Photosynthesis of Gold Nanoplates at the Water/Oil Interface

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Metal nanostructured materials have been the focus of much scientific research for decades because of their unusual optical, electronic, magnetic, catalytic, and other properties that are distinctly different from their bulk counterparts, and therefore, considerable attention from both fundamental and applied research has been paid to the synthesis and characterization of these materials.[1] Particular interest has been focused on the noble metal nanoparticles because of their unique optical and electrical properties and interesting applications of the nanoparticles in many fields such as catalysis,[2,3] optics,[4] sensors,[5] and surface enhanced Raman spectroscopy.[6,7]

Controlling the nanoparticle shape is technologically important, since the optical, electronic, magnetic, and catalytic properties of nanomaterials depend critically not only on particle size but also on particle shape.[8] Several methods have been developed for preparing nanoparticles in a variety of shapes, including rods, prisms, wires, and disks.[9-12] Recently, two-dimensional gold nanoplates have attracted increasing attention because of their potential applications in the areas of electrochemistry and producing new nanodevices.[13] The preparation of nanoplates with controlled size and thickness has been continuously reported by using various synthesis methods. For instance, Lee *et al.*[14] and Chen *et al.*[15] prepared gold sheets of about 10 μm by thermal reduction of HAuCl$_4$ in the bulk phase of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer. Dong *et al.*[16,17] and Sastry *et al.*[18] prepared gold nanoplates of about 1 μm by aspartate or *ortho*-phenylenediamine reduction of HAuCl$_4$ and by biological method, respectively.

In this work, we present a study of the photosynthesis of gold nanoplates at the water/oil interface without any additional templates, surfactants, and reducing agents. We found that hexagonal and truncated triangular crystalline gold nanoplates can be easily formed by irradiating biphasic mixture consists of diethyl ether and aqueous gold salt solution with a conventional fluorescent light. The physicochemical characteristics of the prepared nanoparticles were examined by various analytical tools such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS).

Experimental Section

HAuCl$_4$ was purchased from Aldrich. Other chemicals, unless specified, were reagent grade, and triply distilled water (resistivity greater than 18.0 MΩ·cm) was used when preparing aqueous solutions.

Gold nanoplates were fabricated as follows. 5 mL of freshly prepared HAuCl$_4$ aqueous solution (5, 10, 15, and 20 mM) was taken in a vial along with 5 mL of diethyl ether resulting in a biphasic mixture with the colorless organic part on top and yellow-colored aqueous solution below. The system was then irradiated with a conventional 45-W fluorescent light for 12 hr. A thin film of golden reflectance was formed slowly at the liquid/liquid interface. The interfacial films could be easily transferred to solid substrates. In fact, the biphasic mixture was poured into a Petri dish and the diethyl ether phase evaporated to leave a uniform film on the surface of water. This film was lifted onto mica substrates and carbon-coated TEM grids for further analysis.

The scanning electron micrographs of the samples were taken with field emission scanning electron microscope (FESEM, Phillips Model XL30 S FEG). The TEM images were acquired by using a JEOL JEM-2010 transmission electron microscope operating at 200 kV. XPS measurements were carried out using a VG Scientific ESCALAB 250 spectrometer, using Al Kα X-ray (1486.6 eV) as the light source. The base pressure of the chamber was ~1 × 10^{-10} Torr and the electron take-off angle was 90°.

