Effect of Electric Field on the Morphology of Silver Nanocrystals Prepared by γ-Irradiation

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The flake-like silver nanocrystals were prepared by γ-irradiation in the presence of an electric field. However, only spherical silver nanoparticles were obtained without the electric field.

In recent years, intensive interest has been focused on the preparation of wire-like, rod-like and film-like nanocrystals.[1–5] In order to obtain these oriented nanocrystals, many kinds of templates and substrates were explored. Fan used carbon nanotubules as templates to prepare GaN nanowires.[1] Ethylenediamine was used to prepare CdE (E = S, Se, Te) nanorods via the solvothermal method.[6] Up to now, there is still no report on preparation of silver nanocrystals in the presence of an electric field. In this paper, we report a novel approach to prepare oriented silver nanocrystals. The flake-like silver nanocrystals were prepared by γ-irradiation of an aqueous solution of $AgNO_3$ in the presence of an extra electric field.

All the reagents were analytical-grade and used without further purification. Amount of 0.02 mol $AgNO_3$ was dissolved in 80 ml distilled water to form a homogenous solution. In order to maintain reductive condition, 20 ml isopropyl alcohol was added into the solution. The solution was bubbled with N_2 for 30 min to remove oxygen. Then the solution was irradiated by a 2.22×10^{15} Bq ^{60}Co γ-ray source at the dose rate of 50 Gy/min for 6 h, the total dose was 18 kGy. When irradiated, the solution was placed in an electric field. In this study, two parallel copper plates were connected with an electric source of constant voltage (2000 volts.) and a static electric field was obtained. The intensity (I) of the electric field could be estimated by $I = V/D = 2000\ v/5\ cm = 400\ v \cdot cm^{-1}$. The experiment was carried out in a glass bottle, which was an insulator. There was no electric current in the solution, so high-concentration $AgNO_3$ did not play the role of electrolyte and no electrochemical reaction occurred. A gray product was collected and repeatedly washed by distilled water. Thus, the sample 1 was obtained. As a comparison, the sample 2 was synthesized under the same conditions as those of the sample 1, but without the introduction of an extra electric field.

XRD (X-ray powder diffraction) was carried out on a Rigaku D/max-rA X-ray diffractometer with graphite monochromatized Cu Kα radiation ($\lambda = 1.54178$ Å). The scanning rate of 0.020 °/s was applied to record the patterns in the 2θ range of 30 ° to 80 °. Figure 1(a) showed the XRD pattern of the sample 1, which was prepared in the extra electric field. All the peaks could be indexed as face-center-cubic phase silver (JCPDS Card, no. 4-0783). From Figure 1(a), the narrow and strong diffraction peak (111) indicated preferential crystalline orientation as sample 1. Figure 1(b) showed the XRD pattern of the sample 2.

Transmission electron micrography (TEM) and electron diffraction (ED) were carried out on a Hitachi H-800 transmission electron microscope with accelerating voltage 200 kV. Figure 2 showed TEM images and ED pattern of obtained samples. From

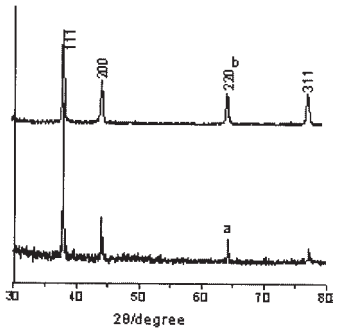

Figure 1. XRD pattern of sample 1(a) and sample 2 (b).

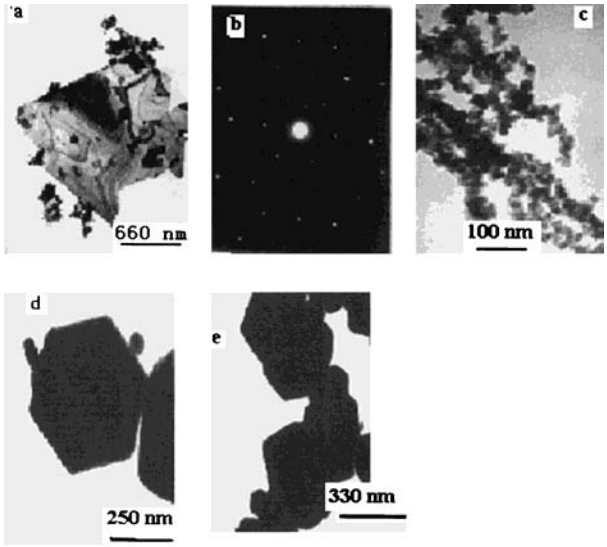

Figure 2. TEM images and ED pattern of as prepared samples. (a) TEM image of nanocrystals prepared in the electric field. (b) ED pattern of nanocrystals in the electric field. (c) TEM image of nanocrystals without the electric field. (d), (e) TEM images of nanocrystal sample 3 and sample 4.

