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Synthesis of highly anisotropic metal nanocrystals and their applications

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ABSTRACT

Highly anisotropic metal nanocrystals such as one dimensional nanowires and two dimensional nanoplates have been of great interest owing to their potential in applications such as transparent electrodes, stretchable electrodes, and barrier films. To control the anisotropic growth of metal nanocrystals, we precisely tuned the kinetic and thermodynamic parameters and consequently could promote the growth reaction toward desirable direction and inhibit the addition of atoms onto the unwanted facets. Therefore, here we would like to introduce the importance of highly anisotropic metal nanocrystals and share recent progress of our research group.

1. INTRODUCTION

Silver metal nanocrystals with controlled shape and morphology such as cubes, octahedra, spheres, prisms, rods, and wires have been intensive studied due to their potential in applications to biosensors, LSPR (Localized Surface Plasmon Raman) sensors, catalysts, electrodes, and solar cells.[1] Such shape controlled silver nanocrystals have been synthesized by solution chemistry using silver salt, solvent, reducing agent, capping agent, and shape controlling additive. Typical solution chemistry utilize polyol medium such as alkanediol and polyalkanediol, or dimethylformamide (DMF) or water in order to dissolve the silver salt and reduce silver cations. The silver atoms produced by reduction of silver cations reach to supersaturation state and begin to be agglomerated to silver nuclei with thermodynamically stale shape in the reaction circumstance. The nuclei are then grown to larger silver nanocrystals by addition of silver atoms to the surface of nuclei. Therefore thermodynamically stable silver nanocrystals will be produced as long as not to control the nucleation and growth stage.

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In general, the surface energy of silver nanocrystals with fcc (faced centered cubic) structure is in the order of {110}>{100}>{111} facet so that the silver nanocrystals tend to reveal {111} facets as many as possible during the nucleation and growth stage. Hence, multiply twined particles (MTPs) bound to {111} facets in their surface are mainly synthesized by uncontrolled reactions. To selectively grow one or two dimensional silver nanowires or plates, the nuclei should be selectively produced or survived in the reaction medium and grown to larger anisotropic silver crystals. Therefore here we tried to find such specific reaction condition to selectively form the nuclei for the formation of silver nanowires and plates.

2. FORMATION OF ANISOTROPIC SILVER NANOCRYSTALS

To form one dimensional silver nanowires, we used polyol method using ethanediol, silver nitrate, PVP (polyvinylpyrrolydone), nitric acid, and sodium chloride. It is known that the silver nanowires are grown from the decahedral seed nanoparticles because the cross-section of silver nanowire has five twinned crystal facets. The crystal structure in the cross-section of silver nanowire reveals five {111} facets and {110} edges; and the outer surface of silver nanowire is bound to {100} facet. Accordingly, to make highly anisotropic silver nanowires we need to selectively form decahedral seed nanocrystals and promote crystal growth toward {111} and {110} facets while capping the {100} facet (see Fig. 1).

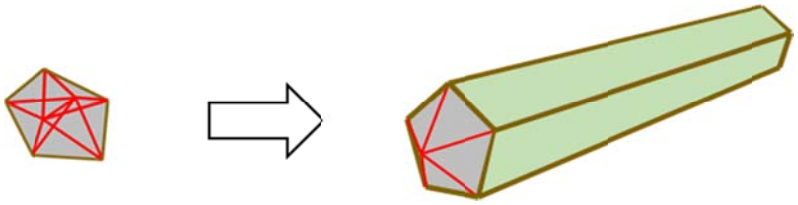

Fig. 1. Schematic illustration of the formation of one dimensional silver nanowires.

