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High-Yield Synthesis of Large Single-Crystalline Gold Nanoplates through a Polyamine Process

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A polyamine process has been demonstrated for the high-yield preparation of single-crystalline gold nanoplates with several 10 μm in size, carried out by heating a concentrated aqueous solution of linear polyethylenimine and HAuCl$_4$ at 100 °C. It suggests that the concentration of reactants is crucial to the formation of nanoplates.

Introduction

In the past few years, metal nanostructured materials have been the focus of much scientific research because of their unusual electronic, optical, magnetic, thermal, 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] On the other hand, the physical and chemical properties of these materials are heavily dependent on their size and shape.[2] As a result, nanostructure production by a size- or shape-controlled procedure has been paid increasing attention and there is great interest in developing new methods for fabricating shape-controlled nanomaterials. Up to now, a variety of methods for preparing spherical metal nanoparticles have been well-documented, and many reviews are now available.[1c,d,3] In the meantime, a few works have reported on the preparation of metal nanostructures with a certain shape. As for silver, nanowires, nanoprisms, nanocubes, nanoplates, nanodisks, and nanobelts have been successfully fabricated.[4] Also, many methods have been demonstrated for the preparation of gold nanostructures with various shapes such as nanowires, nanodisks, and nanoplates.[5]

A polyol process was first demonstrated by Fiévet et al. to prepare metal nanoparticles, carried out by refluxing a solution of the metal precursor in ethylene glycol or a larger polyol which is used as a solvent and a reducing agent.[6] Recently, many approaches based on this polyol method have been widely applied to the production of anisotropic nanostructures with the use of a capping agent such as poly(vinyl pyrrolidone) (PVP) to control the growth rates of various faces of particles.[7] More recently, we have reported a polyamine process for the preparation of stable metal nanoparticles with the use of polyamine to simultaneously act as both the reducing agent and the protective agent. The formation of metal nanoparticles occurs in a single process which involves heating an aqueous solution of metal precursor and polyamine including dendrimer[8] and polyelectrolyte,[9] without the additional introduction of a reducing agent and a protective agent. In this paper, we further report our interesting finding that heating a concentrated aqueous solution of linear polyethylenimine (LPEI) polyelectrolyte[9] and HAuCl$_4$ can convert completely Au^{3+} into two-dimensional gold nanostructures, called nanoplates, through our polyamine process. The resulting nanoplates are large (up to ~40 μm in size) single-crystalline gold with a preferential growth direction along the {111} plane.

Experimental Section

HAuCl$_4$ and LPEI ($M_w = $ ~423) were purchased from Aldrich. All reagents were used as received without further purification. The water was purified through a Millipore system. The gold nanoplates were prepared as follows: in brief, 2 mL of 0.048 M HAuCl$_4$ aqueous solution was mixed with 1.06 M LPEI aqueous solution with a 2:1 molar ratio of LPEI (repeating unit) to gold, and then, the resulting mixture was heated at 100 °C for several minutes, resulting in the formation of a large quantity of golden-sand-like precipitate and leaving a colorless supernatant. The precipitate was used for further characterization.

For characterization by scanning electron microscopy (SEM), some precipitate was placed on an indium tin oxide (ITO) glass

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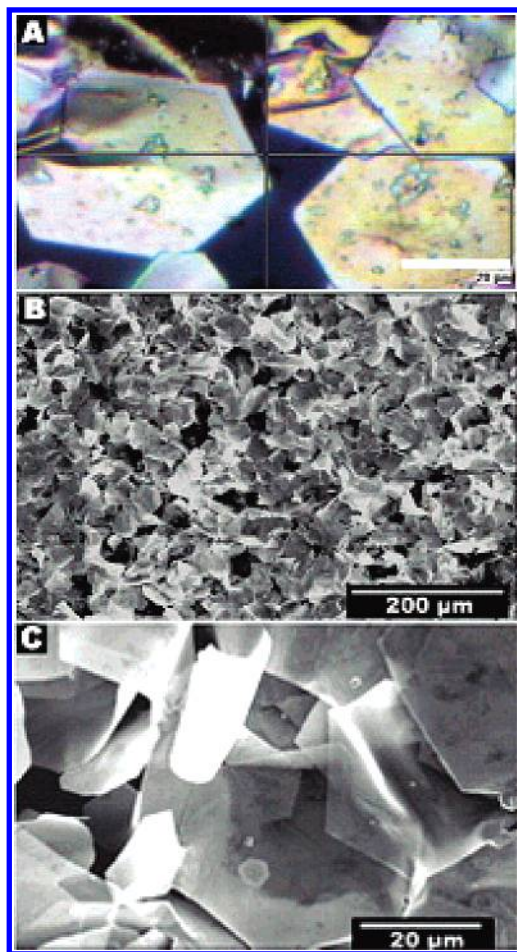(9) Sun, X.; Dong, S.; Wang, E. *Polymer* **2004**, *45*, 2181.

Figure 1. (A) Optical microscopy image (scale bar 20 μm), (B) lower magnification SEM image, and (C) higher magnification SEM image of the resulting precipitate deposited on an indium tin oxide (ITO) glass slide.

slide and air-dried at room temperature. SEM measurements were made on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. The sample for transmission electron microscopy (TEM) characterization was prepared by placing some precipitate or a drop of colloidal gold solution on a carbon coated copper grid and drying at room temperature. The TEM images were taken using a JEOL 2000 transmission electron microscope operating at 200 kV. 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. The sample for XRD characterization was prepared by placing some precipitate on a glass slide.

