept the same, slight change (the size of a few particles started to increase) can be found in Figure 1(C). When the temperature was increased to 90 °C, some relatively large particles can be easily observed in Figure 1(D). The result indicates that the relatively high temperature is not conducive for obtaining monodisperse Ag nanoparticles. Based on the consideration of the condition optimization, naturally, the impact of low temperature was also investigated subsequently. However, when the reaction temperature was decreased to 60 °C, no desirable product can be obtained, even if the reaction time was prolonged to 24 h at near room temperature (30 °C). Instead of this, Ag nanoparticles with a broad size distribution were obtained (Fig. 1(A)).

As shown in Figures 2(B)~(D), the nanoparticles are approximately spherical with an average diameter of 12.0±0.8, 11.8±1.2 or 11.7±1.6 nm, estimated by measuring 200 randomly selected particles in enlarged TEM images, corresponding to 70, 80 and 90 °C, respectively. Obviously, nearly monodisperse nanoparticles with a narrow size distribution can be obtained at 70 °C. With the increasing of reaction temperature, it seems that the average diameter of the nanoparticles reduces a little. Such phenomenon should be attributed to the fact that high

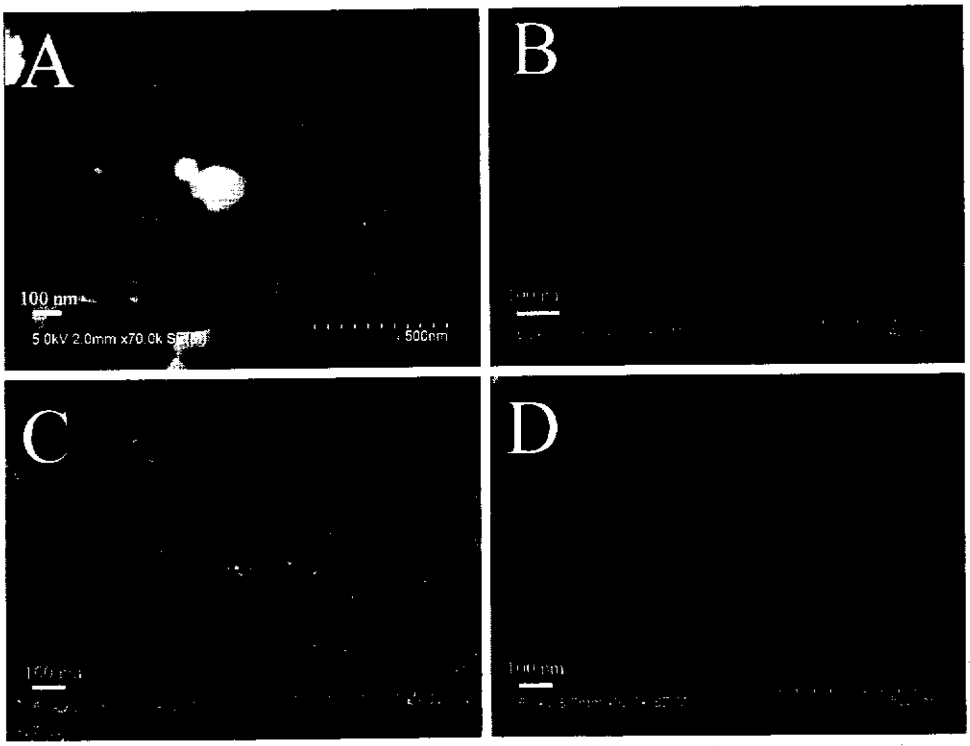

Fig. 1. SEM images of the samples prepared at various conditions: (A) 30 °C, 24 h; (B) 70 °C, 1 h; (C) 80 °C, 1 h and (D) 90 °C, 1 h.

