Large-Scale Synthesis of Micrometer-Scale Single-Crystalline Au Plates of Nanometer Thickness by a Wet-Chemical Route**

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In the past few years metal nanostructures have been the focus of intensive research as a result of their electronic, optical, magnetic, thermal, catalytic, and other properties being distinctly different from their bulk counterparts, and considerable attention, in terms of both fundamental and applied research, has been paid to synthesizing and characterizing metal nanostructures.[1] It has also been demonstrated in nanometer-sized materials that the physical and chemical properties of the structures are closely related to their size and shape.[2] For example, the surface plasmon resonance of metal particles is strongly shape-dependent: the transformation of spherical metal particles into nanometer-sized rods or triangular prisms results in a red-shift and even a split of the corresponding surface plasmon resonance into distinctive dipole and quadrupole modes.[3] A variety of methods have so far been developed to prepare spherical metal nanoparticles,[1d] however, the production of nanostructures by a shape-controlled procedure is still a challenge for materials scientists and there is great interest in developing new methods for fabricating shape-controlled nanoparticles. Many differently shaped nanostructures have been synthesized from metallic Ag by using various chemical approaches, with 1D Ag nanostructures having been fabricated by many research groups.[4] Other Ag nanostructures, such as nanoprisms,[3,5] nanocubes,[6] nanoplates,[7] nanodisks,[8] and nanobelts,[9] have also been fabricated. Much effort has also been made to fabricate Au nanostructures with specific shapes, and many methods have been developed to synthesis 1D Au nanostructures,[10] however, there are very few reports on the synthesis of planar Au nanostructures such as nanodisks[11] and nanoplates.[12] We demonstrate herein a mild wet-chemical route to the large-scale synthesis of micrometer-scale Au nanoplates. In this process $H[AuCl_4]$ is reduced by *ortho*-phenylenediamine in an aqueous medium to form hexagonal single-crystalline Au nanoplates with a preferential growth direction along the Au (111) plane. This result suggests that the molar ratio of *ortho*-phenylenediamine to gold is key to producing Au nanoplates.

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The morphology of the precipitate was characterized by scanning electron microscopy (SEM, Figure 1). The lower magnification image (Figure 1 a) indicates that the precipitate consists of a large amount of particles, while the higher magnification image (Figure 1 b) clearly reveals that the particles are micrometer-scale plates, mainly hexagonal in shape. We can conclude from measurements of the distance between two planes of one plate standing against the glass substrate that these plates are nanoplates, tens of nanometers thick (see Figure 1 b, inset). Small quantities of spherical particles are also observed as by-products. The chemical composition of the particles was further determined by energy-dispersive X-ray spectroscopy (EDS). The EDS spectrum obtained from the precipitate only shows the peak corresponding to Au (data not shown), thus indicating that that the particles are pure metallic Au.

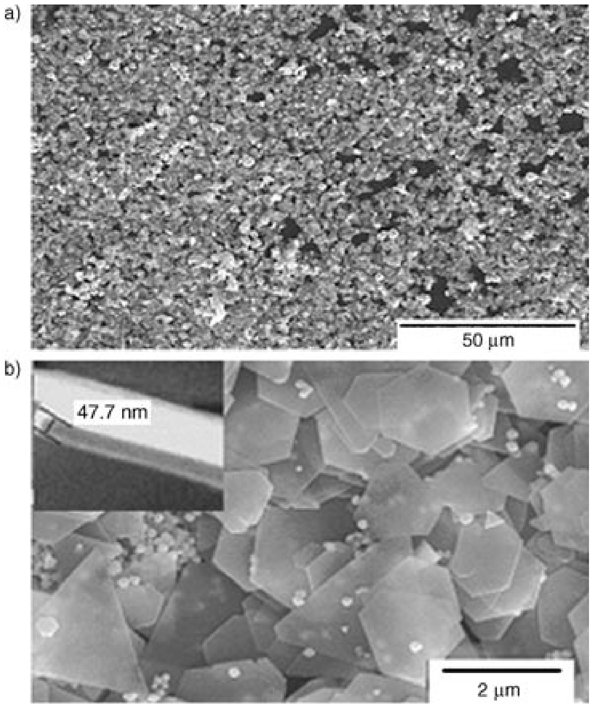

Figure 1. Low magnification (a) and high magnification (b) SEM images of the precipitate. The inset shows that the thickness of a single nanoplate is about 47.7 nm.