Figure 2(a), one could clearly see that the sample 1 was consisted of one bigger and some smaller flake-like nanocrystals. The corresponding ED pattern was shown in Figure 2(b), which indicated the single-crystal nature of the flake-like silver nanocrystals and that the growth of silver nanocrystals was oriented. The results were consistent with the above XRD pattern. Moreover, some irregular nanocrystals was in Figure 2(a), the reason was not clear and it would be studied in our next work. In order to further prove the influence of the external electric field on the morphology of silver nanocrystals, the following experiments were carried out under the same conditions as those of preparing sample 1, but the concentrations of $AgNO_3$ changed 0.04 mol/l

and 0.06 mol/l, thus the sample 3 and 4 were obtained. TEM images showed that the morphologies of the sample 3 and sample 4 were also flake-like (see Figure 2(d) and 2(e)). The main morphological difference among the sample 1, 3, and 4 was their thickness. The above experiments showed that it is reproducible to obtain flake-like silver nanocrystals in a external electric field using γ-irradiation method. In Figure 2(c), only spherical (or quasi-spherical) nanoparticles were displayed. From the TEM images and ED pattern, it could be seen that the extra electric field significantly changed the morphology of as prepared silver nanocrystals.

A possible reason to form flake-like silver nanocrystals could be suggested as follows: Firstly, the radiolysis of aqueous solution initially produced many kinds of particles.[7]

$$H_2O \sim\sim\rightarrow e_{aq}^-, \cdot H, \cdot OH, H_3O^+ \text{ etc.}$$

Among these active particles, ·OH radicals were strong oxidative reagent. It could oxidize silver atoms, which were reduced by e_{aq}^- and ·H. So it should be scavenged. In the experiment, oxidative radicals (·OH radicals) were scavenged by isopropyl alcohol:

$$\cdot OH + (CH_3)_2CHOH \rightarrow H_2O + (CH_3)_2COH\cdot$$

So the reductive condition of the solution was obtained. Then the following reactions occurred:[8,9]

$$Ag^+ + e_{aq}^- \rightarrow Ag^0$$
$$Ag^0 + Ag^+ \rightarrow Ag_2^+$$
$$Ag_2^+ + Ag^+ \rightarrow Ag_3^{2+}$$
$$Ag_3^{2+} + Ag_3^{2+} \rightarrow Ag_4^{2+} + 2Ag^+$$

Finally, these silver ions or silver cluster ions would be reduced by hydrated electrons and agglomerated further. Without the external electric field, the cluster ions agglomeration rate in all directions could be regarded as equal because of random thermal movement, only spherical nanoparticles would be obtained (see Figure 2(c)). While the electric field was introduced, the movement of above cluster ions would contain both random thermal and oriented movements. The oriented movement was induced by the interaction between silver ions (or silver cluster ions) and the extra electric field. The agglomeration rate would be varied in different directions. The agglomeration rate along electric field direction should be superior to that of other directions. It was the difference of agglomeration rate that resulted in the oriented growth of silver nanocrystals.

From the above discussions, it can be found that the key point to form oriented nanocrystals is the interaction between the electric field and silver ions (or cluster ions). The agglomeration rate of cluster ions are different along different directions resulted from this kind of interaction. If silver ions in aqueous solution are replaced by copper ions or nickel ions, and under similar conditions that of sample 1, oriented copper or nickel nanocrysals may be obtained.

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References

1 W. Q. Han, S. S. Fan, Q. Q. Li, and Y. D. Hu, *Science*, **277**, 1287 (1997).
2 J. P. Yang, F. C. Meldrum, and J. H. Fendler, *J. Phys. Chem.*, **99**, 5500 (1995).
3 H. Q. Gao, Z. Xu, D. Sheng, and C. Y. Tie, *Adv. Mater.*, **3** (2) 121 (2001).
4 J. H. Zhan, X. G. Yang, S. D. Li, D. W. Wang, Y. Xie, and Y. T. Qian, *J. Cryst. Growth*, **220**, 231 (2000).
5 W. T. Xu, *J. Cryst. Growth*, **220**, 96 (2000).
6 Y. D. Li, H. W. Liao, D. Yi, Y. Fan, Y. Zhang, and Y. T. Qian, *Inorg. Chem.*, **38**, 1382 (1999).
7 H. Y. Ni, X. W. Ge, H. R. Liu, Z. C. Zhang, Q. Ye, and F. Wang, *Chem. Lett.*, **2001**, 458.
8 E. Janata, A. Henglein, and B. G. Ershov, *J. Phys. Chem.*, **98**, 10888 (1994).
9 M. Mostafavi, M. O. Delocurt, and J. J. Belloni. *Imagine. Sci. Tech.*, **38**, 54 (1994).