Int. J. Bio-Inorg. Hybd. Nanomat., Vol. 1, No. 1 (2012), 33-36 *ISSN: 2251-8533*

International Journal of Bio-Inorganic Hybrid Nanomaterials

Study of the Shape Controlling Silver Nanoplates by Reduction Process

Babak Sadeghi*, Somayeh Rastgo

Department of Chemistry, Tonekabon Branch, Islamic Azad University, Tonekabon, Iran

Received: 14 February 2012; Accepted: 14 April 2012

ABSTRACT

In this work, we report synthesis of silver nanoplates by a simple reduction process of silver nitrate in the presence of polyvinyl alcohol (PVA) and *N,N'*-dimethyl formamide (DMF). The Characterization of the samples were carried out using X-ray diffraction (XRD), Transmission-electron microscopy (TEM) and UV-vis spectroscopy. Absorption spectra of the nanoplates in comparison with that of the silver spherical silver NPs proved a quite different feature due to the silver nanoparticle anisotropic shape. It may be due to the specific interaction between OH groups and Ag^+ ions, which affect the selective growth of various planes of silver nanocrystals.

Keyword: Silver nanoplate; Reduction process; Anisotropic shape feature; Shape controlling nanoparticles.

1. INTRODUCTION

In recent years, controlling the shape as well as size of the metallic NPs has been focus of attention in the chemical and material research fields because it provides an effective strategy for tuning the physical and chemical properties of a metal [1]. In the nanometric material domain, it has been demonstrated that physical properties are usually closely related to the NP shape, independent of the size. In the past decade, synthesis of one- or two-dimensional (1D or 2D) nanostructures of gold and silver have been attracted much more attention for their important potential applications in catalysis [2], sensing [3], recording media [4], optics [5], and so on. However, the control of the particle shape through a general method of synthesis has met limited success although a number of very specific solution chemistry procedures have been reported for preparing rods [6,7] cubes [8], disks [9], belts [10,11] and wires [12] and other special morphologies have been widely fabricated[13-23].

For the synthesis of Ag nanoplates and nanoprisms, an external energy supplied by thermal or photoinduced processes is often required to drive the Ostwald ripening of spherical NPs into the

---

(*) Corresponding Author - e-mail: b_sadeghi@toniau.ac.ir

desired shapes. We recently developed a reduction method for converting Ag nanospheres into the nanorods [24] and nanocomposites [25]. Herein we report an improved synthesis procedure of hexagonal Ag nanoplates that involves a number of steps: (1) formation of Ag nanospheres through reduction of $AgNO_3$ by DMF in the presence of PVA at 80°C, (2) self assembling of the Ag nanospheres into silver nanoplates [24], and (3) formation of Ag nanorods from Ag nanorplates. This method offers great ease of control and a high yield of hexagonal particles. More importantly, this process is driven by a fairly generic mechanism which may be tuned to produce Ag NPs with other shapes (rods, wires, cubes, etc.), thereby paves the way to the shape-control synthesis of Ag nanomaterials.

2. EXPERIMENTAL

2.1. Materials and methods

Materials containing a large fraction of silver nanoplates were synthesized by reduction of silver nitrate in the presence of PVA. The procedure is briefly described as follows: Firstly, 5 ml DMF was refluxed in a three-necked round-bottom flask at 80°C for 2h, then 5 ml DMF solution of 0.02 M silver nitrate and 5 ml DMF solution of 0.05 mM PVA were simultaneously injected dropwise. When the first drops of silver nitrate and PVA/DMF solutions were added, the mixture turned yellow immediately. Continuing the injection, the solution became opaque gradually. By finishing the injection, the solution turned turbid with a grey color in about 15 min indicating the appearance of Ag NPs. The reaction was contining at 80°C for 24 h. After finishing the reaction and the removal of the supernatant, a pink precipitate remained.

