

Shape controlled growth of gold nanoparticles by a solution synthesis

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The shape of gold nanoparticles has been successfully tuned among penta-twinned decahedrons, truncated tetrahedrons, cubes, octahedrons, hexagonal thin plates by introducing a small amount of salt into a *N,N*-dimethylformamide (DMF) solution containing poly(vinyl pyrrolidone) (PVP), and changing the temperature or the concentration of the gold precursor.

Anisotropy is one of the most basic properties of crystals. Different crystal surfaces or directions may exhibit different physical and chemical properties. For example, the {111}, {100} and {110} surfaces of a face centered cubic (fcc) metal such as gold have very different surface atom densities, electronic structures and probable chemical reactivities.¹ Therefore, the controllable preparation of nanocrystals with different shapes and exposed surfaces is very important and challenging. In recent years, intensive approaches have been devoted to the systematic control of the crystal shapes of metal nanoparticles.^{1–4} Particular interest has been focused on the noble metals due to the fact that they are technologically important in many fields such as catalysis,^{4,5} optics,⁶ and surface enhanced Raman spectroscopy.^{7,8} The syntheses of nanoparticles of the noble metals with various shapes have been continuously reported by using various synthesis methods.^{1–3,9–11} For gold nanoparticles, a few reports concerned the synthesis of shape-controlled gold nanoparticles with sizes of about 50 nm or less.^{12,13} Very recently, Yang *et al.* reported the preparation of gold platonic nanocrystals with sizes of 100–300 nm.¹⁴ Herein, we report another simple route to realize successful control of the shape of gold nanoparticles with a size of about 150–200 nm. By introducing a small amount of salt into a *N,N*-dimethylformamide (DMF) solution containing poly(vinyl pyrrolidone) (PVP), or changing the temperature, the shape of gold nanoparticles has been tuned among penta-twinned decahedrons, truncated tetrahedrons, cubes, octahedrons, and hexagonal nanosheets.

Gold nanoparticles were synthesized in DMF as both the solvent and the reductant in the presence of PVP as the capping agent, which had been successfully applied for the preparation of silver nanoparticles.^{15–17} Typically, 0.25 g PVP (Alfa Aesar, *M*_w = 40 000) was mixed with 24.5 mL DMF (Shanghai Chemical Co.) in a flask equipped with a condenser and a thermostat and then the mixture was heated in an oil bath to 140 °C and held there for 4 min. Then, 0.5 mL HAuCl₄ (10 mM) aqueous solution was added dropwise to the hot solution over a period of 90 s. The reaction was continued for another 40 min, keeping the temperature at 140 °C. Magnetic stirring was applied throughout the entire synthesis. For the synthesis of nanoparticles

with another shape, 0.2 mL NaOH or NaCl (10 mM to 50 mM, Shanghai Chemical Co.) aqueous solution and 0.5 mL HAuCl₄ (10 mM) aqueous solution were added simultaneously while keeping all other conditions the same. The samples were separated by centrifugation first, then washed with water and ethanol, and separated by centrifugation to remove the DMF and PVP. Finally, the products were dispersed in ethanol to obtain suspensions for further characterizations.

Fig. 1a and 1b show the typical scanning electron microscopy (SEM, LEO-1530) image and the corresponding X-ray diffraction (XRD, Rigaku Dmax/rC) pattern of the product prepared by reducing 0.5 mL HAuCl₄ (10 mM) aqueous solution, respectively. The XRD pattern indicates that the nanoparticles are the fcc gold (JCPDS, File No. 4-0784). There are no diffraction peaks due to possible impurities. From the SEM image, it is clearly seen that the as-prepared product mainly consists of decahedral nanoparticles with a uniform size of about 180 nm. The decahedron is one of the basic multiply twinned structures, which consists of five tetrahedral crystallites with bare {111} surfaces.^{18–20} Fig. 1c and 1d show the transmission electron microscopy (TEM, FEI Tecnai F30) image of an individual decahedral nanoparticle and its corresponding selected area electron diffraction (SAED) pattern with the electron beam directed along the five-fold axis of the decahedron. The complex diffraction pattern can be well interpreted by five twinned subunits with their common <110> axis along a five-fold axis.²⁰ A high resolution transmission electron microscopy (HRTEM, FEI Tecnai F30) image taken at the top edge of the decahedral nanoparticles confirms that there is a twinned boundary, as shown

