Morphology-controlled Preparation of Silver Nanocrystals and Their Application in Catalysis

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The morphologies of silver nanocrystals have been successfully tuned from wire to versatile rod, cube, and sphere by varying the molecular structure of polyols. Effects of crystal shape on the catalytic performance of silver for hydrogen generation from HCHO solution have also been investigated. It was found that silver nanocubes were more active than nanorods, nanowires, and nanospheres.

Morphological control of metal nanocrystals is a fascinating objective since their unique properties such as catalytic, electronic, and magnetic properties are greatly dependent on their size and shape.[1] At present, a great effort has been devoted to the controlled growth of metallic nanostructures with well-defined shape in recent years.[2,3] Among various methods, the solution-phase synthesis seems a promising route in the preparation of metal nanostructures because of its characteristics of low cost, high yield, and simplicity.[4] Recently, a modified polyol process has been developed by Xia et al. and other groups for the large scare fabrication of metal nanostructures with controllable shapes and diameters.[5–8] In this system, the ethylene glycol serves as both solvent and reducing agent, and PVP acts as both protecting agent to prevent interparticle sintering and surface regulating polymer. The size, shape, and composition of the metal nanoparticles can be well controlled by adjusting the reaction parameters such as temperature, precursor type, and order of addition of reactants. They could further add metal salts and acid such as $FeCl_3$, $NaNO_3$, or HCl to afford novel shapes.[9] Up to now, such versatile features of ethylene glycol enabled researchers to provide metal nanostructures with various shapes under appropriate conditions.

Here, we demonstrate that the variation of the molecular structure of polyols can be an additional powerful way to control the shape of metal nanoproducts. The final silver nanostructures, from nanosphere to nanowire, versatile rod, and nanocube have been obtained quantitatively with different types of polyol. In addition, the catalytic activity of the shape-controlled silver nanocrystals for a novel catalytic reaction, hydrogen production from formaldehyde solution at room temperature, has also been investigated. The silver nanocubes show higher activity than nanorods, nanowires, and nanospheres.

The shape-controlled silver nanocrystals were prepared by a modified polyol method. In a typical process, 1,2-propylene glycol (1,2 PG) (10 mL) that contained poly(vinylpyrrolidone) (150 mM PVP, MW≈50000 calculated in terms of the repeating unit) was placed in a 25-mL vial, capped, and heated with stirring in an oil bath at 160 °C for 1 h. 1 mL of NaCl solution (1 mM in 1,2 PG) was then quickly added, and the vial was recapped. After 5 min, $AgNO_3$ (0.15 M in 1,2 PG) was simultaneously added drop by drop to the stirring solution. The vial was then capped and heated at 160 °C again. The obtained Ag products were washed with acetone and water to remove excess polyols and PVP via centrifugation.

As shown in Figure 1A and Figure S1A,[11] uniform Ag nanowires (98% wire, 2% irregular shapes) with the diameters of 40 ± 3.2 nm have been prepared with 1,2 PG. Figure S1B[11] shows the TEM image of the end of an individual silver nanowire, clearly showing that the twin plane parallel to its longitudinal axis. The corresponding selected area electron diffraction (SAED) (inset) indicates the single crystalline nature of silver nanowires. Figure 1B shows a typical image of the fabricated Ag nanocrystals obtained in the presence of 1,3-propylene glycol (1,3 PG), indicating that a new Ag nanostructure, versatile nanorods, has been prepared. As shown in this TEM image, these versatile nanorods (90% rod and 10% irregular shapes) were 30 ± 2.2 nm in diameter and 400 nm in length and exhibited uneven surfaces because small Ag colloids attached on the silver nanorods. Interestingly, when 1,3-butylene glycol (1,3 BG) was present, uniform Ag nanocubes (92% cubes, 5% triangles, and 3% irregular shapes) with the edge length of 40 ± 5.0 nm were obtained (Figure 1C). It is also clear from the FE-SEM images (Figures S2A and S2B[11]) that their surfaces were smooth and that all corners and edges of these nanocubes were slightly truncated. While 1,4-butylene glycol (1,4 BG) was present, only monodisperse spherical Ag nanoparticles (89% spheres, 7% cubes, and 4% rods) with a mean size of 40 ± 7.0 nm were obtained (Figure 1D). Furthermore, all shape-controlled silver nanoparticles prepared by this modified process possess good reproducibility. The above results clearly suggest that modifying the molecular structures of polyols is a very effective approach

