A Novel Ultraviolet Irradiation Technique for Shape-Controlled Synthesis of Gold Nanoparticles at Room Temperature

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Metal nanoparticles have received much attention during recent years because of their potential applications in microelectronics,[1,2] photocatalyses,[3,4] magnetic devices,[5] chemisorption, aerosols, and powder metallurgies.[6] These applications are strongly dependent on the size, shape (or morphology) and impurities of the metal nanoparticles.[7−9] Nowadays, colloid chemistry is challenged to control not only the metal nanoparticle sizes but the shapes and morphologies of the nanoparticles as well. Shape control is an alternative tool to adjust optical or catalytic properties of the materials.

Gold nanoparticles have been extensively studied in the literature.[10] Many techniques have been exploited to prepare shape-controlled gold nanoparticles. Schönenberger et al.[11] reported the synthesis of Au nanowires using polycarbonate track-etched membranes as templates. Martin and co-workers[12] have explored the optical properties of gold nanowires prepared by electrochemically depositing Au within the pores of alumina membranes. Monodisperse fractions of thiol-stabilized gold nanoparticles have been crystallized into two-and three-dimensional superlattices.[13,14] Esumi[15] has used the HTAC (25−30 wt %) as a template for an ultraviolet irradiation technique to synthesize colloidal Au particles with morphologies from spherical to needle shapes. This was done by adjusting the concentration of $HAuCl_4$ and varying the irradiation time.

In this communication, we report the shape-controlled synthesis of gold nanoparticles using a novel ultraviolet irradiation technique at room temperature. The very slow ultraviolet irradiation photoreduction process may favor the formation of shaped gold nanoparticles. It was found that not only the concentration of gold cations and the irradiation time but also the concentration and the species of polymer capping materials play important roles in the morphology control of the gold nanoparticles.

In a typical preparation procedure, a 30 W, column-like, low-pressure mercury lamp ($\lambda = 253.7$ nm) was used as an ultraviolet irradiation source. Polyvinyl alcohol (PVA, average molecular weight $M_w \approx 80\,000$) was used for the polymer capping material. An 100 mL aqueous solution containing 10^{-4} mol/L $HAuCl_4$ and 3 wt % PVA in a glass beaker about 5 cm away from the mercury lamp was irradiated for 48 h under the present ultraviolet irradiation at 15 °C. The UV−vis absorption spectrum of the resulting solution (sample 1) was recorded using a Shimadzu-200 spectrophotometer. A transmission electron microscope (TEM) image was obtained by dribbling the resulting solution on carbon film.

The UV−vis absorption spectrum of the resulting solution shows an absorption peak at about 525 nm, indicating that the Au nanoparticles have formed after the present ultraviolet irradiation for 48 h.[12]

Figure 1a shows the TEM image of the resulting solution. It can be seen that the Au nanoparticles were produced as platelike triangles about 15 nm in size. Several platelike triangle Au nanoparticles were observed to stack together, indicating that the platelet Au nanoparticles obtained with the present ultraviolet irradiation photoreduction technique may contain a twin or stacking fault normal to the thin direction. This has been suggested in the past for platelet particles as the source of preferred growth at the re-entrant surface. The corresponding electron diffraction (ED) pattern (Figure 1b) reveals that a hexagonal diffraction spot pattern was generated, which demonstrated that the platelike triangular Au nanoparticles prepared with the present ultraviolet irradiation photoreduction technique are highly individuated crystals with a preferential growth direction along the Au(111) plane. The corresponding lattice constant is $a = 0.4023$ nm, which is close to the reported data (JCPDS File No. 4-0784; $a = 0.4078$ nm). The identical X-ray diffraction pattern has also confirmed the preferential growth of the single crystals. We believe that the very slow ultraviolet irradiation photoreduction process may favor the formation of Au single crystals using the PVA for the capping material, which is consistent with the previous result.[16] Platelike triangular Au nanoparticles have been reported in the previous papers,[17,18] and the growth mechanism has been clarified by the Kossel−Stranski theory of face-selective growth of crystals.[19]

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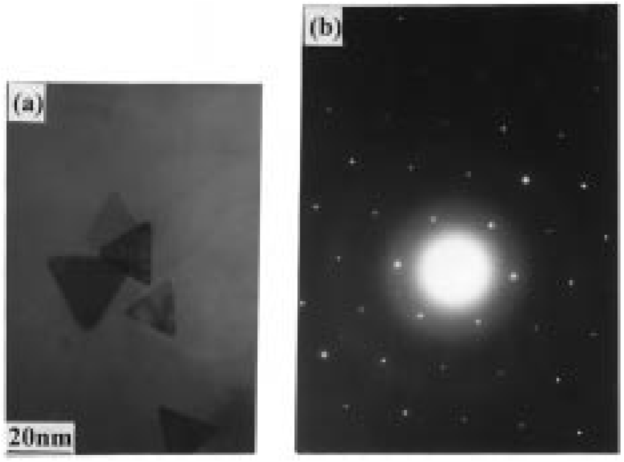

Figure 1. (a) TEM image of the platelike triangular gold nanoparticles prepared by irradiating an aqueous solution containing 10^{-4} mol/l $HAuCl_4$ and 3 wt % PVA for 48 h with the present ultraviolet irradiation. (b) Corresponding electron diffraction (ED) pattern.

