

## Room Temperature, High-Yield Synthesis of Multiple Shapes of Gold Nanoparticles in Aqueous Solution

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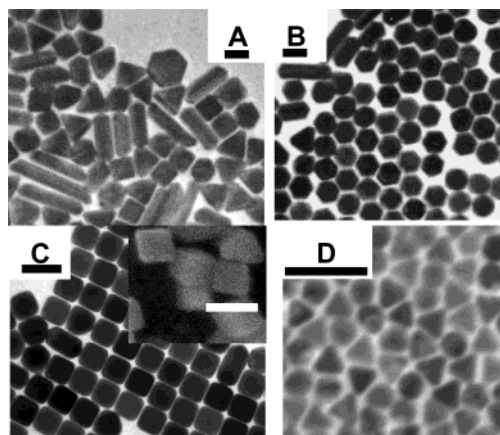
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We describe here that fine control of nanoparticle shape can be achieved by systematic variation of experimental parameters in the seeded growth procedure that we developed to form Au nanorods. This solution-based chemical route produces a number of structural architectures, from rod-, rectangle-, hexagon-, cube-, triangle-, and starlike outlines to branched Au particles in high yield at room temperature in the presence of a single surfactant in aqueous solution.

Bulk solution synthetic methods often produce nanocrystals of multiple sizes and shapes, and hence there is relatively low yield of the desired size and shape.<sup>1</sup> Although colloid chemists have achieved excellent control over particle size for several metallic and semiconductor systems,<sup>2</sup> there has been limited success in gaining control over the shape of the nanocrystals. Controlling size, shape, and structural architecture of the nanocrystals requires manipulation of the kinetic and thermodynamic parameters of the systems via utilization of various additives, light and thermal energies, and their various combinations.<sup>3</sup> We had produced various aspect ratio Ag and Au nanorods, Ag nanowires, and cubic Cu<sub>2</sub>O particles in aqueous solution.<sup>4</sup> On the basis of electron diffraction analysis and high-resolution transmission electron microscopy studies, we proposed a mechanism for the evolution of cylindrical rod shapes in aqueous solution by the seeded growth method.<sup>5</sup> Alivisatos et al., Peng et al., and Cheon et al. utilized high-temperature solution methods to obtain a score of interesting shapes for semiconductor systems.<sup>6</sup> Au particles with hexagonal (icosahedral) and pentagonal (decahedral) profiles have been synthesized by vapor deposition methods.<sup>7</sup> Recently, Chen et al. and Hao et al. reported the synthesis of a mixture of branched gold Au nanocrystals by using two different colloid chemical synthetic protocols.<sup>8</sup>

Our experimental methods involve the preparation of Au seed particles and the subsequent addition of an appropriate quantity of the Au seed solution to the aqueous growth solutions containing desired quantities of cetyltrimethylammonium bromide (CTAB), HAuCl<sub>4</sub>, ascorbic acid (AA), and in some cases a small quantity of AgNO<sub>3</sub> (see Supporting Information (SI)).

The morphology and dimension of the Au nanoparticles depend on the concentrations of the seed particles and CTAB, in addition to the reactants (Au<sup>3+</sup> and AA). All of the above factors were found to be interdependent, thus giving rise to interesting combinations for various shapes (SI, Table 1). For example, at  $1.6 \times 10^{-2}$  M CTAB and  $2.0 \times 10^{-4}$  M Au<sup>3+</sup> ions, nanorods, and other particles with triangular and square outlines were formed, for an AA concentration 1.6 times the Au<sup>3+</sup> ion concentration (Figure 1A). On increasing the AA concentration, rod length and yield decreased, and particles with hexagonal shapes appeared (Figure 1B). Upon a further increase in AA, cube-shaped particles were formed (Figure 1C). Simultaneous adjustment of all four reactant concentrations can produce monodisperse Au nanoparticles with hexagonal and cubic profiles in very high yield (~90%) at room temperature in aqueous solution. Figure 1D shows that smaller particles with