Results and Discussion

The freshly prepared aqueous solution of HAuCl$_4$ with various concentrations of 5, 10, 15, and 20 mM was taken in a vial along with diethyl ether resulting in a biphasic mixture with the colorless organic part on top and yellow colored aqueous salt solution below. After irradiation of this mixture with a conventional 45-W fluorescent light for 12 hr, a thin film of golden reflectance was formed at the water/oil interface. The interfacial film could be transferred to mica substrates and carbon-coated TEM grids. The transferred films were very stable for prolonged time. The physicochemical characteristics of these films were investigated by SEM, TEM, and XPS. In fact, we have chosen the aqueous/ organic biphasic system as a reaction medium for the fabrication of gold nanoplates because nanostructured materials can be readily assembled at the aqueous/organic interface.[19] At the interface, self-assembly of nanostructures is dictated by a minimization of the interfacial energy. From this interfacial entrapment process, gold nanoplates can be easily
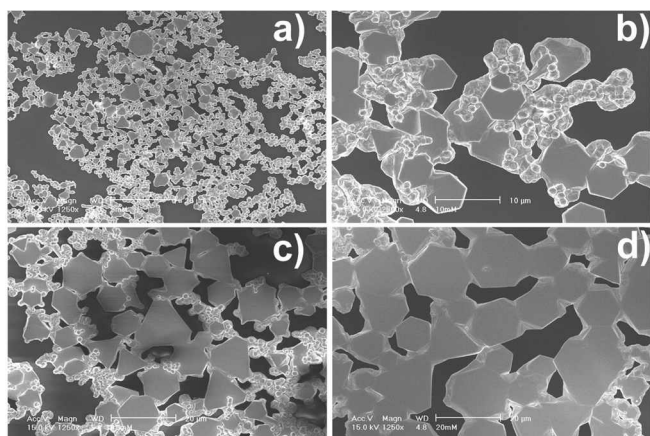
Figure 1. SEM images of the gold nanoplates prepared from (a) 5, (b) 10, (c) 15, and (d) 20 mM HAuCl₄ aqueous solutions.

collected without further purification step such as centrifugation.

Figure 1 shows typical SEM images of the transferred films on mica. From the SEM images, it can be observed that the products are composed mainly of gold nanoplates with a size larger than 1 μm in edge length. Most of nanoplates have hexagonal and truncated triangular shapes. Some small nanoparticles with irregular shapes are also observed, which are byproducts of the reaction. The thickness of the gold nanoplates was estimated to be about 76 nm from the closer inspection of SEM images of some tilted nanoplates (data not shown). As shown in the Figure 1, the size of gold nanoplates gradually increased and the amount of irregular-shaped nanoparticles decreased as the concentration of gold precursor increased from 5 mM to 20 mM. From this observation, we can assume that the concentration of HAuCl₄ should be a dominant factor for the regulation of the formation of gold nanoplates.

Figure 2 shows the high-magnification TEM images of isolated gold nanoplates. TEM images clearly show that the photochemical reduction of gold ions leads to the formation of nanoplates with truncated triangular and hexagonal geometries with very smooth edges. Continuous and randomly distributed pairs of bending contours, which are frequently encountered in the bright-field TEM image of nanobelts, can be found across the flat crystal faces. The bending contours are caused by the warping of the atomic planes with respect to the direction of the incident electron beam.[20] The single-crystalline structure of these nanoplates was further confirmed by their corresponding electron diffraction patterns. Insets of Figure 2 show the selected-area electron diffraction (SAED) patterns of corresponding nanoplates. The SAED patterns were obtained by aligning the electron beam perpendicular to the triangular and hexagonal facets of the nanoplates lying flat on the TEM grid. The hexagonal symmetry of the diffracted spots suggests that each gold nanoplate was a single crystal bounded by {111} facets, and their {111} planes tend to be preferentially oriented parallel to the surface of the supporting substrate. All these observations indicate the faceted morphology of gold nanoplates
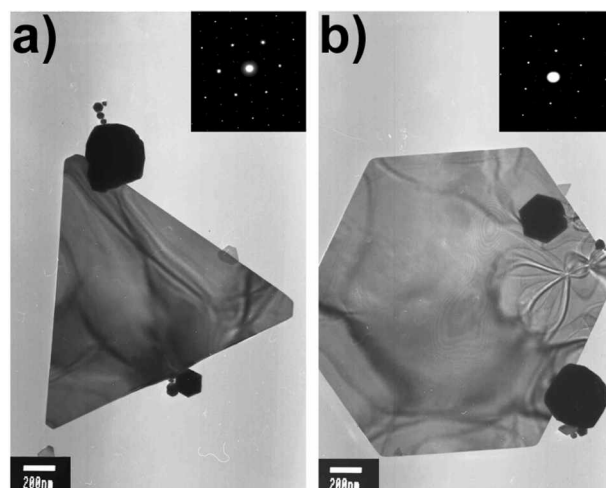

