Controlled Fabrication of Decahedral Gold Nanostructures by a Thermal Approach

Min Zhou,[1] Shenhao Chen,*[1,3] Haiqing Sun,[2] and Xiuyu Liu[1]
[1]*Department of Chemistry, Shandong University, Jinan 250100, P. R. China*
[2]*School of Materials Science and Engineering, Shandong University of Science and Technology, Qingdao 266510, P. R. China*
[3]*State Key Laboratory for Corrosion and Protection, Shenyang 110016, P. R. China*

(Received February 26, 2007; CL-070212; E-mail: shchen@sdu.edu.cn)

Multiple-twinned gold nanostructures with decahedral shape have been prepared in aqueous solution by a one-step thermal process method. The decahedra of nano-gold can be obtained by heating aqueous PVP/$HAuCl_4$ solution. In this process, poly(vinyl pyrrolidone) (PVP) acted as both reducing agent and shape-controlling surfactant. By control of the reaction condition, decahedral, icosahedral, and plate-like gold nanostructures have been obtained.

Metal nanostructures have drawn considerable interests in the past years because of their unique optical, electrical, and magnetical properties.[1,2] Exciting progress has been made towards strategies to selectively preparing anisotropic metal nanoparticles.[3] Among them, Au nanocrystals are particularly interesting because they have unique electrical and optical properties. Various approaches have been reported for fabricating gold nanocrystals with various morphologies, such as rods,[4] wires,[5] prisms,[6] and plates.[7] Notwithstanding such various methods, there still remain many shapes that are unattainable in selective manner by existing methods. It is interesting to note that only recently have decahedral gold nanocrystals been reported. Xie and co-workers[8] prepared multiple-twinned gold nanoparticles with decahedral shape by a polyol method. In their process, chloroauric acid was reduced by ethylene glycol to form the multiple-twinned Au nanocrystals in the presence of PVP molecules at 200 °C under the extra condition of autogenous pressure. Yacaman et al.[9] recently reported the formation of twinned (including decahedra) gold nanocrystals using polyol process in the presence of PVP. Five-twinned with decahedral shape may exhibit intrinsic physical and chemical properties differing from untwinned structures owing to their lattice symmetry and specific surface structural characteristics. Herein, we report a simple one-step preparation of decahedral gold nanocrystals in aqueous solution by thermal chemical reduction method. In this work, PVP serves as both a stabilizer and a reductant for controlled preparation of gold nanostructures with different shapes. Upon adjusting the chain length of the PVP, the decahedral, icosahedral and plate-like structures with dominating distribution were fabricated, respectively.

PVP has been extensively used in the chemical preparation of many types of colloidal nanocrystals. The major role of PVP has been assigned as a stabilizer or a capping agent to protect the product from agglomeration. Here, we use the reducing and shape-introducing power of PVP for preparation of gold nanostructures with different shapes. Typically, the solution for preparation of decahedral gold nanostructures, which consisted of 2.5 mM $HAuCl_4$ and 10 g/L PVPK17 was heated to 95 °C. The color of the solution turned iridescent purple within 60 min, indicating formation of gold nanoparticles. The size and shape of the products were carried out by using a JSM-6700F scanning electron microscope (SEM) operating at 10 kV. The TEM photographs were taken with a Hitachi H-800 TEM at an accelerating voltage of 200 kV. The crystal structure of the products was examined using an X-ray diffractometer (XRD, Rigaku D/Max 2200PC diffractometer with Cu Kα radiation).

Figure 1a shows a typical SEM image of the products prepared by the simple thermal reduction process. The representative SEM image demonstrates that the as-prepared particles are consisted of decahedral nanostructures with an edge length of ca. 1200 nm. Figure 1b shows an individual decahedral particle, from which one can clearly resolve the exact shape. Each decahedron demonstrates fivefold rotational axes clearly. Figure 1c gives a geometrical model that corresponds to the decahedron shown in the same figure. The energy-dispersive X-ray spectroscopy (EDS) pattern (Figure 1d) obtained from the product only shows the peak corresponding to Au, thus indicating that the particles are pure metallic Au (the peak of C comes from carbon coating for SEM measurement). The yields of decahedral and plate-like particles calculated from Figure 1a were ca. 12 and 8%, respectively. Most of particles were dominated with spherical and spherical-like particle.

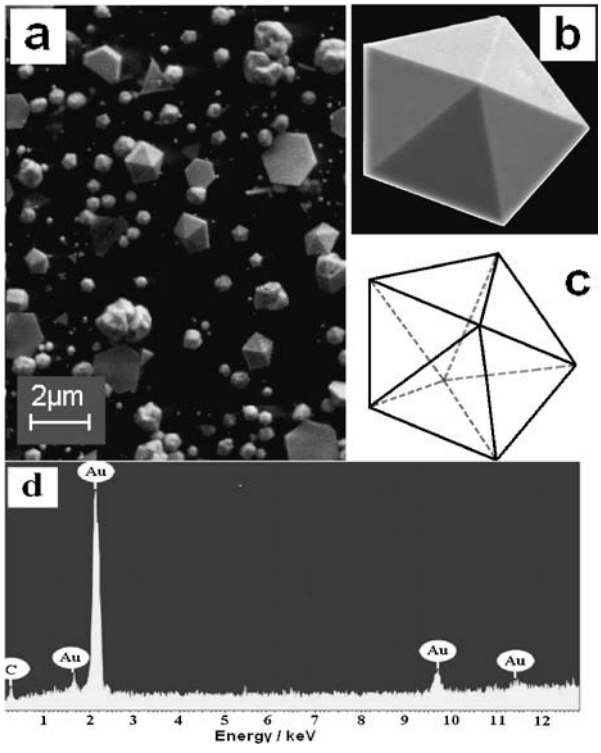

Figure 1. SEM (a) image of the decahedral Au nanocrystals; (b) individual decahedral Au particle and its geometrical structure (c); EDS (d) spectrum of the Au products.

