

Poly(vinyl pyrrolidone)-capped five-fold twinned gold particles with sizes from nanometres to micrometres

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Abstract

Poly(vinyl pyrrolidone)-capped multiple twinned gold (Au) particles with decahedral shape have been synthesized by a simple and convenient solvothermal wet chemical method. In the process, hydrogen tetrachloroauric acid (HAuCl₄·3H₂O) was reduced by ethylene glycol (EG) to form the multiple twinned Au nanocrystals in the presence of poly(vinyl pyrrolidone) (PVP) molecules at 200 °C under the extra condition of autogenous pressure. The decahedral nanoparticles take up about 10% of the total amount and have the usual size distribution from several tens to hundreds of nanometres. Some larger microsized five-twinned Au particles with perfect decahedral shape have also been observed in the final product. Furthermore, x-ray photoelectron spectroscopy (XPS) measurements verified that PVP molecules are adsorbed on the surface of the Au particles. Based on the experimental results, a growth mechanism has been suggested to elucidate the formation of the small decahedral Au nanoparticles as well as their evolution into perfect large decahedral Au particles with the size of several micrometres.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The five-fold twinning structure, widely existing in natural biological [1] and mineral substances [2] such as viruses, proteins, halobios, and natural diamond, has attracted considerable attention not only in crystal growth and crystallography research but also in the field of material design, thin film growth, and cluster physics. In biology, the natural starfish with its elegant pentagonal shape is a typical example of the special structure [3], while in mineralography and material science, natural diamond and noble metals with five-twinned structure have been found from as early as the 19th

century [4]. The synthesis of artificial materials, e.g., thin films and particles, with five-twinned structure originated in the middle of the 20th century. Segall [5] was the first to report pentagonal Cu grains with pyramidal shape in cold-rolled Cu by thermal etching. Later, the five-twinned structure was found in various metal materials such as Au, [6] Ag [7], Ni [8], Pt [9], Pd [10], Ru [11], Rh [12] and their alloys [13]. In recent years, the synthesis of noble metal nanoparticles has attracted intensive investigation due to their unique optical, electronic, thermal, and catalytic properties. The special shape of the metal nanoparticles plays a very important role in tailoring the properties. Nanoparticles with various shapes (for example, cubes [14], prisms [15], plates [16], rods [17], and wires [18]) have been prepared by employing different

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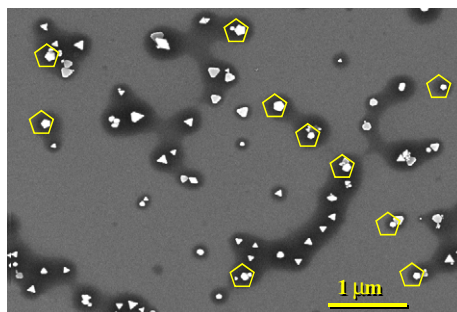


Figure 1. A typical SEM image of obtained Au nanoparticles, in which the particles with decahedral shape have been circled using pentagonal labels.

methodologies. Five-twinned nanoparticles with decahedral shape may exhibit physical and chemical properties differing from those of untwinned nanoparticles due to their intrinsic structural characteristics concerning surface energy and the lattice symmetry. Thus, it appears very interesting to find a new approach to synthesize noble metal nanoparticles with five-fold twinned structure.

In this paper, we explore a new strategy to prepare colloidal five-twinned Au nanoparticles by a simple and convenient solvothermal wet chemical method. In the process, hydrogen tetrachloroauric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) was reduced by ethylene glycol (EG) to produce the five-twinned Au nanocrystals with the shape of a decahedron in the presence of poly(vinyl pyrrolidone) (PVP) molecules at 200°C under the extra condition of autogenous pressure. Transmission electron microscopy (TEM) and field emission scanning electron microscopy (FE-SEM) have been used to observe the topographies of the thus-obtained product. Surprisingly, large five-fold twinned Au particles with perfect decahedral shape have been found in final product, which have not been observed in previous studies using the wet chemical method. To shed light on the mechanism of formation and growth of the five-twinned Au nanoparticles, FE-SEM images of the Au particles with various possible topographies of the intermediate process have been collected. In addition, x-ray photoelectron spectroscopy (XPS) measurements have also been conducted to show the existence of the PVP molecules on the surface of the Au particles, further elucidating the role of the stabilizer in the formation and growth of the five-fold twinned Au nanoparticles.