Figure 2 shows the transmission electron microscopy (TEM) image (Figure 2 a) of a single Au nanoplate as well as the related selected area electron diffraction (SAED) pattern (Figure 2 b) obtained by focusing the electron beam on a nanoplate lying flat on the TEM grid. Interestingly, some patterns are observed on the nanoplate plane. The other four dark dots marked with arrows are spherical Au particles formed as by-products. The SAED pattern reveals that a hexagonal symmetry diffraction spot pattern is generated, thus demonstrating that the Au nanoplate is a single crystal with a preferential growth direction along the Au (111) plane.[13]

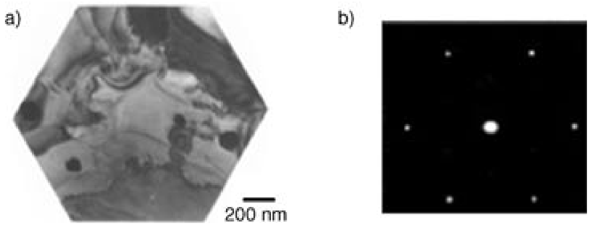

Figure 2. Typical TEM image (a) and corresponding electron diffraction pattern (b) of a single hexagonal Au nanoplate lying flat on a TEM grid.

The crystalline nature of the nanoplates was further confirmed by recording the X-ray diffraction (XRD) pattern. The XRD pattern (Figure 3) shows sharp peaks corresponding to the (111), (200), (220), (311), and (222) diffraction peaks of metallic Au, and thus indicates that the precipitate is composed of pure crystalline Au.[14] Note that the ratio of the intensity between the (200) and (111) diffraction peaks is much lower than the standard file (JCPDS; 0.061 versus 0.33). These observations confirm that our nanoplates are primarily dominated by (111) facets, and thus their (111) planes tend to be preferentially oriented parallel to the surface of the supporting substrate.

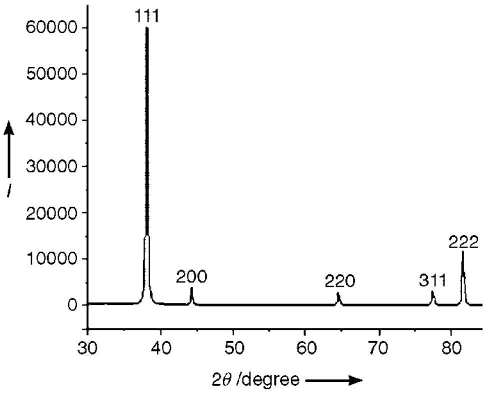

Figure 3. XRD pattern of the Au products.

It is well-known that Au nanostructures dispersed in liquid media usually display a very intense color because of surface plasmon resonance (SPR). Figure 4 shows a photograph and an absorption spectrum of the resulting Au particles sus-

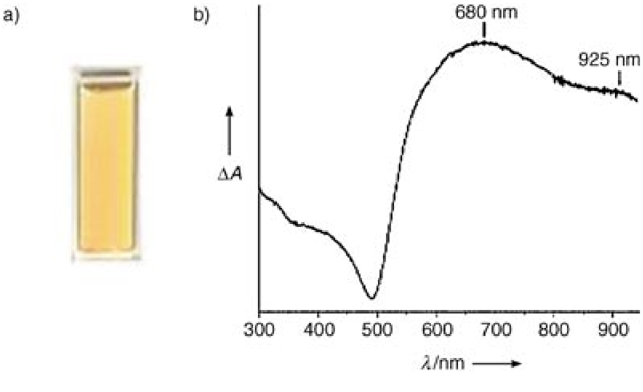

Figure 4. Photograph (a) and UV/Vis spectrum (b) of the Au particles suspended in water.

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pended in water. It has been reported that a solution of spherical colloidal Au is red,[15] but interestingly our suspension is gold-yellow in color (Figure 4a). It is also documented that the SPR band of Au nanostructures strongly depends on the size, shape, and aggregation of the nanostructures,[16] and that spherical Au particles show an SPR band at approximately 520 nm that is usually red-shifted to longer wavelengths with increasing particle size.[17] The resulting suspension shows two SPR bands located at about 680 and 925 nm which arise from the longitudinal plasmon resonance of Au particles,[18] thus providing another piece of evidence for the formation of anisotropic Au particles.[17]

We have found in our previous study that $H[AuCl_4]$ can be reduced by polyamine-containing polyelectrolytes and dendrimers to form Au nanoparticles.[19] More recently, it has been shown that $H[AuCl_4]$ can also be reduced by *ortho*-phenylenediamine to form spherical Au particles with the concurrent formation of poly(*ortho*-phenylenediamine) nanobelts as a result of the oxidative polymerization of *ortho*-phenylenediamine monomers by $H[AuCl_4]$.[20] In our present study we also obtained a precipitate of Au nanoplates and belts. Analysis of these belts by SEM shows that they contain C and N, thus indicating that they are oxidative products of *ortho*-phenylenediamine. These belts can be washed away with tetrahydrofuran (THF) to leave purified Au particles.