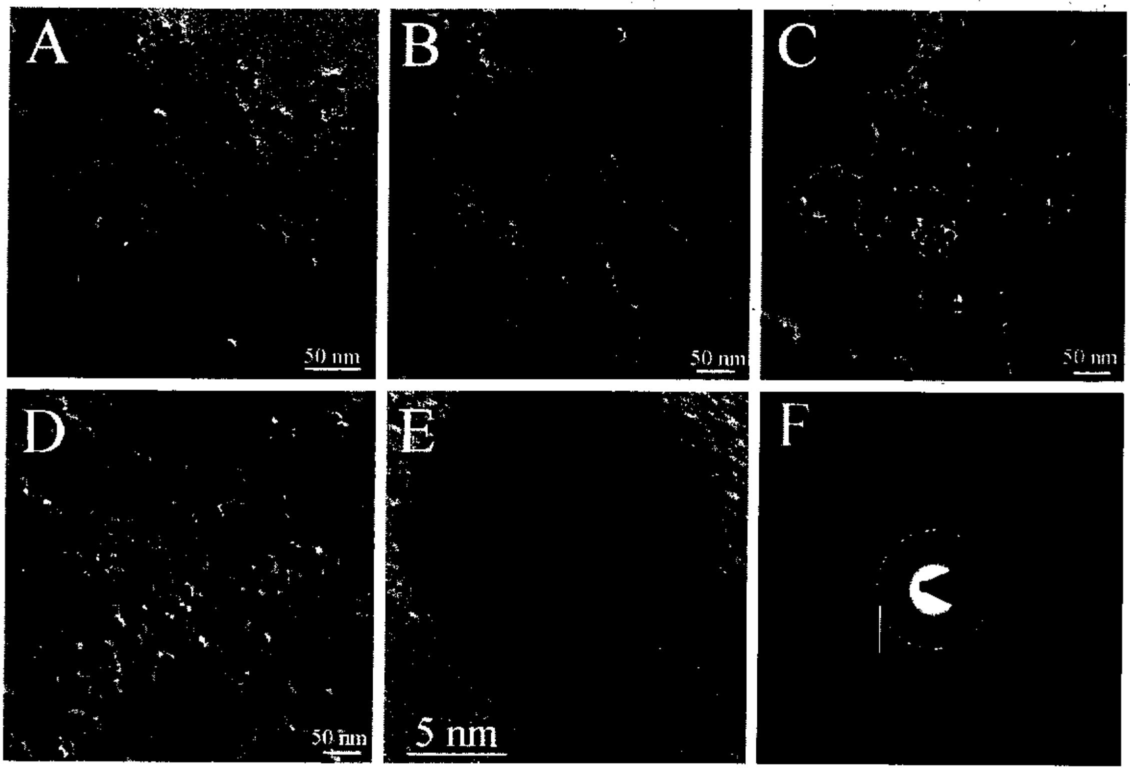

Fig. 2. TEM images of the samples prepared at various conditions: (A) 30 °C, 24 h; (B) 70 °C, 1 h; (C) 80 °C, 1 h; (D) 90 °C, 1 h. (E) HR-TEM image and (F) SAED pattern of the sample (B).

temperature can accelerate reduction reaction rate and thus is helpful to enhance the nucleation rate of Ag particles. The quick nucleation is beneficial to obtaining some relative smaller particles. However, the size deviation of these nanoparticles increases distinctly at the relatively high temperature, especially at 90 °C. Compared with high temperature (90 °C), low temperature (30 °C) produced more distinctly polydisperse distribution for the resulting Ag nanoparticles (Fig. 2(A)).

The HR-TEM image (Fig. 2(E), taken from an individual particle from Fig. 2(B)) presents clear lattice fringes, indicating that the Ag nanoparticle is highly crystallized. The SAED pattern (Fig. 2(F)) of Ag nanoparticle (Fig. 2(B)) shows discontinuous diffraction rings consisting of diffraction spots, indicating that the nanocrystals are polycrystalline, which is also confirmed by the lattice fringes with different orientations in the HR-TEM figure. The observed diffraction rings can be assigned to (111), (220), (222), (311) and (331) reflections, confirming the formation of face-centered cubic silver.[10]

The optical absorptions of the silver nanoparticles have been measured using UV-vis spectrometer; results are shown in Figure 3. As can be seen, silver nanoparticles have a distinct absorption peak at $\lambda_{max} = 408$ nm for the sample prepared at 70 °C, which is a typical excitation of surface plasma for metallic Ag nanospheres.[11] When the reaction temperature was increased to 80 or 90 °C, the maxima of the absorption peaks all show a blue shift to $\lambda_{max} = 401$ nm, whereas it shifted to $\lambda_{max} = 420$ nm when the temperature was decreased to 30 °C. It is well known that the absorption peak position is correlated to the average size of particles. According to this principle, we can conclude that the average size of the four samples follows the order: A (30 °C) > B (70 °C) > C (80 °C) ≈ D (90 °C), which is consistent with the results of TEM.

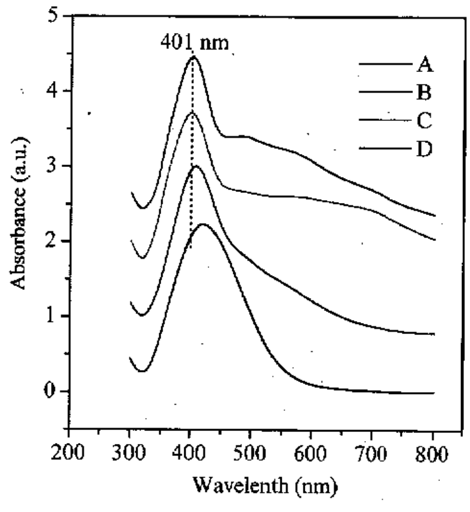

Fig. 3. UV-vis absorption spectrum of the samples prepared at various conditions: (A) 30 °C, 24 h; (B) 70 °C, 1 h; (C) 80 °C, 1 h and (D) 90 °C, 1 h.

Apart from the peak position, the other difference is the peak width. A similar peak width can be observed for the samples synthesized at 70, 80 and 90 °C, which are obviously narrower than that of the sample prepared at 30 °C. Such results indicate that uniform Ag nanospheres are more easily obtained at relatively high temperature than that at low temperature. However, it does not mean that the higher the temperature is, the more uniform the nanoparticles size is. Moreover, the appearance of the shoulder peaks for the samples (Figs. 3(C) and (D)) indicates that some particles with relatively large size have formed, which is also supported by the forgoing SEM and TEM results.