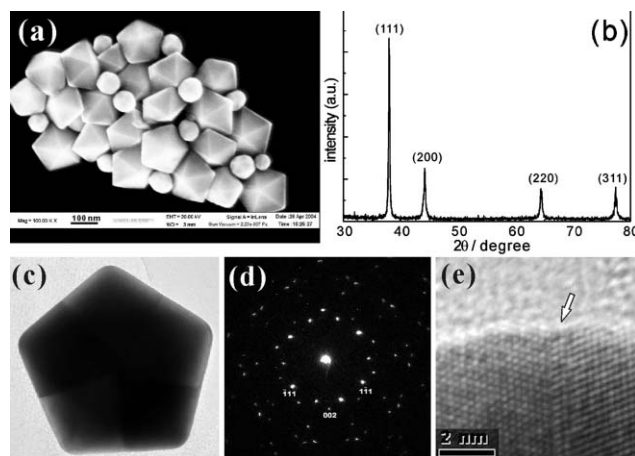


Fig. 1 (a) SEM image of decahedral gold nanoparticles; (b) XRD pattern (with CuK α radiation) of as-synthesized gold nanostructure; (c), (d) TEM image and the corresponding SAED pattern of an individual decahedral gold nanoparticle; (e) HRTEM image of the decahedral nanoparticles at the top corner of the nanoparticle shown in (c).

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in Fig. 1e. As a result, the decahedral nanoparticles are five-fold twinned nanoparticles.

Multi-twinned particles (MTPs) including five-fold twinned decahedral nanoparticles have been found in many fcc metals.^{18–20} Five-fold twinned decahedral nanoparticles are composed of five equal tetrahedral subunits bound together by $\{111\}$ twinned planes. All the ten bare facets of the decahedral particle are $\{111\}$ planes, having the lowest surface free energy for an fcc metal. In terms of energy minimization, it is favorable to form decahedral MTPs thermodynamically in comparison with single crystal particles when the surface free energy of $\{111\}$ is low. By varying the surface energies of various crystal faces, it is then possible to tune the shape of the particles, from MTPs to single crystals. For example, lowering the surface energy of the $\{100\}$ surface to some extent, the single crystal will become thermodynamically stable according to analysis of the energies of MTPs relative to single crystals.¹⁸ It has been well demonstrated that the adsorption of chemical species on the surface has a very dramatic effect on the surface energies.²¹ For the small particles, the ratio of surface free energy to the total energy becomes very important, and may be structure determining.²² In the present case, the gold nanoparticles were prepared in solution and with the presence of the so-called capping agent PVP. Inevitably, adsorption of PVP and the solvent molecules on the reduced gold particles takes place. Although there is no direct evidence for selective surfactant adsorption abilities on the different crystal faces, we can assume that the surface free energies of $\{111\}$ surfaces in the presence of the given concentration of PVP and the solvent are the lowest, the same as that in vacuum, resulting in the formation of $\{111\}$ facets and the decahedral MTPs. To control the shape of the particles, we can tune the surface free energies of different facets by adsorption of additives on the surfaces. Some simple ionic salts have been found to be effective in varying the surface energy of gold nanocrystals in our experiment and elsewhere.¹⁴ Fig. 2a shows the typical SEM images of gold nanoparticles prepared by introducing a small amount of NaOH (0.2 mL, 10 mM) into the solution. It is clear

that the shape of the nanoparticles has dramatically changed. Many truncated cubes appear among the particles, which are single crystals as checked by electron diffraction (ED) (inset of Fig. 2a). The hexagonal surfaces are $\{111\}$, while the square ones are $\{100\}$. With an increase in the amount of NaOH, the percentage of single crystal particles increases. Fig. 2b shows the SEM image of the gold nanoparticles prepared by adding 0.2 mL NaOH (20 mM) into the solution. More than 90% of the nanoparticles are cubes with an average size of 150 nm, which are single crystals with $\{100\}$ surfaces, through the SAED analysis in the inset of Fig. 2b. Besides the cube nanoparticles, it is found that there are a few nanoparticles with a truncated decahedral shape. By introducing a small amount of NaCl (0.2 mL, 10 mM) instead of NaOH, similar cube nanoparticles can be obtained as shown in Fig. 2c.

