

Nanosilver Fabrication under the Control of Ligands Containing Pyridyl Group in Solution Phase with Photoreduction Method

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Nanosilver was prepared by photoreduction method and the size and shape of the nanosilver can be easily controlled by changing the organic capping reagent such as pyridine, nicotinic acid, 2,2'-dipyridylamine and 2,2'-bipyridine. Using different capping reagents, different shapes of nanosilvers, such as nanoribbon, nanotriangle or nanowire, can be obtained under mild condition.

It is well known that the size and shape of nanomaterials play a crucial role in their various applications.¹ Many efforts have been made for the controlled syntheses of these materials. To the best of our knowledge, up to now "hard templates"² and "soft templates"³ are often employed to synthesize nanosilver. Electrochemical⁴ and photoinduced⁵ approaches have also been studied. By these methods, silver nanoparticle,⁶ nanorod,^{5a} nanowire,^{2a,7} nanoprism,^{5b,8} and nanocube⁹ have been successfully synthesized in lab. Nevertheless most of these methods are complicated and time consuming. To control the shape and size of nanomaterial is still a desirable yet elusive goal.

Here we wish to report a nanosilver fabrication under the control of the ligands that contain pyridyl group. By changing the organic ligands we can easily control the shape and size of the nanosilver under mild condition. The typical procedure of our synthesis is simply to expose the mixture of silver nitrate and the organic ligands to ultraviolet irradiation at room temperature for only two minutes.

In the preliminary experiment, nicotinic acid was used as the ligand. After exposing the mixture of 0.10 M of silver nitrate (10 mL) and 0.35 g of nicotinic acid to ultraviolet irradiation for two minutes, ribbon-like nanosilver (Figure 1A) was formed as the predominant product. The highly magnified TEM images showed that they were assembled by many microcrystals (Figure 1B) and the SAED (selected area electron diffraction) pattern (Figure 1C) showed the corresponding multicrystal nature of these materials. Though we can change the shape and size of these nanowires a little by adjusting the concentration of the silver nitrate (Figure 1D), there was no significant change in the shape and size. So we attempted to find new approaches to control the shape and size of nanomaterials substantially.

Considering that the mixture of pyridine and formic acid has a better solubility than that of nicotinic acid and also this mixture contains both donor nitrogen atom and carboxylic functional group, which are similar to the donor nitrogen atom and carboxylic groups in nicotinic acid, the ligand was changed to the mixture of pyridine and formic acid. Figure 2A showed the TEM images of the nanosilver synthesized in the presence of the mixed ligands. Almost perfect silver nanotriangles were fabricated concomitant with some truncated triangular silver nanoplates. The SAED pattern (Figure 2B) showed face-cen-

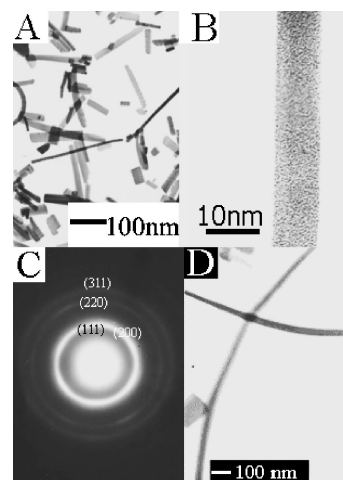


Figure 1. a) The typical TEM images of the ribbon like nanosilver obtained by the ultraviolet irradiation of the mixture of 0.35 g nicotinic acid and 0.12 g solid AgNO_3 in 10 mL distilled water (AgNO_3 0.07 M) for 120 seconds; b) The highly magnified TEM image of the selected nanoribbon; c) The corresponding SAED pattern of the ribbon like nanosilver; d) The TEM images of the nanosilver with better aspect ratio obtained by the ultraviolet irradiation of the mixture of 0.35 g nicotinic acid and 0.085 g solid AgNO_3 in 10 mL distilled water (AgNO_3 0.05 M) for 120 seconds.

tered cubic (FCC) single crystal nature of these materials and the corresponding XRD pattern agreed well with previous report data (JCPDS No. 04-0783). Uniform contrast in TEM images clearly demonstrated that these shaped nanosilvers were not tetrahedrons but thin plates. From the SAED pattern, we assume that the silver nanoplate is mainly covered by {110} facet, which is the highest energy facet among all the facets of silver crystal.¹⁰ On the basis of our experimental result and the previous report^{7,9} we proposed the mechanism for the formation of different shape nanosilver as below. Firstly, all the ligands act as capping reagents. Under the ultraviolet light, the silver ions are reduced to silver atoms and assemble to form the silver microcrystal particle. The large quantity of organic ligands containing nitrogen atom are easily attached to the surface of these microcrystal and slow down the growth speed of the crystal facet. Particularly, the lone pair electrons in pyridyl nitrogen are exposed enough to increase the coordination ability. Different facets of this microcrystal have different adsorption ability. The facets that attached more ligands grow more slowly than those attached fewer ligands. As a result, the facets that attached fewer ligands tend to assemble one by one to fabricate specific shape. In this situation, the pyridine tends to attach to the {110} facet and suppress the growth rate of this facet. Because of the