2.2. Characterization process

The Powder X-ray diffraction (XRD) pattern was recorded on a Seisert Argon 3003 PTC using nickel-filtered XD-3α Cu Ka radiations (λ =1.5418 Å). Absorbance mode was recorded on a Hitachi spectrophotometer model U-2101 PC. The soluble form of the sample was prepared by suspending a small amount of powder in ethanol. TEM was performed on a Philips EM208 and microscope operated at 100 kV. Sample was prepared by dispersing the powder in ethanol. Imaging was enabled by depositing a few drops of suspension on a carbon coated 400 mesh Cu grid. The solvent was allowed to evaporate before imaging.

3. RESULTS AND DISCUSSION

A typical X-ray diffraction (XRD) pattern of the products is shown in Figure 1, and the peaks were assigned to the diffraction of (111) and (200) planes of fcc silver respectively, with the cell parameter calculated to be 4.084 Å in agreement with the literature report (PCPDF NO. 04-0783), and other peaks corresponding to (220), (331), and (222) diffraction were not observed. Compared with the two diffraction peaks, one notes that the intensity of the (200) peak is much stronger than that of the (111) peak, indicating that the formed Ag nanoplates are abounding in (100) facets, and that the (100) planes are preferentially oriented parallel to the substrate. The (111) diffraction peak probably originated from the existence of Ag nanorods, NPs, as well as possible (111) facets on the truncated corners of the Ag nanoplates.

It is worth noting that the ratio between the intensity of the (200) and (111) peaks was about 3.5, which was higher than previous reports [26, 27, 28]. The face-centered cubic (fcc) structure of silver metal confers its tendency to nucleate and into NPs with their surfaces bounded by the lowest energy (111) facets, with the most of the previous methods, in particular the chemical synthesis, being mainly confined to those of the preparation of nanowires, rods, or spheres [29].

Figure 2(A,B) shows the TEM images of the individual hexagonal silver nanoplate. They show that the nanoplates have very sharp edges with average width of 60 nm, and their thickness is about 5 nm.

The absorption spectrum of the nanocrystals dispersed in solution shows three peaks centered at 2.2 eV, 2.85 eV, and 3.6 eV with a shoulder around

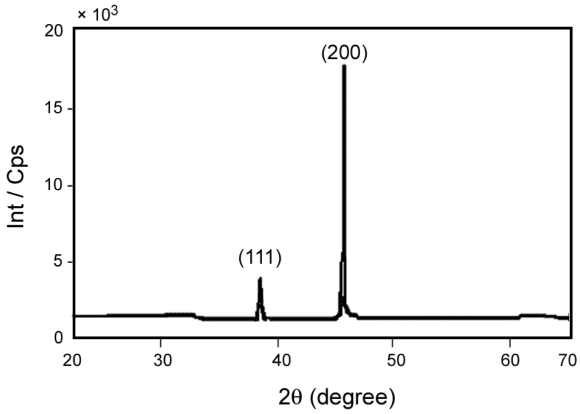

***Figure 1:** XRD of Ag/PVA nanoplates, generated by DMF.*

3.3 eV (Figure 3). This agrees with the red-pink color of the solution obtained at the end of the synthesis. The peaks are related to surface plasmon (SP) bands characteristic of noble metal nanocrystals such as silver [30]. The absorption spectrum in Figure 3 is that of a collection of silver nanocrystals differing by their shape (spheres and disks). It is now well known that the SP band positions strongly depend on the nanocrystals shape. For a sphere a single SP band is expected [30]. This is well illustrated by the absorption spectrum of 5 nm spherical silver nanocrystals, which shows a single peak centered at 3.1 eV [31]. Such an absorbance might contribute to the overall spectrum obtained experimentally, in the same energy range. In that case, four SP modes are expected and their position depends on the particle size, shape, and aspect ratio. Hence the following are expected: 1) a high energy peak of low intensity around 3.5 eV, 2) a complex structure made of several resonances between 2.5 and 3 eV, 3) and a peak at lower energy that will strongly depend on the nanodisk size and aspect ratio.