It is worthwhile mentioning that the quantity of *ortho*-phenylenediamine in the solution is an important factor in determining the morphology of the final Au particles. Control reactions in which excess *ortho*-phenylenediamine was added under otherwise identical conditions only gave isolated or aggregated spherical Au particles. Figure 5 shows typical SEM images of Au products obtained with initial *ortho*-phenylenediamine to gold ratios of of 3:1 (Figure 5a) and 8:1 (Figure 5b), and clearly indicates the formation of aggregated and isolated spherical Au particles, respectively. Other control reactions also gave similar results. These results indicate that the quantity of *ortho*-phenylenediamine in the solution is key to yielding Au nanoplates. We suggest that *ortho*-phenylenediamine molecules serve as a soft template and kinetically control the growth rates of various faces of Au particles by selectively adsorbing on to the crystallographic planes, thus resulting in the formation of large single-crystalline Au nanoplates. However, it is not clear at present how the *ortho*-phenylenediamine molecules influence the growth of different crystal planes of the Au nanoplates, and the detailed mechanism needs further investigation.

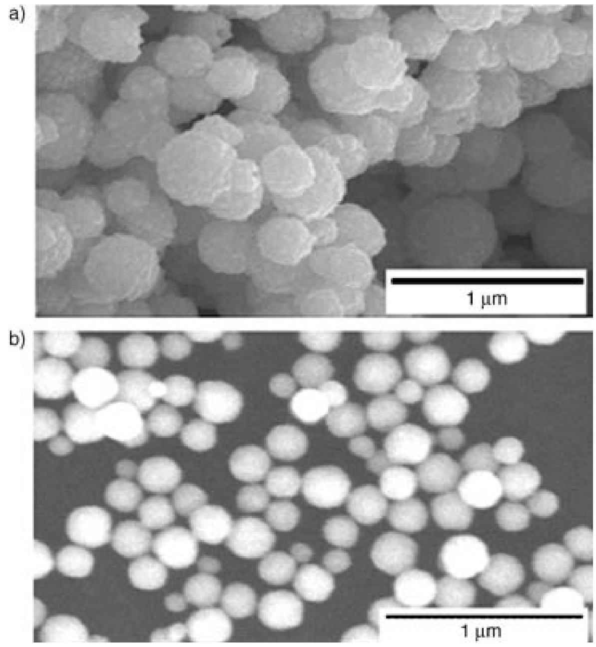

Figure 5. Typical SEM images of Au particles obtained with an initial *ortho*-phenylenediamine to gold ratio of 3:1 (a) and 8:1 (b).

In conclusion, we present our preliminary findings that micrometer-sized hexagonal single-crystalline Au nanoplates can be synthesized on a large scale by a mild wet-chemical route, carried out by the chemical reduction of $H[AuCl_4]$ with *ortho*-phenylenediamine in aqueous media at room temperature and ambient pressure. Two surface plasmon absorption bands at about 680 and 925 nm are found for these Au nanoplates. The study suggests that the quantity of *ortho*-phenylenediamine in the solution is key to producing Au nanoplates. The importance of the platelet-like gold particles is not restricted to optics; exceptionally interesting materials with unique mechanical properties can be obtained with such colloids.[21]

Experimental Section

$H[AuCl_4]$ was purchased from Aldrich and *ortho*-phenylenediamine from Beijing Chem. Co. All reagents were used as received without further purification. The water used was purified through a Millipore system. In a typical experiment, an aqueous solution of 48 mM $H[AuCl_4]$ (3 mL) was added to water (5 mL). An appropriate volume of an aqueous solution of freshly prepared *ortho*-phenylenediamine (80 mM) was quickly added to the solution under vigorous stirring at room temperature to obtain a 1:1 molar ratio of *ortho*-phenylenediamine to gold. A large quantity of precipitate was observed several minutes later, which was collected by centrifugation, washed several times with THF and water, then suspended in water. The resulting suspension was used for further characterization.

The samples for SEM and XRD characterization were prepared by placing 100 µL of the suspension on a glass slide, and allowing the solvent to slowly evaporate at room temperature. The sample for the TEM study was similarly prepared by placing a drop of the suspension on a carbon-coated copper grid. The UV/Vis spectra were collected on a CARY 500 Scan UV/Vis/near IR spectrophotometer. The SEM images were obtained on a XL30 ESEM FEG scanning electron microscopy operating at 20 kV. The TEM images were recorded on a JEOL 2000 transmission electron microscopy operating at 200 kV. The XRD pattern was collected on a D/Max 2500 V/PC X-ray diffractometer using Cu (40 kV, 200 mA) radiation.

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