Results and Discussion

The morphology of the precipitate was first characterized with optical microscopy, as shown in Figure 1A. The image clearly indicates the formation of large plates (up to ~40 μm in size). SEM was used to further characterize the precipitate. The lower magnification image (Figure 1B) indicates that the precipitate consists of a large quantity of plates, mainly hexagonal in shape. The higher magnification image (Figure 1C) shows that these plates are transparent with several 10 nm in thickness (exact data not obtained), revealing that they are nanoplates. Energy-dispersive X-ray spectroscopy (EDS) indicates that the nanoplate is gold (data not shown).

Please note the following experimental facts: (1) There are no gold byproducts with other shapes except the nanoplates existing in the resulting precipitate. (2) Adding $NaBH_4$ to the colorless supernatant after the termination of reaction gives no gold particles, which indicates that
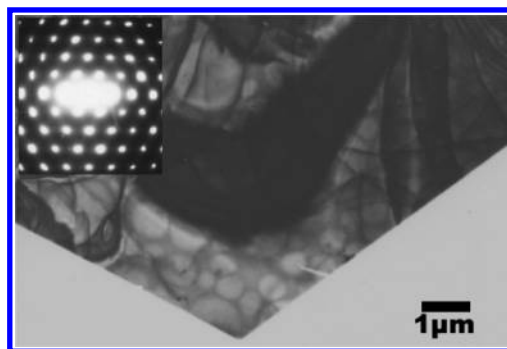

Figure 2. TEM image of a part of a single gold nanoplate and the corresponding selected area electron diffraction (SAED) pattern (inset).
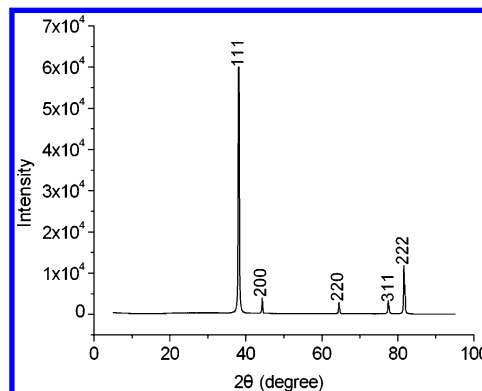

Figure 3. XRD pattern of the resulting gold nanoplates deposited on a glass slide.

$HAuCl_4$ in the mixture is depleted by LPEI. These two pieces of evidence indicate that this heat-treatment-based polyamine process is a high-yield approach for the preparation of large gold nanoplates.

A typical TEM image of a part of a single gold nanoplate is presented in Figure 2.[10] The Cu grids can be clearly observed, providing another piece of evidence for the transparent and thin nature of the gold nanoplate thus formed. The inset of Figure 2 shows the corresponding selected area electron diffraction (SAED) pattern obtained by focusing the electron beam on the nanoplate lying flat on the TEM grid. The SAED pattern reveals that a hexagonal symmetry diffraction spot pattern is generated, demonstrating that the gold nanoplate is a single crystal with a preferential growth direction along the gold {111} plane.[11]

The crystalline nature of the gold nanoplates was further confirmed by the corresponding XRD pattern (Figure 3). The five sharp peaks can be assigned to the {111}, {200}, {220}, {311}, and {222} diffraction peaks of metal gold, respectively, indicating that the precipitate is composed of pure crystalline gold.[12] Also mentioned is that the ratio of intensity between the {200} and {111} diffraction peaks is much lower than the standard file (JCPDS) (0.054 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.

In this synthesis, the use of concentrated reactants was critical to the formation of gold nanoplates. When the

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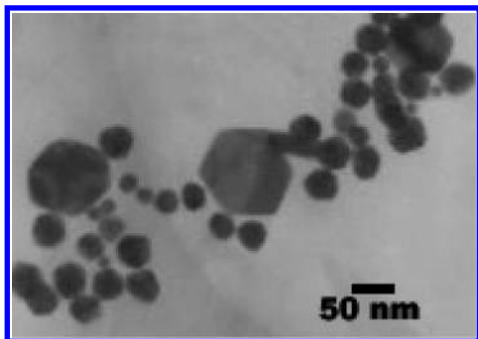(12) Maye, M. M.; Zheng, W.; Leibowitz, F. L.; Ly, N. K.; Zhong, C.-J. *Langmuir* **2000**, *16*, 490.

Figure 4. TEM image of gold nanoparticles obtained by decreasing the concentration of reactants to $^1/_{100}$ at 100 °C.

synthesis was performed under a low concentration of reactants, we only obtained a purple colloidal gold solution. Figure 4 shows a typical TEM image of the gold product obtained by decreasing the concentration of reactants to $^1/_{100}$, under otherwise identical conditions. Clearly, the resulting gold product mainly consists of small nanoparticles with an irregular shape. Some hexagonal nanoparticles are also noticed in the same sample. Our observations may suggest that LPEI can provide strong kinetic control over the growth rates of various faces of gold particles in a concentrated LPEI−HAuCl$_4$ aqueous

solution by becoming selectively adsorbed on the crystallographic planes, which results in the formation of large single-crystalline Au nanoplates. However, it is not clear at the present time how the LPEI influences the growth of different crystal plans of the gold nanoplates and the detailed mechanism requires further investigation.

Conclusion

The present work demonstrates the high-yield synthesis of large single-crystalline gold nanoplates through a polyamine process by heating a concentrated LPEI−HAuCl$_4$ aqueous solution at 100 °C. It was found that the concentration of reactants is the key to producing gold nanoplates. As-prepared gold nanoplates with a large Au-(111) face may hold promise for scanning tunneling microscopy (STM) substrates. In addition, exceptionally interesting materials with unique mechanical properties can be obtained with such colloids.[13]

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