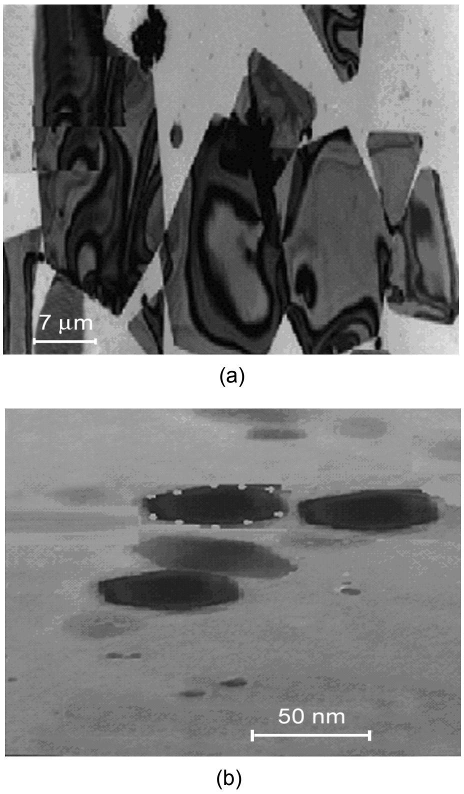

***Figure 2:** TEM images of the silver nanoplates prepared by DMF.*

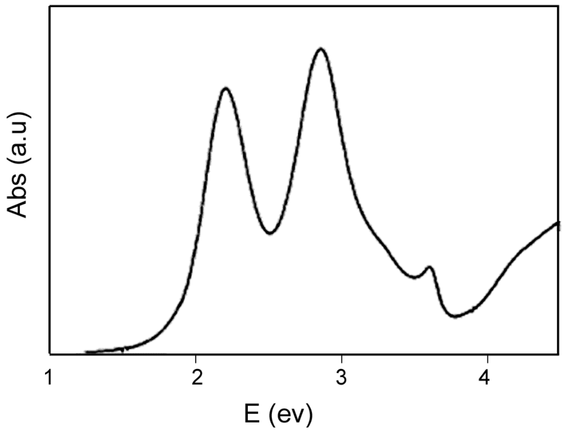

***Figure 3:** Absorption spectrum of the solution obtained at the synthesis and containing spheres and nanoplates.*

The catalytic mechanism of hydrogen generation on these colloidal silver nanocrystals with different shape is still under investigation.

It is hoped that these new results would also provide data for theoreticians to develop simulations concerning nanodisks.

4. CONCLUSIONS

"In conclusion, a new approach to the synthesis of silver nanodisks with highly anisotropic optical properties is described in this work. The control of the aspect ratio will provide an interesting way to tune the absorption spectrum because of the main low energy absorption peak would be shifted in a large energy range. In any case, it seems reasonable to conclude that the change in the absorption spectrum of silver nanocrystals is clearly due to the shape anisotropy feature with the appearance of various absorption peaks.

"The unusual intensity of the (200) diffraction peak is a result of the strong tendency of the Ag NPs to assemble into 2D arrays on the solid surface [32].

ACKNOWLEDGMENT

This work was financially supported by the Islamic Azad University, branch of Tonekabon research ministry and also a fund from Executive Director of Iran-Nanotechnology Organization (Govt. of Iran).