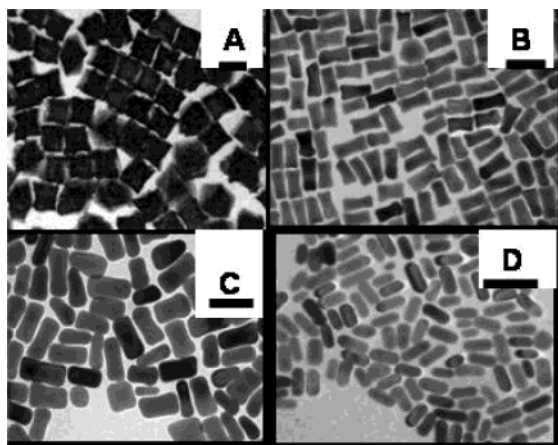


**Figure 1.** TEM (inset SEM) images of Au nanoparticles synthesized under different conditions. [AA] increases from A to C; and seed concentration increases from C to D. Scale bar = 100 nm. See also SI, Table 1.

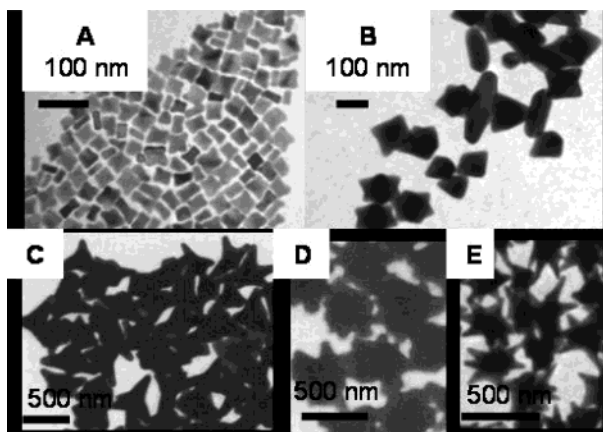
triangular outlines were the major product instead of cubic ones, when the seed concentration was raised, keeping other parameters the same as for the cubic shapes.

The formation of various shapes is likely the outcome of the interplay between the faceting tendency of the stabilizing agent and the growth kinetics (rate of supply of Au<sup>0</sup> to the crystallographic planes).<sup>3a,7,9</sup> Detailed structural and morphological analyses are required to clearly understand these phenomena. For example, both fcc cubooctahedral and icosahedral particles may show hexagonal profiles under TEM. It is believed that, as in the case of Pt<sup>0</sup>-polymer systems reported by El-Sayed et al., the shape of the fine Au seeds produced in the presence of CTAB is faceted with the most stable {111} faces solvent-accessible.<sup>9</sup> CTAB molecules appear to bind more strongly to the {100} than the {111} faces.<sup>5</sup> Thus, lower CTAB and higher AA concentration conditions favor the faster formation and deposition of Au<sup>0</sup> onto the {111} faces, leading to their disappearance and the formation of {100} faces, thereby producing cubic shapes. Under similar (or slightly higher) CTAB concentrations and slightly lower AA concentration conditions, one could expect truncated octahedra with both {100} and {111} faces. The formation of truncated fcc shapes has also been previously observed in the presence of passivating agents for gold nanocrystals.<sup>7a</sup>

A good yield of cube-shaped particles could be obtained even at low [AA] conditions, such as for a [AA] =  $1.6 \times [\text{Au}^{3+}]$ , if a small quantity of AgNO<sub>3</sub> were added to the system (Figure 2A). These particles appeared to have rough surfaces. The edge length of these particles was function of both [Au<sup>3+</sup>] and [seed]. However, noncubic shapes form especially upon decreasing or increasing the concentrations of Au<sup>3+</sup> ions. If CTAB concentration is increased from  $1.6 \times 10^{-2}$  to  $9.5 \times 10^{-2}$  M, a very high yield (~97%) of gold particles with rectangular outline to cylindrical rod-shapes are formed, depending on the concentration ratio of seed particles to