In our previous studies, we found that nitric acid dissolves the MTP silver nanocrystals preferentially and as a result, single crystalline silver nanocrystals are selectively formed because the reverse etching reaction tends to eliminate thermodynamically unstable {110} facet so that the MTP silver nanocrystals with many {110} facets, decahedral silver nanocrystals with ten of {110} facets, and single crystals without {110} facets are disappeared in this order. This implies that certain etching condition yields to selective formation of decahedral silver nanocrystals. In addition, chloride anion makes silver chloride precipitate by reaction with silver cation and the silver chloride precipitate is gradually dissolved in hot reaction medium. The dissolved silver chloride releases silver cation and chloride anion while the silver cation is reduced to silver atom by polyol medium and the chloride anion stabilizes the produced

silver nanocrystals. In air condition, the chloride ions also act as oxidative etchant removing silver MTP nanocrystals. Therefore, to promote the selective formation of one dimensional silver nanowires, both nitric acid and chloride ions are required. The produced silver nanowires by introduction of specific amount of nitric acid and sodium chloride were shown in Fig. 2.

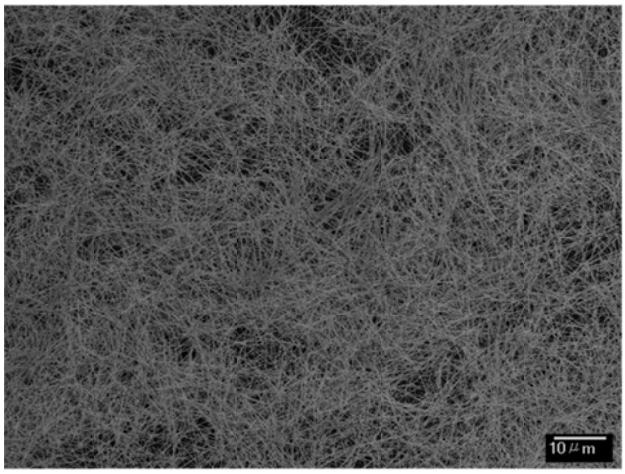

Fig. 2. SEM image of silver nanowires prepared by polyol synthesis.

The two dimensional silver nanoplates were synthesized by slow reduction reaction condition to reveal thermodynamically favored {111} facet which is corresponded to top and bottom face of silver nanoplate. To reduce the reaction rate, we preceded the reduction reaction with PVP (polyvinypyrrolidone) because PVP has hydroxyl group in both end of polymeric main chain.[1] In addition, we used non-reducing medium such as NMP (N-methylpyrrolidone) or DMF to dissolve silver salts. The produced silver nanoplates by slow reaction rate were shown in Fig. 3.

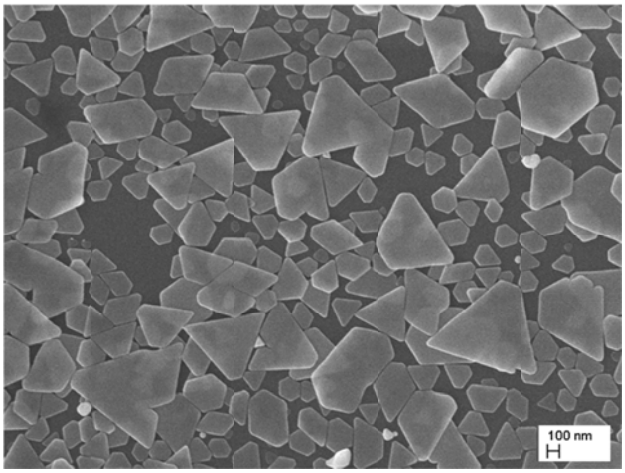

Fig. 3. SEM image of two dimensional silver nanoplates prepared by slow reduction reaction.

3. CONCLUSIONS

One and two dimensional anisotropic silver nanowires and nanoplates could be synthesized by selective formation of nuclei and promotion of selective growth of certain facets by kinetic and thermodynamic reaction control. These anisotropic silver nanocrystals can be applicable to flexible or stretchable electrodes.

4. REFERENCES

[1] M.H. Kim, J.-J. Lee, J.-B. Lee, K.-Y. Choi, CrystEngComm, 2013,15, 4660-4666.