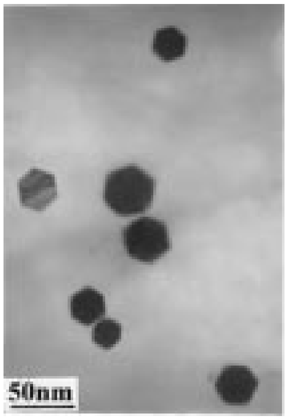

Figure 2. TEM image of the hexagonal-shaped gold nanoparticles prepared by irradiating an aqueous solution containing 10^{-3} mol/L $HAuCl_4$ and 3 wt % PVA for 48 h with the present ultraviolet irradiation.

Irradiation time was investigated to study the influence on the morphology of the shaped Au in sample 1 obtained with the present irradiation photoreduction technique. The result shows that Au nanoparticles obtained grew into more regular platelet triangular shapes as the irradiation time was extended. No changes of the morphology of the shaped Au nanoparticles were observed after the irradiation time was extended to 48 h. The reason for this is may be that there was enough time for the reduction of $HAuCl_4$ into elemental Au, which aggregated and grew into Au nanoparticles with more regular shape.

Further study indicates that the platelike triangular Au nanoparticles have grown larger and developed into hexagonal shapes with the increase of the concentration of $HAuCl_4$. Figure 2 shows the TEM image of the Au nanoparticles prepared by irradiating the solution (sample 2) containing 10^{-3} mol/L $HAuCl_4$ and 3 wt % PVA for 48 h. It was found that the crystal morphology of the Au nanoparticles is predominately hexagonal about 25 nm in size rather than the triangular shape favored in the sample 1. The corresponding ED pattern showed that these hexagonal Au nanoparticles also obtained highly crystallized single crystals with a preferential growth direction along the Au(111) crystal plane. We think that the variation of the Au morphology may result from the excess gold source in the solution, which facilitates the formation of hexagonal Au nanoparticles.

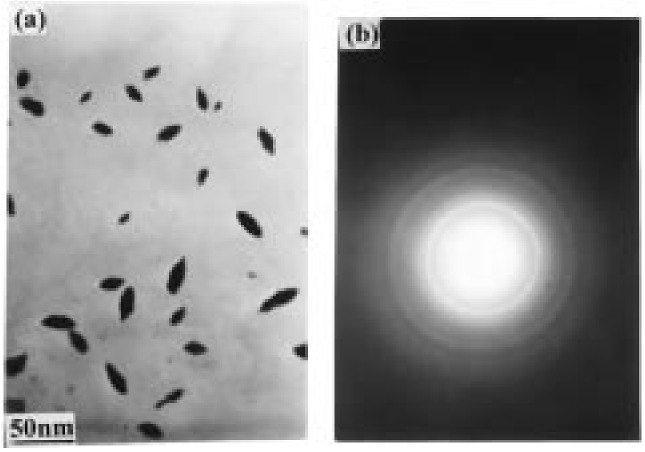

Figure 3. (a) TEM image of the quasi-ellipsoidal shaped gold nanoparticles prepared by irradiating an aqueous solution containing 10^{-4} mol/L $HAuCl_4$ and 3 wt % PEG for 48 h with the present ultraviolet irradiation. (b) Corresponding electron diffraction (ED) pattern.

The concentration of PVA also plays an important role in the morphology of the produced Au nanoparticles. Further studies demonstrated that only spherical Au nanoparticles were obtained if the PVA concentrations were lower than 1.0 wt % in the presence of 10^{-4} mol/L $HAuCl_4$ for the same period of irradiation. Increasing the PVA concentration in the system was found to be favorable for the formation of the polyhedral-shaped Au nanoparticles. The influences of concentrations of the PVA and Au cations on the shape of the Au nanoparticles are very similar to that obtained by El-Sayed et al.,[8] who reported that the ratio of the concentration of the capping polymer material to the concentration of the platinum cations can control the shapes and sizes of platinum nanoparticles.

Dramatic morphology variations of Au crystals were observed when polyethylene glycol (PEG, average molecular weight $M_w \approx 20\,000$) was used for the polymer capping material. In the same system as sample 1, with PEG in place of PVA, the Au nanoparticles about 25 nm in size displayed quasiellipsoidal morphology, as shown in Figure 3a. The corresponding ED pattern (Figure 3b) shows the gold polycrystalline diffraction rings. The morphology variation of the Au nanoparticles resulting from the alternation of the polymer capping materials revealed that polymer capping materials acting as molecularly dissolved surface modifiers and steric stabilizers may influence the crystallization of the growing Au nucleus site in a specific manner.[20] The more detailed influence mechanism of the polymer capping materials on the morphology of the Au nano-

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particles prepared with the present ultraviolet irradiation technique will be investigated further.

In summary, shape-controlled gold nanoparticles have been synthesized using a novel ultraviolet irradiation technique at room temperature. The very slow ultraviolet irradiation photoreduction process may favor the formation of the shaped-gold nanoparticles. It was found that not only the concentration of Au cations and the irradiation time but also the concentration and the species of the polymer capping materials play important roles in the morphology control of the produced Au nanoparticles. Increasing $HAuCl_4$ concentration in the system with PVA for the polymer capping material facilitated the platelike triangular Au nanoparticles to grow larger and to develop into hexagonal shapes, which may result from the excess gold source in the solution. The prolongation of irradiation time facilitated the formation of the Au nanoparticles with more regular shape. Meanwhile, increasing the concentration of PVA was favorable for the formation of the Au nanoparticles with polyhedral shapes. Au nanoparticles with the quasiellipsoidal morphology were obtained with PEG in place of PVA as the polymer capping material.

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