Figure 2. High-magnification TEM images of isolated gold nanoplates with (a) truncated triangular and (b) hexagonal geometries. Insets show corresponding SAED patterns.
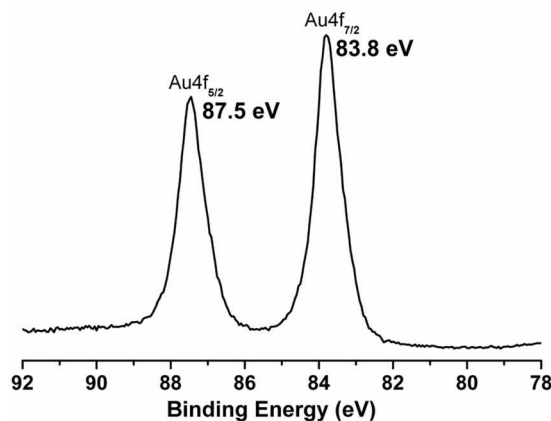

Figure 3. High-resolution Au 4f XPS features obtained from the gold nanoplates.

and their inherent anisotropy, which is an important feature since many optical and electronic properties of crystalline materials depend on their orientation.

To gain more insight into the prepared nanoplates, XPS measurements have been performed. XPS turned out to be a powerful tool for the investigation of metal nanostructures.[21] High-resolution Au 4f X-ray photoelectron spectrum of the gold nanoplates is shown in Figure 3. As shown in the figure, Au 4f XPS spectrum obtained from the gold nanoplates films was characterized by peaks with binding energies of 87.5 eV for $4f_{5/2}$ and 83.8 eV for $4f_{7/2}$, both distinctive for Au metal.[21] We could not observe any features associated with Au^+ and Au^{3+}, indicating that gold ions are fully reduced.

In this work, the conventional fluorescent light illumination to the biphasic mixture consists of diethyl ether and aqueous metal salt solution has been used as a new approach to the synthesis of metal nanoplates. All the previous photochemical or photocatalytic methods for the preparation of metal nanostructures are based on the use of UV light. Direct photochemical excitation of metal ion precursors under 254

nm irradiation can lead to the generation of metal nano-particles in aqueous solution. For example, the photolysis of $AuCl_4^-$, $PtCl_6^{2-}$, or Ag^+ by 254 nm induced the formation of metal nanoparticles in the presence of surfactants that prevent nanoparticles from agglomerating.[22] Recently, we found that palladium nanoparticles can be easily formed by irradiating biphasic mixture consists of diethyl ether and aqueous K_2PdCl_4 solution with a conventional fluorescent light.[23] The formation of palladium nanoparticles by visible light irradiation can be ascribed to the fact that aqueous $PdCl_4^{2-}$ solution shows a prominent broad absorption feature centered at 420 nm. The irradiation of fluorescent light can thus induce photochemical excitation of metal ion precursor, and can lead to the formation of nanoparticles. Since the aqueous $AuCl_4^-$ solution exhibits a considerable absorbance at 400-500 nm, same mechanism can be applied to the gold nanoplates system. However, it is not clear at the present time how the light irradiation influences the growth of different crystal plans of the gold nanoplates and the detailed mechanism requires further investigation.

Conclusions

We have shown that large-size single-crystal gold nano-plates can be successfully prepared by photochemical reduction of gold ions with conventional fluorescent light excitation. The size of gold nanoplates can be controlled by adjusting the concentration of gold precursor. Our synthetic approach does not require any additional templates, surfac-tants, and reducing agents, and thus offers not only an attractive possibility for the fabrication of thin film micro-circuits and devices, but also can offer a very efficient and economic route for the preparation of nanostructures. Currently, we are attempting to synthesize other metal nanoplates by using various metal precursors.

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