The presence of NaOH or NaCl in the solution might have influenced strongly the surface energy of various gold crystal planes because of the competitive adsorption between the ions of the added salt and the original adsorbates, which is of influence on the growth rate of various facets during the crystal growth. It is reasonable to suppose that the $\{100\}$ surface becomes the most stable surface in the presence of NaOH or NaCl and turns into the face with the lowest growth rate, because the $\{100\}$ facets appear in the resulting gold nanoparticles, and the $\{100\}$ facets become larger with an increase in the amount of the additives. More evidence for the change of the surface energy of various crystal faces comes from the very few coexisting MTPs. Only a transitional decahedral shape can be found instead of a decahedron. Such a phenomenon can be attributed to a kinetic occurrence, leading to different growth rates for the different crystal faces. However, the change of the surface energies by the adsorption of foreign species may be the origin of this kinetic problem. At the present time, we do not have direct evidence for a quantitative value of the decrease of the $\{100\}$ surface energy. However, the transformation from decahedral MTPs to the single crystal nanoparticles can be well explained.

The adsorption abilities of chemical species vary with the temperature, and therefore, the shape can also be controlled by the reaction temperature. Fig. 2d shows an example of the gold nanoparticles prepared in the presence of 0.2 mL NaOH (20 mM) at the reaction temperature of 147 °C. The SEM observations have shown that the shapes of the nanoparticles change to an octahedron, and the size of the particles is about 150 nm. The octahedron particle is one of the basic shapes of a single crystal, where the eight bare facets are all $\{111\}$ surfaces. The ED confirms the crystallinity of the octahedron particles as shown in the inset of Fig. 2d. It should be pointed out that the change of the reaction temperature varies not only the surface energies, but also kinetic factors such as the addition rate of reduced gold atoms.

Finally, we found that the concentration of the aqueous solution also affected the morphology of the products. The hexagonal nanosheets appeared with the increase of the HAuCl_4 concentration. One particular example shows that the successful preparation of gold hexagonal nanosheets is realized by adding 0.5 mL of 45 mM HAuCl_4 aqueous solution to the reaction mixture while keeping the concentration of PVP constant, as shown in Fig. 3a. Large quantity nanocrystals are hexagonal nanosheets with an average width and thickness of 900 nm and 60 nm, respectively (see Fig. 3b). The size of a nanosheet is defined here as the distance

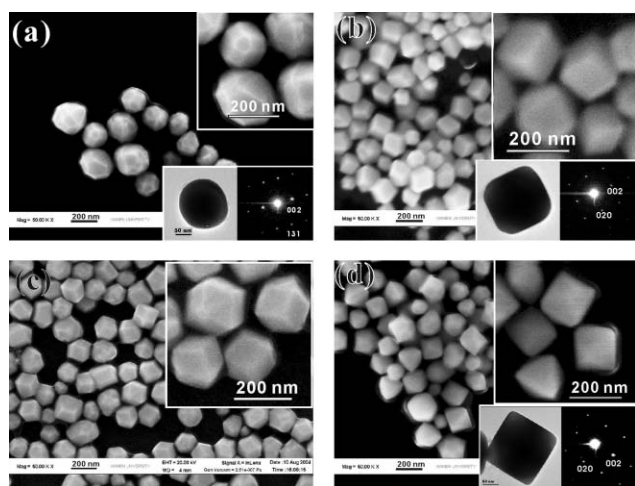


Fig. 2 SEM images of the as-prepared truncated tetrahedral (a), cube (b), cubic (c), octahedral (d) gold nanoparticles. Insets in the figures show the enlarged SEM image (top-right), the TEM image of an individual typical nanoparticle (left) and its corresponding SAED pattern (right). The SAED patterns can be indexed as diffractions from the $[310]$ zone axis for (a), $[100]$ zone axis for (b) and $[100]$ zone axis for (d), respectively.