2. Experimental details

All chemical reagents were obtained from Acros and used as received. The synthesis process can be concisely described as follows. 5 ml $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (0.1 M) and 5 ml PVP (K30, $M_w = 40000$) (0.3 M) EG solutions were first added to 10 ml EG solvent in a Teflon vessel with 50 ml capacity. The container was then sealed in a stainless-steel bomb. The whole system was heated and maintained in an oven at 200°C under autogenous pressure for 2 h. After the reaction finished, the container was cooled under room temperature conditions naturally. Finally, an EG colloidal solution of Au particles with jacinth colour was obtained.

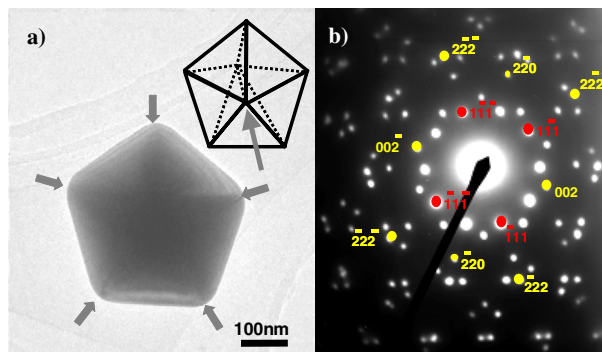


Figure 2. A typical TEM image of a decahedral Au nanoparticle (a), in which arrows demonstrate twinned boundaries among subcrystals, and the selected area electron diffraction (SAED) image and indexed partial diffraction pattern for the Au nanoparticle (b). The inset in (a) schematically illustrates how the electron beam travels along the direction parallel to the five-fold axis of the Au nanoparticle.

In addition, some precipitates could also be found in the final product. In order to separate the Au particles from the EG solvent and residual PVP, the Au particle colloidal solution was first filtered to remove the precipitates, and then poured into 100 ml acetone solvent to naturally precipitate for 72 h. Afterwards, the upper liquid was removed to leave the precipitates. The thus-obtained precipitates were repeatedly washed with anhydrous ethanol again to ensure the complete removal of residual EG solvent and PVP, and subsequently dried in a vacuum for further morphology and spectroscopic characterizations. The morphology and structure of the product were characterized by scanning electron microscopy (SEM, Philips XL30 S-FEG) and transmission electron microscopy (TEM, JEOL 2010 with an accelerating voltage of 200 kV). X-ray photoelectron spectroscopy (XPS) measurements were performed on a VGESCALAB MKII x-ray photoelectron spectrometer with a $\text{Mg K}\alpha$ (1253.6 eV) excitation source.

3. Results and discussion

The solid product obtained can be easily dissolved in EG or ethanol. On depositing and drying a drop of EG solution of the product on an n-Si(100) substrate, we found many small decahedral Au nanoparticles besides those with other shapes such as triangles and hexagons, as shown in the SEM image in figure 1. The decahedral Au nanoparticles usually take up about 10% of the total amount and have a size distribution from tens to hundreds of nanometres. It appears that the decahedral Au nanoparticles are not a single product, but coexist or compete with the Au nanoparticles with single crystalline and other twinning structures. The occurrence of this phenomenon also indicates that both the nucleation and growth of the Au nanoparticles are considerably complicated in the reaction system under the given conditions. To further elucidate the structure of the decahedral Au nanoparticles in detail, TEM has been used to image the small Au nanoparticles. Figure 2(a) demonstrates a typical TEM image of an obtained decahedral Au nanoparticle. A nearly perfect pentagonal shape with each angle of about 108° can be clearly seen. Selected area electron diffraction (SAED) was performed by focusing the electron

