Large-scale, Solution-phase Production of Microsized, Single-crystalline, Hexagonal Gold Microplates by Thermal Reduction of $HAuCl_4$ with Oxalic Acid

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Heating an aqueous oxalic acid/$HAuCl_4$ solution results in the formation of microsized, single-crystalline, hexagonal gold microplates on a large scale.

The importance of the two-dimensional (2D) gold particles is not just in optics, and exceptionally interesting materials with unique mechanical properties can be obtained with such structures;[1] therefore, effective but simple strategies for fabricating 2D gold particles must be found. To date, the reports on the preparation of 2D gold particles including plates and disks with nanometer thickness, called nanoplates or nanodisks, are well-documented in the literature. For example, Ibano et al. demonstrated a photoreduction method for the preparation of gold nanoplates using anionic phospholipid as a protective reagent;[2] Tsuji et al. prepared gold nanoplates with a microwave-polyol method;[3] Wang et al. obtained gold nanoplates in amphiphilic block copolymer-based liquid crystalline phase with the help of a small amount of cationic surfactant;[4] Simakin et al. obtained gold nanodisks by laser ablation of Au target in water by a Cu vapor laser;[5] More recently, some kind of amine-containing compounds including amino acids,[6] organic small molecule,[7] and polyelectrolyte[8] have been successfully used as a reducing reagent as well as a soft-template for the generation of gold nanoplates at room temperature or elevated temperature.

However, in all above reported studies, the thickness of 2D gold particles is below 100 nm. In this letter, we present the fabrication of gold plates (several micrometers in size) with a thickness above 100 nm, called gold microplates, by a thermal reduction process carried out by heating an aqueous oxalic acid/$HAuCl_4$ solution. It is found that the size and the thickness of as-prepared plates can be controlled by the amount of oxalic acid used. The resulting gold microplate is a single crystal with a preferential growth direction along the gold (111) plane. It is also found that the concentration of reactants has heavy influence on the formation of these gold plates. To the best of our knowledge, this is the first report on the production of gold microplates from an aqueous oxalic acid/$HAuCl_4$ solution.

In a typical experiment, 200 μL of 0.12 M aqueous $HAuCl_4$ solution was diluted to 10 mL by adding water, followed by the introduction of 0.048 M aqueous oxalic acid solution with 1:1 molar ratio of oxalic to gold. The resulting solution was heated at 100 °C for several min, and a large quantity of golden precipitate occurred. The precipitate was used for further characterization. Scanning electron microscopic (SEM) data were collected by a XL30 ESEM FEG scanning electron microscope. Transmission electron microscopic (TEM) data were obtained from a JEOL 2000 transmission electron microscope. X-ray diffraction (XRD) analysis was carried out on a D/Max 2500 V/PC X-ray diffractometer using Cu (40 kV, 200 mA) radiation.

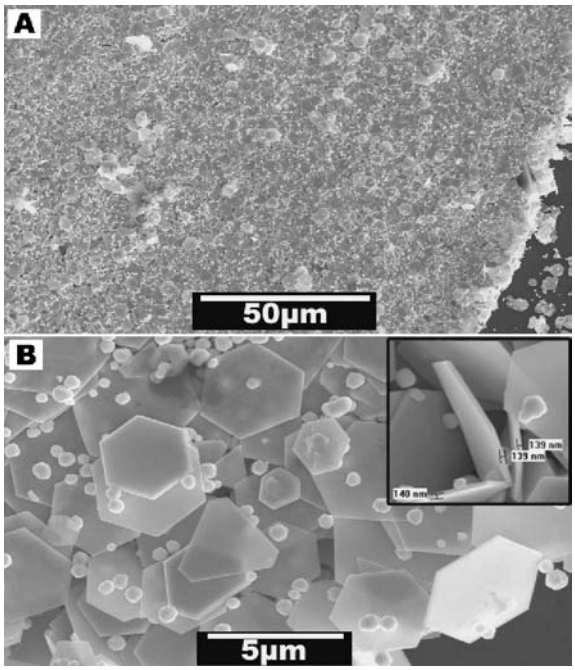

Figure 1. Lower magnification (A) and higher magnification (B) SEM image of the precipitate obtained at 1:1 molar ratio of oxalic acid to gold at 100 °C.

Figure 1 shows typical SEM images. Lower magnification image (Figure 1a) indicates that the precipitate consists of a large quantity of tightly stacked 2D structures. Energy-dispersive X-ray spectroscopy (EDS) confirms that the products are gold. Higher magnification image (Figure 1b) further shows that these 2D structures are hexagonal plates with several micrometers in size. By measuring the distance between two planes of one plate standing against the substrate we obtain the thickness of as-produced plates. The thickness of these plates is ≈140 nm (inset), revealing that they are microplates. Also observed are some small nanoparticles with irregular shapes, which are by-products of the reaction.