**Figure 2.** TEM images showing cubic to rod-shaped gold particles produced with low AA concentrations in the presence of a small quantity of silver nitrate. [CTAB] was increased from  $1.6 \times 10^{-2}$  M (A), to  $9.5 \times 10^{-2}$  M (B,C,D).  $[\text{Au}^{3+}]$  decreased from (B) to (C), whereas seed concentration increased from C to D. Scale bar = 100 nm. See also SI, Table 1.



**Figure 3.** TEM images of branched Au nanoparticles, varying in the dimension and number of branches, prepared under various combinations of [seed]/ $[\text{Au}^{3+}]$  ratio, and the concentrations of CTAB and AA. Tetrapods (A), star-shape (B), larger tetra-pods (C), and multi-pods (D and E). See also SI, Table 1.

$\text{Au}^{3+}$  ions (Figure 2B, C and D). Preliminary high-resolution TEM data show that the rectangular blocks are single-crystalline in structure. The role of silver nitrate is not clearly understood (see SI). In electroless metal plating, reduced  $\text{Ag}^+$  ions act as sacrificial seeds for the reduction of  $\text{Au}^{3+}$  ions to form Au tubes/rods.<sup>10</sup> It is believed that this mechanism is not operative in our case, since no particle formation was detected in the absence of seeds in our experimental time scale. El-Sayed et al. have proposed that silver ions could assist in the template elongation by pairing with  $\text{Br}^-$  ions of CTAB.<sup>11</sup>

A lowering of the ratio of concentrations of seed to  $\text{Au}^{3+}$  ions along with an increase in the concentration of AA can result in the formation of branched Au particles, depending on the concentrations of CTAB and silver nitrate (Figure 3). However, silver nitrate was not essential for the branching. The yield of the branched particles

produced was as high as  $\sim 70\%$ . The four arms in larger tetrapods were clearly out of plane. The release of stress/strain effects in the growth of Au nanoparticles had been previously observed to give rise to anomalous shapes.<sup>7</sup> However, it has been reported in the case of semiconductor systems that the formation of branched structures requires first a relatively high supply of branches of various kinds is determined by a balancing act between the concentration buildup and the competition of ligand/stabilizing molecules for the particle surface.<sup>6a,b,e,12</sup> Very recently, Chen et al. also proposed that forced reduction of gold ions by ascorbic acid through the addition of NaOH is key for branching of particles.<sup>8a</sup> Vis-NIR absorption spectra of the samples containing Au nanocrystals of various shapes show clear differences in optical absorption properties (SI, Figure 1).

In conclusion, we used a simple solution-based seed-mediated growth method where one could controllably vary the morphology and dimension of the Au nanocrystals by the manipulation of the synthetic parameters. Moreover, these various shapes were produced in aqueous solution at room temperature and by utilizing only one surfactant, CTAB.