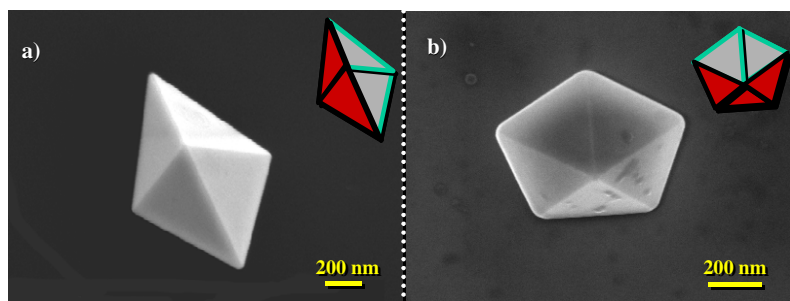


Figure 3. SEM images of double (a) and triple (b) twins. The insets in (a) and (b) illustrate possible geometries.

beam along the direction parallel to the five-fold axis of the Au nanoparticle lying on carbon-coated TEM Cu grid. Figure 2(b) shows an SAED pattern obtained from the Au nanoparticle; it shows a complex five-fold symmetry instead of the single-crystalline pattern for face-centred-cubic (FCC) Au. Further analysis of the diffraction pattern reveals that it is actually formed by the overlap of five sets of individual diffraction patterns. Each set of diffraction spots corresponds to those of the [110] zone axis direction, as partly labelled in figure 2(b). Others can be theoretically created by sequentially rotating the set four times, by 72° each time. The complex SAED pattern distinctly implies that the decahedral Au nanoparticles consist of five adjoining tetrahedral subcrystals bounded by {111} planes along a common $\langle 110 \rangle$ edge. However, it is well known that a complete space-filled structure, i.e. a perfect decahedron, cannot be achieved only by compact splicing of five tetrahedral subunits of the regular FCC structure. There always exists an intrinsic gap of 7.4° in order to achieve a 360° cycle because the theoretical geometrical angle is about 70.52° between two (111) planes in a tetrahedral subunit. In fact, when the decahedral crystals are very small, e.g. several nanometres, extended lattice defects may favour filling the gaps. Thus, the twinned crystals can still exhibit a diffraction pattern with five-fold symmetry. It seems from figures 2(a) and (b) that the 7.4° gap has been averaged into five gaps between adjacent tetrahedrons; however, further observation finds that some peripheral diffraction spots show a little elongation and exhibit asymmetry in the pattern, showing an inhomogeneous relaxation of elastic strains. This also means that the intrinsic angular gap of 7.4° is not distributed evenly into the five gaps. Scientifically speaking, the five-fold axis in the decahedral Au nanoparticle can be only regarded as that of pseudo-five-fold symmetry.

Before understanding how the 7.4° angular gap distributes into the five gaps among the tetrahedral subunits, an essential and important issue should be addressed, that is, the origin of the small five-twinned Au nanoparticle. The formation mechanism of the five-twinned structure is highly disputed due to material diversity and the differences in the preparation processes. In principle, two possible mechanisms, i.e., nucleation-based and growth-mediated, have been suggested to explain the formation of the five-twinned structures. The former [19] assumes that the small nanocrystal initially nucleates by a non-crystallographic atom packing process, and afterwards gradually transforms to a five-twinned structure