REFERENCES

1. (a) Wang Z.L., *J. Phys. Chem. B.*, B.**104m** (2000), 1153-1175. (b) El-Sayed M.A., *Acc. Chem. Res.*, **34**(2001), 257-264. (c) Murphy C.J., Jana N.R., *Adv. Mater.*, **14**(2002), 80-82. (d) Wiley B., Sun Y., Mayers B., Xia Y., *Chem. Eur. J.*, **11**(2005), 454-463.
2. Moreno-Manas M., Pleixats R., *Acc. Chem. Res.*, **36**(2003), 638-643.
3. Spadavecchia J., Prete P., Lovergine N., Tapfer L., Rella L., *J. Phys. Chem. B*, **109**(2005), 17347-17349.
4. Sun S.H., Murray C.B., Weller D., Folks L., Moser A., *Science*, **287**(2000), 1989-1992.
5. Kamat P.V., *J. Phys. Chem. B*, **106**(2002), 7729-7744.
6. Zijlstra P., Bullen C., Chon J.W.M., Gu M., *J. Phys. Chem. B*, **110**(2006), 19315-19318.
7. Wu H.Y., Huang W.L., Huang M.H., *Cryst. Growth. Des.*, **7**(2007), 831-835.
8. Sun Y.G., Xia Y.N., *Science*, **298**(2002), 2176-2179.
9. Millstone J.E., Park S., Shuford K.L., Qin L., Schatz G.C., Mirkin C.A., *J. Am. Chem. Soc.*, **127**(2005), 5312-5313.
10. Sun Y., Mayers B., Xia Y., *Nano Letter*, **3**(2003), 675-679.
11. Wang L.Y., Chen X., Chai Y.C., Hao J.C., *Colloid. Surf. A*, **293**(2007), 95-100.
12. Vasilev K., Zhu T., Wilms M., Gillies G., Lieberwirth I., Mittler S., Knoll W., Kreiter M., *Langmuir*, **21**(2005), 12399-12403.
13. Yamamoto M., Kashiwagi Y., Sakata T., Mori H., Nakamoto M., *Chem. Mater.,* **17**(2005), 5391-5393.
14. Sanchez-Iglesias A., Pastoriza-Santos I., Perez-Juste J., Rodriguez-Gonzalez B., Garcia de Abajo F.J, Liz-Marzan L.M., *Adv Mater.*, **18**(2006), 2529-2534.
15. Kwon K., Lee K.Y., Lee Y.W., Kim M., Heo J., Ahn S.J., Han W., *J. Phys. Chem. C*, **111**(2006), 1161-1165.
16. Qu Y., Porter R., Shan F., Carter J.D., Guo T., *Langmuir*, **22**(2006), 6367-6374.
17. Gao J., Bender C.M., Murphy C.J., *Langmuir*, **19**(2003), 9065-9070.
18. Zhou M., Chen S.H., Zhao S.Y., *J. Phys. Chem. B*, **110**(2006), 4510-4513.
19. Kim F., Song J.H., Yang P., *J. Am. Chem. Soc.*, **124**(2002), 14316-14317.
20. McGilvray K.L., Decan M.R., Wang D., Scaiano J.C., *J. Am. Chem. Soc.*, **128**(2006), 15980-15981.
21. Filali M, Meier M.A.R., Schubert U.S., Gohy J.F., *Langmuir*, **21**(2005), 7995-8000.
22. Singh N., Lyon L.A., *Chem Mater.*, **19**(2007), 719-726.
23. Gole A., Murphy C.J., *Chem Mater.*, **16**(2004), 3633-3640.
24. Sadjadi M.A.S., Sadeghi B., Meskinfam M., Zare K., Azizian, *J. Physica E,* **40**(2008), 3183-3186.
25. Sadeghi B., Pourahmad A., *Advanced Powder Technology*, **22**(2011), 669-673.
26. Yu D., Yam V.W., *J. Am. Chem. Soc.*, **126** (2004), 13200-13201.
27. Sun Y., Xia Y., *Science*, **298**(2002), 2176-2179.
28. Lee Y.T., Im S.H., Wiley B., Xia Y., *Chem. Phys. Lett.*, **411**(2005), 479-483.
29. (a) Sun Y., Mayers B., Herricks T., Xia Y., *Nano Lett.*, **3**(2003), 955-960. (b) Yin Y., Li Z.Y., Zhong Z., Gates B., Xia Y., Venkateswaran S., *J. Mater. Chem.*, **12**(2002), 522-527.
30. U. Kreibig, M. Vollmer, 1993. Optical properties of metal clusters, Springer (Berlin).
31. Taleb A., Petit C., Pileni M.P., *J. Phys. Chem. B*, **102**(1998), 2214-2220.
32. J.V. Gilfrich, I.C. Noyan, R. Jenkins, T.C. Huang, R. Synder, D. Smith, M.A. Zaitz,P.K. Predecki, 1997. *Advances in X-Ray Analysis*, Plenum Press (New York and London).