Figure 2 shows the X-ray diffraction (XRD) pattern from the as-prepared products. The diffraction peaks can be assigned to the (111), (200), (220), (311), and (222) facets of metal gold, confirming that the precipitate is composed of crystalline gold.[7] No impurity peaks were observed, indicating the high purity of the final products. It is worthwhile mentioning that the ratio of intensity between the (200) and (111) diffraction peaks is much lower than the standard file (JCPDS 4-784) (0.067 versus 0.33), indicating that the product are primarily dominated by (111) facets and their (111) planes tend to be preferentially oriented parallel to the surface of the supporting substrate.[6] The crystal-

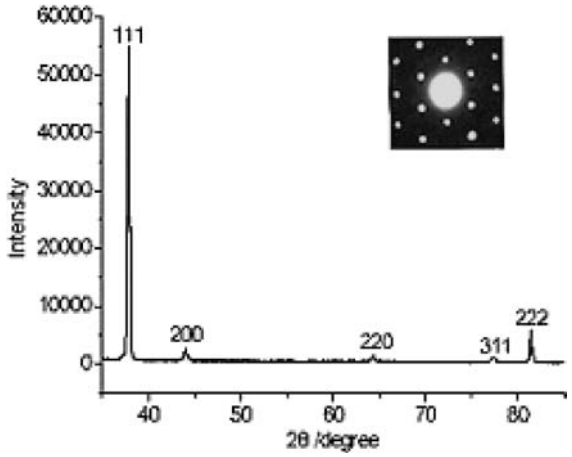

Figure 2. X-ray diffraction (XRD) pattern of the precipitate obtained at 1:1 molar ratio of oxalic acid to gold at 100 °C. Inset: selected area electron diffraction pattern (SAED) of one microplate.

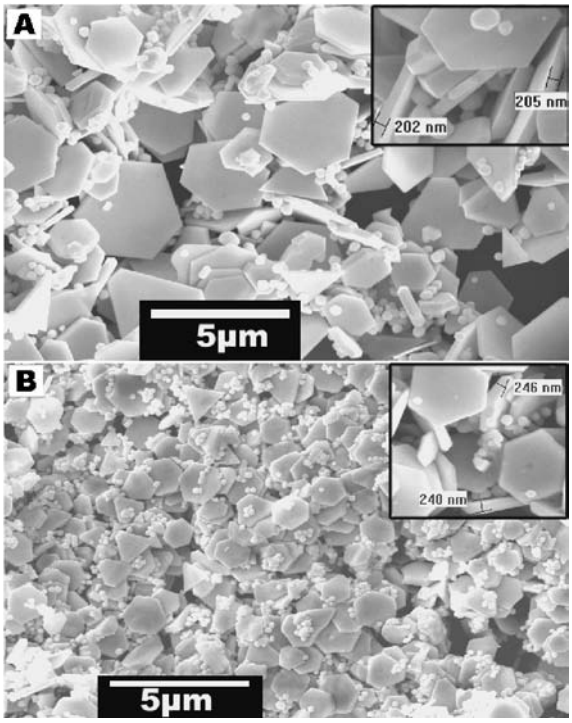

Figure 3. SEM images of the precipitates obtained at 3:1 (A) and 9:1 (B) molar ratio of oxalic acid to gold at 100 °C.

line nature of the microplates was further confirmed by corresponding selected area electron diffraction pattern (SAED) obtained by focusing the electron beam on one microplate flatlying on TEM grid. The SAED pattern gives a hexagonal symmetry diffraction spot pattern (inset), also indicating that the gold microplate thus formed is a single crystal with a preferential growth direction along the gold (111) plane.[7]

We examined the influence of the amount of oxalic acid used on the formation of gold microplates. Figure 3 shows typical SEM images of the precipitates obtained at 3:1 (Figure 3a) and 9:1 (Figure 3b) molar ratio of oxalic acid to gold at 100 °C, indicating the formation of microplates on a large scale. It is clearly seen that increasing molar ratio leads to decreasing

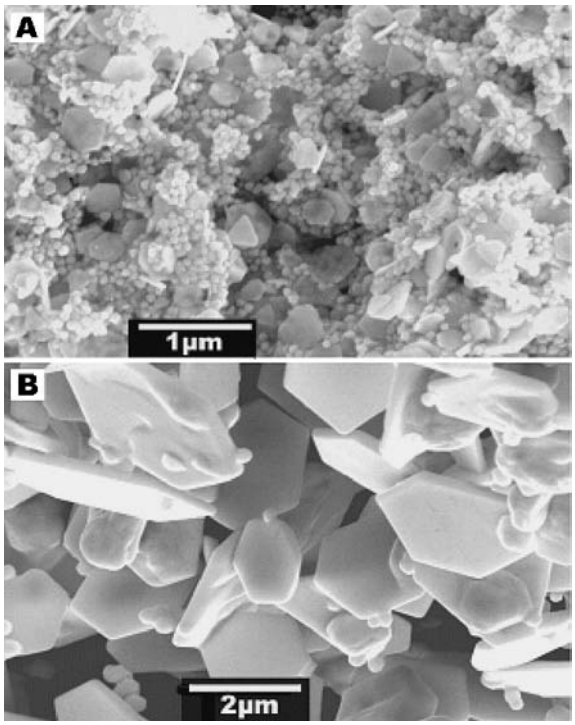

Figure 4. SEM images of the precipitate obtained by decreasing the concentration of reactant to one-fifth (A) and by increasing the concentration of reactants to fivefold (B) at 100 °C.

plate size. Also note when the molar ratio is increased to 3:1 and 9:1, the plate thickness is increased to ≈205 and ≈245 nm, respectively (inset).

Finally, the influence of concentration of reactants on the formation of gold microplates was also examined. When the concentration was decreased to one-fifth, the precipitate consisted of a large quantity of small nanoparticles and microplates (Figure 4a). However, when the concentration was increased to five-fold, the precipitate mainly consisted of microplates and one plane of some plates became rather rough (Figure 4b).

In summary, heating an aqueous oxalic acid/$HAuCl_4$ solution has been proven to be an effective and facile approach for the large-scale production of microsized, single-crystalline, hexagonal gold microplates. Both the size and the thickness of these plates can be controlled by the molar ratio of oxalic acid to gold. We also find that the concentration of reactants strongly influences the formation of the gold plates.

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