by layer-by-layer growth. In this case, the angular gap can be uniformly accommodated into the five-twinned particle. The latter, growth-mediated mechanism, i.e., the tetrahedral stacking mechanism [20], assumes that small five-twinned nanoparticles can be constructed by cyclic twinning operations induced by mis-stacking of atoms or mismatch of lattices during particle growth. At the initial growth stage, twinning could occur on pre-existing tetrahedra produced in the nucleation process. The formation of secondary and tertiary twins is a key step in favour of the five-twinned particles. In this case, the 7.4° angular gap is very difficult to be equally assigned among the five twinning boundaries. In our previous study [21] on five-twinned Ag nanoparticles, various secondary and tertiary twinned Ag nanoparticles were observed. In the present case, twins and triple Au twins have also been found in the final product, as shown in figures 3(a) and (b). Thus, we think that the growth-mediated mechanism may dominate the formation of the small five-twinned Au nanoparticles in this reaction system under the given conditions. It is worth noting that we cannot exclude the case of the five-twinned Au nanoparticle being formed directly by joining five equal-sized tetrahedra together, although the possibility is considerably low.

Besides the smaller five-twinned Au nanoparticles, larger decahedral Au particles with a size of several micrometres have also been observed in the obtained precipitates. The formation of micrometre-sized noble metal particles with five-fold twinned structure is a very important research subject in material science. Understanding the evolution mechanism of the five-twinned Au particle from nanometre-scale to micrometre-scale may help one to controllably design a particle material with a special structure. Most of the previous experimental and theoretical investigations on five-twinned particles have been focused on metallic clusters formed by atom arranging and packing from a few up to several hundreds of atoms in a rare gas environment. The nucleation-based mechanism has been suggested to explain the formation of five-twinned metallic nanoparticles, in which a non-crystallographic packing of atoms first occur and then is complemented by layer-by-layer growth to develop the five-twinned structure. It has been calculated [22] that the stable or quasi-stable size limit of the five-twinned Ag nanoparticles is about 300 nm from the point of view of energy balance considerations involving elastic strain, surface and twin boundary energy, etc. However, five-twinned

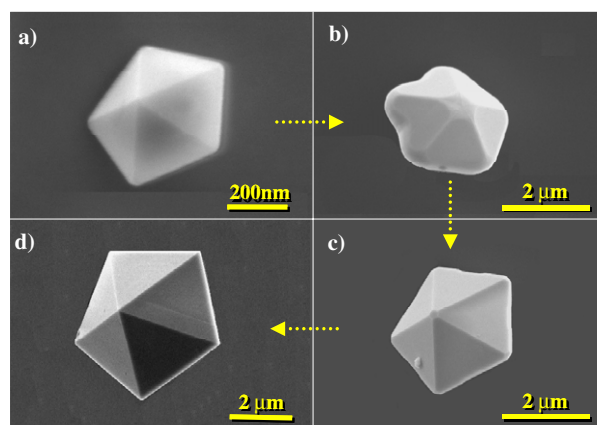


Figure 4. SEM images of decahedral Au particles with various sizes and shapes. The direction arrowed from (a) to (d) shows the possible growth process of a decahedral Au particle from nanometre to micrometre.

structures found in practice always exceed the size limit on the basis of thermodynamic considerations. One reason is that crystal growth usually happens far from the thermodynamic equilibrium state. However, the shape evolution may be determined not only by thermodynamics factors such as surface energy but also by those of dynamics such as the difference of growth rates among various crystal planes [23]. Figure 4 provides a series of scanning electron microscope (SEM) images of the five-twinned Au particles. Au particles with perfect or star-like decahedral shape and different sizes were found in the final product. The emergence of the Au particles with various shapes and sizes is characterized by high dynamics. Figure 4(a) shows a typical smaller perfect five-twinned Au nanoparticle. Figures 4(b) and (c) demonstrate larger star-like decahedral Au particles with micrometre sizes. It can be seen in figure 4(b) that reentrant edges and a new face perpendicular to the pentagonal axis occur on a star-like decahedral Au particle, while the reentrant edges and pentagonal top are gradually disappearing on another star-like decahedral Au particle (see figure 4(c)). The different appearances of the two kinds of Au particle may represent possible intermediate growing stages when smaller decahedral Au particles evolve toward perfect bigger ones with micrometre size. The observed shape evolution implies that growth along twin boundaries may initiate the growth process of small decahedral Au nanoparticles. It is obvious

that the growth rate along twin boundaries is much faster than those along the directions of other crystal facets. An apparent perfect decahedral Au particle with larger micrometre size (see figure 4(d)) can be finally formed from the source of smaller five-twinned Au nanoparticle via the possible intermediate states of the star-like particles with reentrant edges.