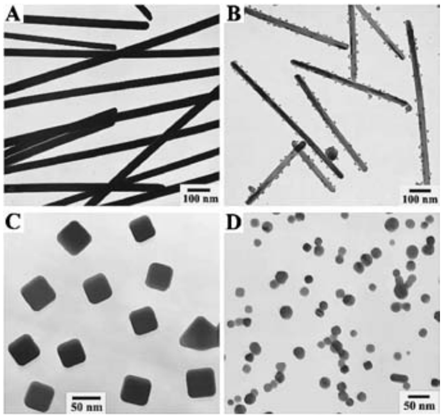
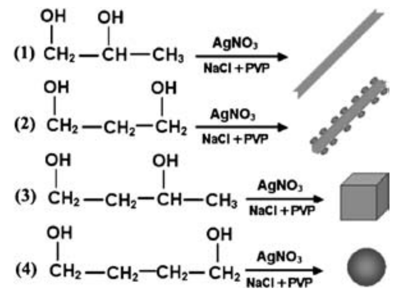


Figure 1. TEM images of colloidal Ag particles: (A) Ag nanowires prepared in 1,2 PG, (B) versatile Ag nanorods prepared in 1,3 PG, (C) Ag nanocubes prepared in 1,3 BG, (D) Ag nanospheres prepared in 1,4 BG.



Scheme 1. The relationship between molecular structures of polyols and shapes of silver nanoproducts.

for morphologies evolution of Ag nanoproducts.

Scheme 1 indicates the relationship between molecular structures of polyols and shapes of silver nanoproducts. It can be concluded that neighboring OH groups in 1,2 PG are favorable for anisotropic growth of single-crystalline silver nanowires, while the bridging OH groups in 1,3 PG are advantageous to fabricate silver nanorods. However, the bridging OH groups connected a methyl group in 1,3 BG are favorable for anisotropic growth of single-crystalline silver nanocubes. The two OH groups on the C-1 and C-4 positions of polyol facilitate the anisotropic growth of spherical silver nanoparticles, which may be due to the large separation of OH groups. It is well known that the hydroxy groups of polyol can coordinate with metal cations to form complexes.[10] According to the Nernst equation, the potential of the Ag^{+}/Ag pair can be greatly affected by the formation of complexes. This coordination effect can significantly vary the reduction rate and thus favor the formation of nanocrystals through kinetic control. On the other hand, diverse position of OH groups of polyol may greatly affect chemical and physical properties of the reaction medium, such as the reduction rate and selective growth of metal nanocrystals.

The X-ray diffraction (XRD) patterns of variously shaped silver nanoproducts are shown in Figure 2. The five peaks are all assigned to diffraction lines of the (111), (200), (220), (311), and (222) planes of the face-centered cubic (fcc) silver, respectively. As shown in curve a, the ratio between the intensities of (200) and (111) diffraction peaks was higher than the conventional value (0.6 versus 0.4), indicating that the nanocubes were abundant in (100) facets. As a direct result of the 2-D structure of the versatile nanorods, the ratio between the relative intensities of the (111) and (200) planes is higher than that of nanowires (curve c), suggesting the relative abundance of (111) planes. However, the ratio of diffraction peaks for spherical nanoparticles is similar to that of conventional bulk silver (curve d). This XRD observation agrees well with the above TEM results and further confirms the high shape uniformity of the silver nanocrystals.