**Supporting Information Available:** Experimental details and absorption spectra for different shapes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) Murphy, C. J. *Science* **2002**, *298*, 2139–2141.
- (2) (a) Schmid, G.; Ed. *Clusters and Colloids: From Theory to Applications*; VCH: New York, 1994. (b) Watzky, M. A.; Finke, R. G. *J. Am. Chem. Soc.* **1997**, *119*, 10382–10400. (c) Jana, N. R.; Peng, X. *J. Am. Chem. Soc.* **2003**, *125*, 14280–14281.
- (3) (a) Ahmadi, T. S.; Wang, Z. L.; Green, T. C.; Henglein, A.; El-Sayed, M. A. *Science* **1996**, *272*, 1924–1925. (b) Pileni, M. P.; Ninham, B. W.; Gulik-Krzywicki, T.; Tanori, J.; Lisiecki, I.; Filankembo, A. *Adv. Mater.* **1999**, *11*, 1358–1362. (c) Li, M.; Schnablegger, H.; Mann, S. *Nature* **1999**, *402*, 393–395. (d) Jin, R.; Cao, Y. C.; Hao, E.; Mettraux, G. S.; Schatz, G. C.; Mirkin, C. A. *Nature* **2003**, *425*, 487–490. (e) Sun, Y.; Xia, Y. *Science* **2002**, *298*, 2176–2179. (f) Sun, Y.; Xia, Y. *Adv. Mater.* **2002**, *14*, 833–837. (g) Sun, Y.; Mayers, B.; Herricks, T.; Xia, Y. *Nano Lett.* **2003**, *3*, 955–960.
- (4) (a) Jana, N. R.; Gearheart, L.; Murphy, C. J. *J. Phys. Chem. B* **2001**, *105*, 4065–4067. (b) Jana, N. R.; Gearheart, L.; Murphy, C. J. *Adv. Mater.* **2001**, *13*, 1389–1393. (c) Jana, N. R.; Gearheart, L.; Murphy, C. J. *Chem. Commun.* **2001**, 617–618. (d) Gao, J.; Bender, C. M.; Murphy, C. J. *Langmuir* **2003**, *19*, 9065–9070. (e) Gou, L.; Murphy, C. J. *Nano Lett.* **2003**, *3*, 231–234.
- (5) Johnson, C. J.; Dujardin, E.; Davis, S. A.; Murphy, C. J.; Mann, S. *J. Mater. Chem.* **2002**, *12*, 1765–1770.
- (6) (a) Peng, X.; Manna, L.; Yang, W. D.; Wickham, J.; Scher, E.; Kadavanich, A.; Alivisatos, A. P. *Nature* **2000**, *404*, 59–61. (b) Manna, L.; Scher, E. C.; Alivisatos, A. P. *J. Am. Chem. Soc.* **2000**, *122*, 12700–12706. (c) Manna, L.; Milliron, D. J.; Meisel, A.; Scher, E. C.; Alivisatos, A. P. *Nat. Mater.* **2003**, *2*, 382–385. (d) Peng, Z. A.; Peng, X. *J. Am. Chem. Soc.* **2002**, *124*, 3343–3353. (e) Peng, X. *Adv. Mater.* **2003**, *15*, 459–463. (f) Lee, S.-M.; Jun, Y.-W.; Cho, S.-N.; Cheon, J. *J. Am. Chem. Soc.* **2002**, *124*, 11244–11245.
- (7) (a) Yacaman, M. J.; Ascencio, J. A.; Liu, H. B.; Gardea-Torresdey, J. J. *Vac. Sci. Technol. B* **2001**, *19*, 1091–1103. (b) Yang, C. Y.; Heinemann, K.; Yacaman, M. J.; Poppa, H. *Thin Solid Films* **1979**, *58*, 163–168. (c) Renou, A.; Gillet, M. *Surf. Sci.* **1981**, *106*, 27–34.
- (8) (a) Chen, S.; Wang, Z. L.; Ballato, J.; Foulger, S. H.; Carroll, D. L. *J. Am. Chem. Soc.* **2003**, *125*, 16186–16187. (b) Hao, E.; Bailey, R. C.; Schatz, G. C.; Hupp, J. T.; Li, S. *Nano Lett.* **2004**, *4*, 327–330.
- (9) Petroski, J. M.; Wang, Z. L.; Green, T. C.; El-Sayed, M. A. *J. Phys. Chem. B* **1998**, *102*, 3316–3320.
- (10) Menon, V. P.; Martin, C. R. *Anal. Chem.* **1995**, *67*, 1920–1928.
- (11) Nikoobakht, B.; El-Sayed, M. A. *Chem. Mater.* **2003**, *15*, 1957–1965.
- (12) Peng, Z. A.; Peng, X. *J. Am. Chem. Soc.* **2001**, *123*, 1389–1395.

JA047846D