Furthermore, PVP molecules may play a very important role in the formation and evolution process of the five-twinned Au nanoparticles. Tsuji and co-workers [24] have investigated the effect of PVP on the size and morphology of an obtained Au product in EG solution by a microwave-assisted polyol method. They found that only large spherical Au particles were produced in the reaction solution without adding PVP. When PVP existed in the EG solution, large triangular or hexagonal Au nanoplates as well as nanorods or nanowires were created. Their sizes could be systematically adjusted by changing the ratio of $\text{HAuCl}_4/\text{PVP}$. The authors think that PVP can act as a kinetic controller of the growth rates along various crystalline facet directions by adsorption and desorption processes. However, it is still unclear if PVP molecules can adsorb on the surfaces of the Au products and how they interact with the Au surfaces if they are adsorbing.

To resolve these doubts, we first dispersed the Au precipitate prepared by our polyol method in ethanol, and then deposited a droplet of the colloidal solution on a n-Si(100) substrate for FE-SEM observation. Figure 5 shows SEM images of the small Au nanoparticles with various shapes. A layer of thin film can be clearly seen to homogeneously cover the surfaces of the Au nanoparticles with various shapes. Obviously, the transparent shell cannot be washed off by using the solvent, although EG and PVP are easily soluble in ethanol. It is possible that a layer of PVP is adsorbing on the surfaces of bare Au nanoparticles. To elucidate the components of the film layer, x-ray photoelectron spectroscopy (XPS) technique was employed. Before the experiment, the obtained Au precipitates were again repeatedly washed with ethanol to guarantee complete remove of EG and residual PVP, as described in the experimental section. As is known, previous several XPS studies [25–28] on PVP-capped Ag nanostructures have indicated that the oxygen and nitrogen atoms of the pyrrolidone unit in PVP molecule may interact with the Ag surfaces to favour the adsorption of PVP. It has been proposed that the difference of interaction extent between PVP and various crystalline facets leads to anisotropic growth of Ag nuclei and further to the formation of various shaped Ag nanostructures [29]. Figure 6(a) shows a typical

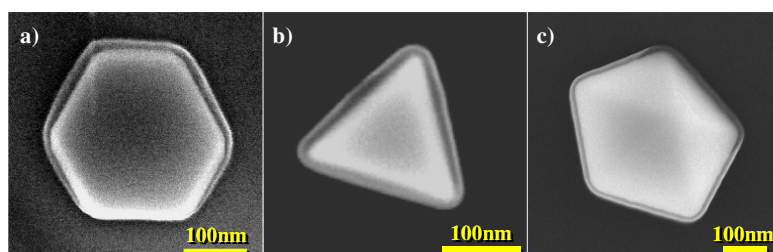
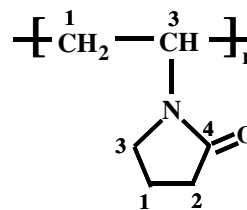


Figure 5. SEM images of smaller Au nanoparticles with various shapes: (a) pentagon, (b) hexagon, (c) triangle; a layer of transparent thin film can be seen to homogeneously cover the surfaces of the Au nanoparticles.