The above results indicate that temperature plays an important role in the size and the size distribution of Ag nanocrystals. According to publications,[3,15] the sizes and the size distribution of nanocrystals depend mainly on Ag ions monomer concentration and the growth velocity, respectively. In a sense, it is difficult to obtain monodisperse nanocrystals with small size at low temperature because of the kinetic control[12] which is in favor of the formation of nanocrystals with anisotropic structure and a broad size distribution. Such phenomenon has also been observed in our product (Fig. 2(A)). It is generally thought that the size distribution of nanoparticles can be focused down to a very narrow range at relatively high temperature, because high temperature can accelerate reaction and thus is helpful to enhance the product (Ag monomer) concentration. At higher monomer concentration, the critical size becomes smaller so that all the particles grow nearly at the same time.[15] As a result, smaller particles grow faster than the larger ones, which is beneficial for forming monodisperse nanoparticles. However, at higher temperature, some smaller particles may be easily consumed by some relatively larger particles during the growth process based on Ostwald ripening.[16,17] The relatively high temperature may accelerate Ostwald ripening process when the ploy dispersed nucleation occurred at such temperature range. According to this analysis, some relatively larger particles formed gradually, which is supported by our experiment result (Figs. 1(D) and 2(D)). Thus, an appropriate temperature (70 °C) is helpful to obtain monodisperse silver nanocrystals in this case, which can avoid the formation of polydisperse particles caused by the Ostwald ripening at high temperature and the kinetic control at low temperature.

4. CONCLUSIONS

Compared with other procedures involving high temperature, high cost Ag precursor or complex process, a facile one-pot route is proposed in this article (low temperature, low cost Ag precursor and simple process) for the synthesis of nearly monodisperse Ag nanocrystals with a narrow size distribution. The results indicate that a proper reaction temperature is helpful to synthesize monodisperse silver nanoparticles.

Acknowledgments: This work is supported by Natural Science Foundation of the Higher Education Institutions of Anhui Province, China (KJ2012A036, KJ2011A034), National Nature Science Foundation of China (21171003, 21101002) and Key Laboratory of Oil and Gas Fine Chemicals, Ministry of Education and Xinjiang Uyghur Autonomous Region, Xinjiang University (XJDX0908-2011-02).

References and Notes

1. Z. Cao, H. Fu, L. Kang, L. Huang, T. Zhai, Y. Ma, and J. Yao, *J. Mater. Chem.* 18, 2673 (**2008**).
2. P. Li, Q. Peng, and Y. Li, *Chem. Eur. J.* 17, 941 (**2011**).
3. N. Zheng, J. Fan, and G. D. Stucky, *J. Am. Chem. Soc.* 128, 6550 (**2006**).
4. M. Darroudi, A. Zak, M. Muhamad, N. Huang, and M. Hakimi, *Mater. Lett.* 66, 117 (**2012**).
5. K. Abe, T. Hanada, Y. Yoshida, N. Tanigaki, H. Takiguchi, H. Nagasawa, M. Nakamoto, T. Yamaguchi, and K. Yase, *Thin Solid Films* 327–329, 524 (**1998**).
6. A. Tang, S. Qu, Y. Hou, F. Teng, Y. Wang, and Z. Wang, *J. Solid State Chem.* 184, 1956 (**2011**).
7. X. Z. Lin, X. Teng, and H. Yang, *Langmuir* 19, 10081 (**2003**).
8. Y. Ma, W. Li, J. Zeng, M. McKiernan, Z. Xie, and Y. Xia, *J. Mater. Chem.* 20, 3586 (**2010**).
9. Y. Yin, C. Erdonmez, and A. P. Alivisatos, *J. Am. Chem. Soc.* 128, 12671 (**2006**).
10. Z. Chen and L. Gao, *Mater. Res. Bull.* 42, 1657 (**2007**).
11. L. Piao, K. H. Lee, B. K. Min, W. Kim, Y. R. Do, and S. Yoon, *Bull. Korean Chem. Soc.* 32, 117 (**2011**).
12. M. Yamamoto, Y. Kashiwagi, and M. Nakamoto, *Langmuir* 22, 8581 (**2006**).
13. M. Yamamoto and M. Nakamoto, *J. Mater. Chem.* 13, 2064 (**2003**).
14. P. Huang, J. Lin, Z. Li, H. Hu, K. Wang, G. Gao, R. He, and D. Cui, *Chem. Commun.* 46, 4800 (**2010**).
15. Y. Yin and A. Alivisatos, *Nature* 437, 664 (**2005**).
16. J. Hu, M. Chen, X. Fang, and L. Wu, *Chem. Soc. Rev.* 40, 5472 (**2011**).
17. X. Lou, L. A. Archer, and Z. Yang, *Adv. Mater.* 20, 3987 (**2008**).

Received: 28 March 2012. Accepted: 29 May 2012.