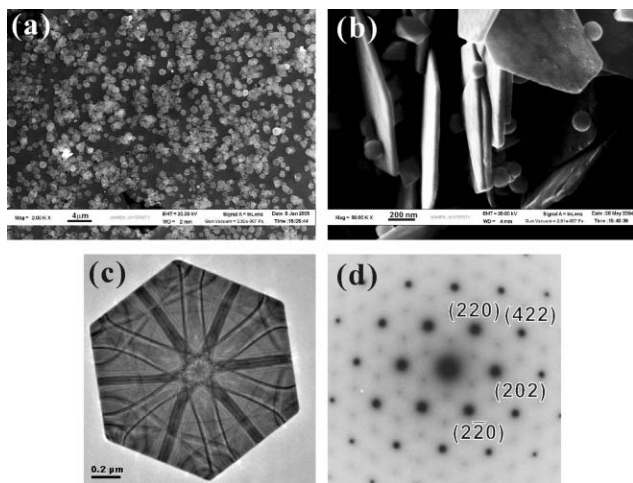


Fig. 3 SEM images of the as-prepared hexagonal nanosheets (a) and (b). TEM image of an individual typical nanosheet (c) and its corresponding SAED pattern (d).

from one edge of the hexagonal nanosheet to the opposite side. Fig. 3c and 3d show the TEM image of a single Au nanosheet and the related SAED pattern obtained by directing the electron beam onto a nanosheet. The diffraction spots can be indexed as the diffractions of a [111] zone axis, indicating that the surface of the nanosheet is a (111) lattice plane. Some additional weak diffraction spots at 1/3 and 2/3 of $\langle 422 \rangle$ diffraction were observed, which can be explained as diffractions from a flat thin plate.²³ Furthermore, the band-like patterns shown on the surface of the nanosheet in Fig. 3c are due to deformation or bending of the nanosheet during the irradiation of the electron beam, which is most frequently observed in metal foils.²⁴ The growth of the thin plate can be attributed to the lowest growth rate along (111) facets, which is similar to the case of the growth of decahedral particles. However, in the nucleation stage it could be different. Therefore, the growth of the thin plate with (111) as bare surface is also due to the lowest surface free energy of (111) surfaces in the corresponding experimental conditions, being consistent with the above proposed mechanism.

It is known that the optical properties of gold nanoparticles depend on the size and the shape of the particles. The UV-Vis spectra of the as-prepared products show such shape dependent UV-Vis spectra as shown in Fig. 4. The spectra show adsorption peaks due to the surface plasmon resonance at 583 nm for decahedral particles, 588 nm for nanocube, and 550 nm, 695 nm for nanosheets, respectively. The spectra are consistent with previous experimental and theoretical results.^{13,14,25,26} The two absorption peaks for the nanosheets correspond to the surface plasmon resonance in the direction normal to (550 nm) and parallel to (695 nm) the nanosheet surface, respectively. The sharp absorption peak for the nanocubes indicates that they are fairly uniform in shape and size.

In summary, we have successfully controlled the shape of gold nanoparticles by a simple wet chemical synthesis. Gold nanoparticles with decahedral, truncated cube, cube, octahedral shapes and hexagonal thin plates have been synthesized. A preliminary

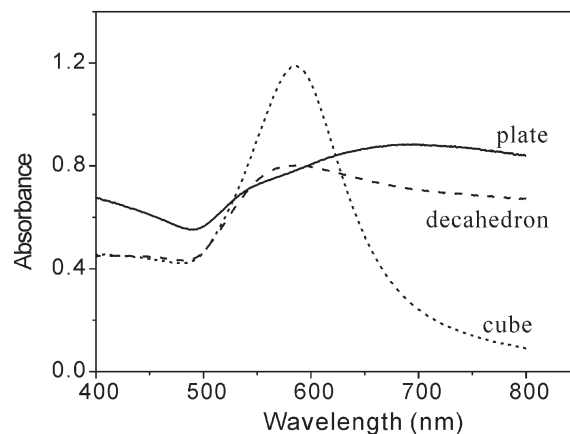


Fig. 4 UV-Vis spectra for the gold nanocrystals with different shapes: decahedron, cube, thin plate.

mechanism based on the change of surface free energy has been proposed to account for the transformation of nanoparticles among various shapes, which can be extended to control the nanoparticle shape of other fcc metals.

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