XPS spectrum of the Au particles. The existence of carbon, nitrogen and oxygen signals verifies the presence of PVP molecules on the surface of the Au particles. Au binding energy peaks with various core levels have also been observed. Figures 6(b)–(e) demonstrate high-resolution XPS regions of various elements for the Au particles. For clarity, the XPS C(1s) spectra have been fitted by multiple Gaussians. The C(1s) spectra could be decomposed into four peaks by this curve fitting. Peak positions at 285.0, 285.4, 286.2 and 287.9 eV have been obtained, which can be attributed to the carbon atoms numbered from 1 to 4 for the PVP molecule (see scheme 1), respectively, depending on the different chemical environments. In the O(1s) region, the peak at 531.7 eV can be attributed to carboxyl (C=O) oxygen. Compared with pure PVP (531.3 eV), the O(1s) peak from carboxyl (C=O) oxygen shifts 0.4 eV to higher binding energy, indicating that the electron density decreases around the carboxyl (C=O) oxygen due to interaction between the PVP molecule and the Au particle core. The N(1s) peak (399.8 eV) seems not to be influenced by the Au particle core. The XPS spectra of the Au particles in the Au region are shown in figure 6(e). The two peaks at 83.6 and 87.5 eV result from Au 4f 7/2 and Au 4f 5/2, respectively. It appears that the peaks shift toward low binding energy relative to bulk Au atoms (84.0 eV for Au 4f 7/2, 87.7 eV for Au 4f 5/2). In general, the Au 4f core-level energy is very sensitive to the chemical environment around the Au core, and particularly to the electron-donating ability of the polymeric ligand and to the strength of the interaction between the Au and the polymeric ligand. The shift shows that electrons are inclined to transfer from the carboxyl (C=O) oxygen of PVP to the Au interface, further implying a stronger interaction between them, which may affect the aggregation of reduced Au atoms, arrangement of Au atoms on the interfaces of the Au particles, and further induce the formation of twinning planes, as well as anisotropic growth of created small Au clusters.



Scheme 1. Configuration of PVP repeated unit with carbon numbering.

4. Conclusions

In summary, poly(vinyl pyrrolidone) (PVP)-capped five-fold twinned Au nanoparticles have been successfully synthesized by a simple and convenient wet chemical method. In the process, hydrogen tetrachloroauric acid (HAuCl₄·3H₂O) was reduced by ethylene glycol to form the five-fold twinned Au nanocrystals in the presence of the PVP molecules at 200 °C under an extra autogenous pressure condition. A growth-mediated mechanism has been suggested to elucidate the formation of the small decahedral Au nanoparticles. The PVP molecules may play a very important role in the formation process of the five-fold twinned Au nanoparticles. In addition, the small decahedral Au nanoparticles can evolve into larger apparently perfect decahedral Au particles with a size of several micrometres. The investigation provides a new insight into the formation and evolution of Au nanoparticles with a five-fold twinned structure.

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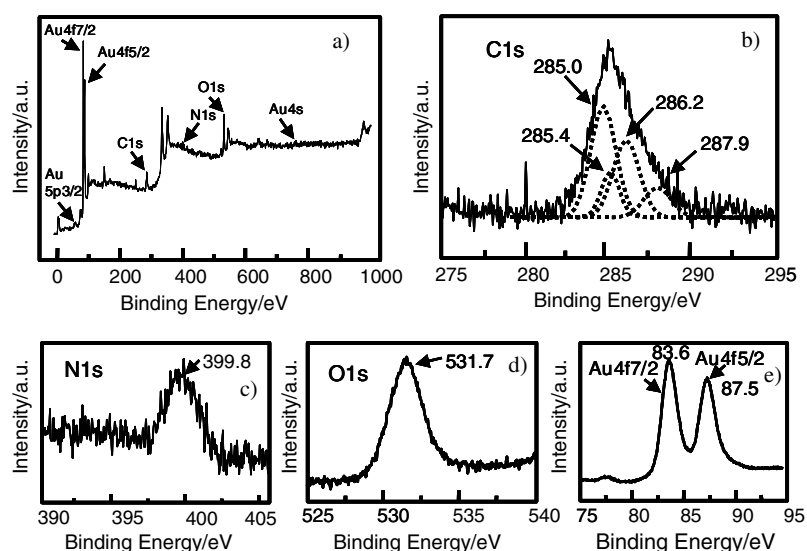


Figure 6. XPS spectra of PVP-capped Au particles (top left) and C 1s, N 1s, O 1s, and Au 4f regions.

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