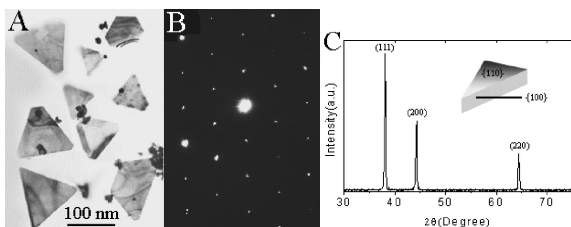


Figure 2. a) The TEM images of the silver nanotriangular synthesized by UV photoreduction of the solution of 0.12 M silver nitrate (containing 1 ml pyridine and 1 ml formic acid in 10 ml) for 120 seconds. b) The SAED pattern of the triangular nanosilver. c) XRD pattern of triangular nanosilver.

π - π interaction between pyridines, the adsorbed pyridines array orderly and produce a cover layer on the surface, resulting in the formation of the triangle nanosilver, as shown in Figure 2A, B. The exact mechanism for the formation of different shape nanosilver via this solution-phase approach is still not clear and is under investigation in our group. Here we just proposed a hypothesis that is consistent with the experiment results.

In terms of this hypothesis, the ligand contains the pyridyl group can be attached to the surface directionally. Therefore, it is possible that the ligand containing multi-pyridyl group will be adsorbed to multi-facet of silver microcrystal. As a result, the anisotropic growth of the microcrystal could be limited in a certain direction, resulting in the formation of specific shape nanosilver. Actually, when 2,2'-dipyridylamine (DPLA), a ligand with three donor nitrogen atoms, was employed as the capping reagents, as expected, longer and thinner silver nanowires were obtained. They are about 10 μ m in length and 100 nm in width (Figure 3A, B). We only got multicrystalline nanosilver whose

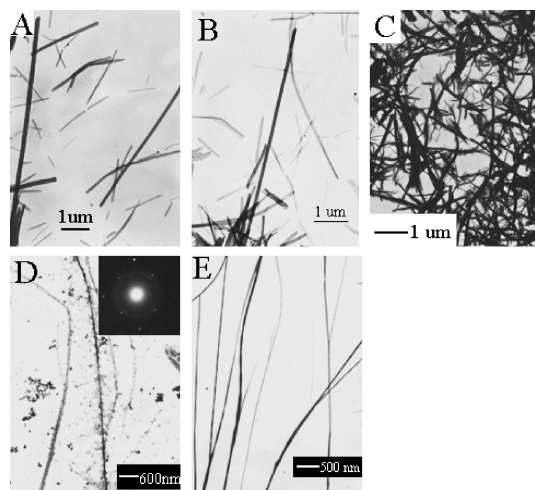


Figure 3. a, b, c) The typical TEM images of the silver nanowire obtained by the UV photoreduction of the mixture of 0.07 M silver nitrate and 0.30 g 2,2'-dipyridylamine for 120 seconds. The mean width is about 100 nm and the length is up to 10 μ m. d) TEM images of the materials shown in A after being heated in boiling water for ten hours. The inset is the SAED pattern of the silver nanowire in the middle of the picture. e) The TEM images of the silver nanowire obtained by UV photoreduction of the mixture of 0.07 M silver nitrate and 0.30 g 2,2'-bipyridine for 120 seconds. The mean width is about 60 nm and the average length 100 μ m.

SAED pattern was the same as that ribbon-shaped silver (Figure 1C) at room temperature. But they can be changed into single crystals (Figure 3D) when heated in boiling water for several hours. Inspired by this experiment, 2,2'-bipyridine (BP) was employed as ligand. In comparison with DPLA, BP is more rigid because the two pyridyl groups connect directly. Moreover, the span between the two pyridyl groups in BP is shorter than that in DPLA. As a result of this limitation, much longer and thinner silver nanowire (Figure 3E) was formed. This nanowire is average 100 μ m in length and 60 nm in width, and the aspect ratio is almost as high as 1700. On the other hand, the morphology and dimension of nanosilver can be affected by many factors such as concentration of AgNO_3 and ligand, the reaction temperature and solvent. Generally, the increase of concentration of AgNO_3 leads to the formation of ribbon-shaped nanosilver and reduces the aspect ratio. How these factors affect the shape and size of nanosilver is investigated in detail in our lab.

In conclusion, we have applied organic ligands containing pyridyl group as the capping reagents to control the shape of the silver nanostructure. In the presence of the ligand, the nanosilver can be fabricated under ultraviolet at room temperature for only two minutes. By changing the capping reagents, moreover, different shape of nanosilvers can be obtained under mild condition. The more detailed investigation about the fabrication mechanism is still in progress in our group.

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