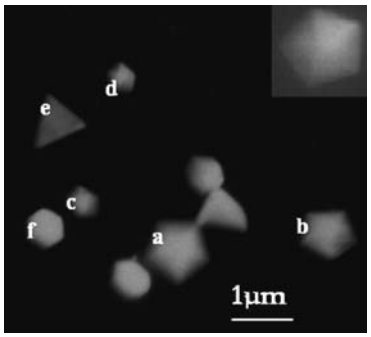

Figure 2. TEM image of the decahedral Au nanocrystals, the inset shows an individual decahedron.

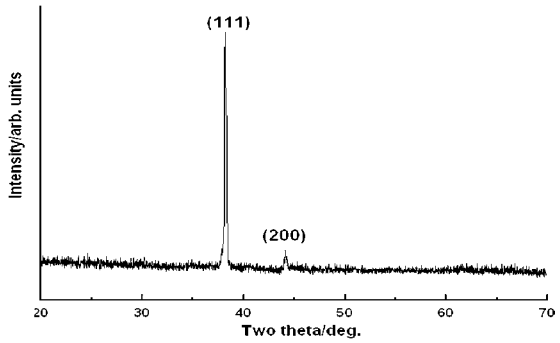

Figure 3. X-ray diffraction pattern of gold products. Labeled peaks correspond to the characteristic diffraction peaks of elemental Au^0.

To further elucidate the structure of the decahedral Au nanoparticles in detail, TEM has been used to image the products. Figure 2 demonstrates a typical TEM image of the as-prepared decahedral Au nanoparticle. The image indicates that the nanocrystals consist of decahedral structure. A nearly perfect pentagonal shape can be clearly seen. The particles contain a characteristic fivefold symmetry, which is more clearly shown in Figure 2 for particles a, b, c, and d. These Au decahedral particles have sizes from 500 to 1200 nm, in agreement with the SEM characterization. In our TEM observations, some of the particles are triangular (Figure 2, particle e) and hexangular plates (Figure 2, particle f), whose shapes and sizes are also consistent with SEM image.

The phase purity and high crystallinity of the Au decahedra is also supported by XRD, as shown in Figure 3. The two peaks of the as-prepared nanoparticles can be assigned to the (111) and (200) of pure crystalline Au with face-centered cubic (fcc) structure. Lisiecki et al.[10] reported that the decahedron consists of five tetrahedral crystallites with bare {111} surface. Noted that the intensity ratio between the (111) and (200) peaks for the as-prepared samples was much larger than the conventional bulk intensity ratio (JCPDS, File No. 4-0784). This phenomenon reveals that surfaces of the nanoparticles are predominantly composed of {111} facets.

The morphology of the as-obtained nanostructures was found to strongly depend on the reaction conditions. It is worth noting that the chain length of PVP is an important factor in determining the morphology of the final Au particles. Three PVP polymers with different chain lengths, PVPK90 ($n \approx 3240$), PVPK30 ($n \approx 360$), and PVPK17 ($n \approx 90$) were investigated in the present study. Different chain length of PVP was used under otherwise identical condition; different shapes of the Au products were obtained. Figure 4a shows typical SEM image of Au products obtained with PVPK90 and clearly demonstrates a large number of microsized plates. However, when PVPK30 was used for preparation of gold nanoparticles, icosahedral and plate-like nanostructures were main products (Figure 4b). These results indicate that it is possible to tune the shape of the gold nanocrystals by simply controlling the chainlength of PVP. However, it is not clear at present how the PVP influences the growth of different crystal planes of the Au nanostructures in detail, and the mechanism needs further investigation.

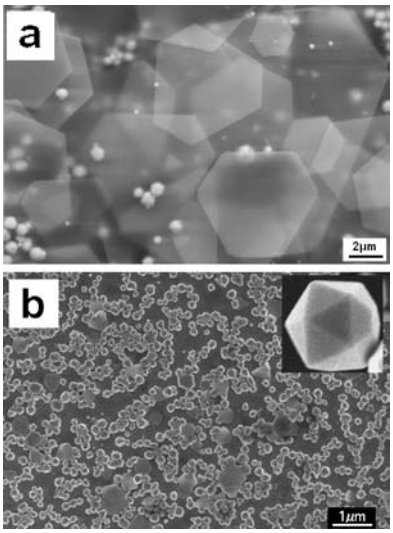

Figure 4. SEM images of gold products prepared in the presence of PVPK90 (a) and PVPK30 (b). The inset of (b) shows an individual icosahedron.

In conclusion, we present our preliminary findings that decahedral Au nanostructures can be obtained by a simple one-step wet-chemical route; which is carried out by the thermal process of $HAuCl_4$ with PVP in aqueous media. By using PVPs with different chain length, decahedral, icosahedral, and plate-like Au nanostructures were obtained. The successful preparation of gold nanocrystals exemplifies a very facile, generic strategy for fabrication of gold nanoparticles with various shapes. The exquisite shape-controlled preparation can be achieved through regulating experimental parameters and demonstrates a strategy that may be generally applicable to other material systems.

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