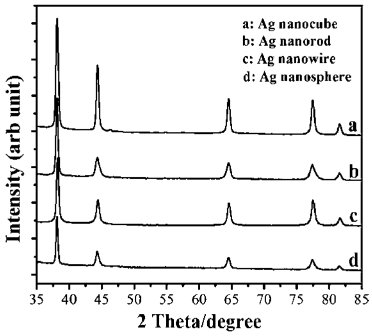


Figure 2. XRD patterns of colloidal Ag nanoparticles: (a) Ag nanocubes, (b) versatile Ag nanorods, (c) Ag nanowires, (d) Ag nanospheres.

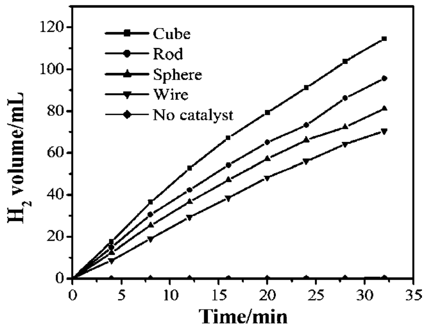


Figure 3. Catalytic activities of colloidal Ag nanoparticles: Reaction condition: $T = 25\,^{\circ}\mathrm{C}$; HCHO concentration 0.48 $\mathrm{mol{\cdot}L^{-1}}$; NaOH concentration $1.0\,\mathrm{mol{\cdot}L^{-1}}$; silver catalysts 1.0 mg.

Finally, the catalytic behaviors of the silver nanoproducts with various shapes were explored for HCHO liberating hydrogen gas as a probe. The comparison in the catalytic activity for the silver nanocubes, nanowires, nanorods, and nanospheres was shown in Figure 3. It can be seen that the catalytic activities were greatly dependent on the structural and morphology of colloidal silver catalysts, indicating that this hydrogen generation reaction over silver nanocatalyst is a structure-sensitive reaction. Among these silver nanocrystals, the silver nanocubes showed higher activity than that of other shaped silver nanoparticles. During 32 min, the average hydrogen generation rate was calculated to be 3571, 2988, 2534, and 2199 $\mathrm{mL\,min^{-1}\,g^{-1}}$ on nanocubes, versatile nanorods, sphere, and nanowires, respectively. The catalytic mechanism of hydrogen generation reaction by these colloidal silver nanocrystals with different shape is still under investigation.

Financial supports from the National Basic Research Program of China (nos. 2003CB214500 and 2007CB613305) are greatly acknowledged.

References and Notes

1 A. Miyazaki, T. Asakawa, Y. Nakano, I. Balint, *Chem. Commun.* **2005**, 3730.

2 Y.-Y. Yu, S.-S. Chang, C.-L. Lee, C. R. C. Wang, *J. Phys. Chem. B* **1997**, *101*, 6661.

3 V. M. Cepak, C. R. Martin, *J. Phys. Chem. B* **1998**, *102*, 9985.

4 M. Tsuji, M. Hashimoto, Y. Nishizawa, M. Kubokawa, T. Tsuji, *Chem.—Eur. J.* **2005**, *11*, 440.

5 Y. Sun, B. Gates, B. Mayers, Y. Xia, *Nano Lett.* **2002**, *2*, 165.

6 Y. Bi, G. Lu, *Chem. Mater.* **2008**, *20*, 1224.

7 D. Geng, G. Lu, *J. Phys. Chem. C* **2007**, *111*, 11897.

8 J.-H. Lee, K. Kamada, N. Enomoto, J. Hojo, *Chem. Lett.* **2007**, *36*, 392.

9 B. Wiley, Y. Sun, B. Mayers, Y. Xia, *Chem.—Eur. J.* **2005**, *11*, 454.

10 C. J. Halkides, C. T. Farrar, D. J. Singel, *J. Magen. Reson.* **1998**, *134*, 142.

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