Solvothermal Preparation of Single-crystalline Gold Nanorods in Novel Nonaqueous Microemulsions

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(Received January 26, 2005; CL-050118)

Single-crystalline gold nanorods have been prepared by one-step, seedless solvothermal reduction of $HAuCl_4 \cdot 4H_2O$ in cetyltrimethylammonium bromide (CTAB)/octane + butanol/formamide microemulsions. Formamide provides not only reduction but also sites occupied by Au^{3+} ion through replacing "water pools" in the traditional microemulsions.

The properties and application of nanostructured materials are strongly dependent on the size, morphology, and crystallinity. Preparation of anisotropic gold nanorods and nanowires, which show potential application in the optoelectronic field, have been reported.[1–3] Most of nanosized gold synthesis was performed with the $NaBH_4$ as reducing agent in the reverse micelle system, which may lead to too fast reduction rate. Polyol,[4,5] aspartate,[6] *N*,*N*-dimethylformamide,[7] dimyristoyl-L-phosphatidyl-DL-glycerol,[8] metallic Ag,[9] poly (ethylene oxide) blocks,[10] hydrazine,[11] glucose,[12] *meso*-2,3-dimercaptosuccinic acid,[13] and sodium citrate[14] were reportedly used as reducing agents of Au^{3+} to prepare metallic Au in the certain conditions such as at room temperature, under the microwave irradiation, at reflux, by electrochemical process or photoirradiation.

Though microemulsions are widely used as microreactors or nanoreactors to prepare nanomaterials, the microemulsions have almost all limited their inside cores to water pools until now. Self-assembly of surfactants in nonaqueous systems has recently been a hot topic as both a basic investigation and an attractive way to prepare water-free or water-sensitive materials. Formamide has been investigated as a solvent for micelle formation of surfactants, it has been found that micelle aggregates of some ionic surfactants can be formed in formamide solvent.[15] So we try to expand the microemulsions from aqueous pools (water cores) into nonaqueous pools (formamide cores). To our knowledge, this nonaqueous microemulsion is the first time used as nanoreactors for the synthesis of Au nanorods.

Solvothermal reduction route is widely used to prepare novel metal materials, because of its advantages such as high temperature and high pressure.[16] Until now, solvothermal reduction route has rarely been reported to the synthesis of gold nanomaterials.[17] Herein we report one-step seedless formamide-thermal reduction route to anisotropic single crystalline gold nanorods of high crystallinity by the reduction of $HAuCl_4 \cdot 4H_2O$ in CTAB/octane + butanol/formamide microemulsions.

In the glove-box filled with argon, the mixture of 1.09 g of CTAB, 2.74 mL of butanol, 1.2 mL of formamide, and 24 mL of octane was stirred for 10 min, and then 0.0245 g of $HAuCl_4 \cdot 4H_2O$ was added and further stirred for 10 min. The solution was transferred into a Teflon-lined stainless autoclave and kept at 130 °C for 20 h, 180 °C for 10 h and 180 °C for 20 h, respectively. After cooled to room temperature naturally, yellow colloids were obtained. The products were separated by centrifugation, washed with absolute ethanol several times, and dried at 80 °C in vacuum. The products were characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM) and X-ray diffraction (XRD).

Figure 1 shows TEM images of the typical samples by the solvothermal reduction at 180 °C for 10 h. Nanorods were observed. Nanorod has the diameter of about 135 nm and a length of ≈4 μm (shown in Figure 1a). Figure 1b shows a high magnification TEM image of a randomly chosen individual Au nanorod with a diameter of about 130 nm and a length of ≈1 μm (aspect ratios is ca. 8). One can see that the nanorod has the smooth edges, and its corresponding selected area electron diffraction (SAED, shown in the inset of Figure 1b) indicates that the gold nanorod is single crystalline. It can be indexed with the fcc symmetry. Some branch-like Au nanostructures were also observed (shown in Figure 1c). It confirms the formation of Au microemulsions in the reaction system and the diffusion of Au from one droplet to another in the transient droplet dimers.

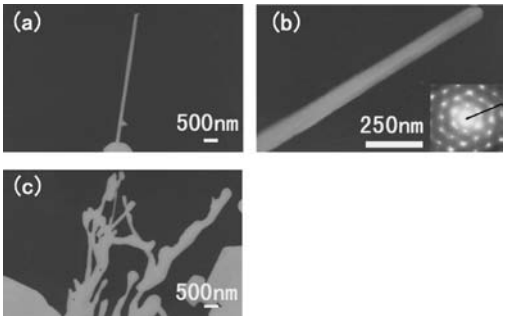

Figure 1. TEM images of the individual Au nanorod at 180 °C for 10 h (a). The high magnification with the inset is the SAED pattern (b). Branch-like Au nanostructures (c).

We also investigated the effect of reaction temperature and reaction time over the morphologies of the samples. By increasing heating time up to 20 h at 180 °C, nanorods with 230–480 nm in diameters and 6 μm in lengths (aspect ratios are ca. 12–26) were obtained (Figures 2a and 2b). Electron diffraction patterns of these nanorods reveal the similar single crystalline structures. Compared with the reported process to synthesize single-crystalline Au nanorods,[18] our method is a simple one-step process instead of multi-processes: formation of $AuCl_4^-$–surfactant complexes, photolysis of the complexes and the growth of Au particles, and the nanorods obtained in our experiments are larger in size. The relative ratio of number of Au nanorods to total number of Au nanostructures was estimated to be about 50%, the yield of

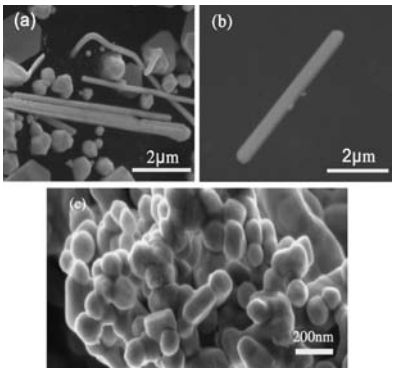

Figure 2. SEM images of the samples. (a) Several Au nanorods, (b) single Au nanorod obtained at 180 °C for 20 h. (c) Au nanoparticles at 130 °C for 20 h.

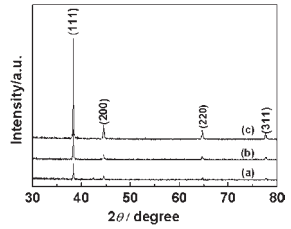

Figure 3. XRD patterns of typical samples prepared by solvothermal reduction at (a) 130 °C for 20 h, (b) 180 °C for 10 h, (c) 180 °C for 20 h.

Au nanorods is higher than that of (4%)[19] and (10%)[4] reported previously. When heating temperature was reduced to 130 °C, time even increased as long as 20 h, only elongated particles with diameters of about 150 nm were observed (Figure 2c).

Figure 3 shows XRD patterns of the typical samples, (a) is nanoparticles obtained at 130 °C for 20 h, (b) nanorods at 180 °C for 10 h, (c) size-increased nanorods at 180 °C for 20 h. The products are a single phase of well-crystallized elemental Au with a fcc structure, which is consistent with the result of SAED. This indicates that formamide reduced $HAuCl_4 \cdot 4H_2O$ to form metallic Au at the high temperature and high pressure. It is worth noting that the intensities of the peaks and the ratio between the intensities of the (111) and (200) or (111) and (220) planes increase from Figure 3a to Figure 3c (higher than their responding conventional values), which is attributed to the increased crystallinity and anisotropic growth. These results are consistent with the TEM and SEM analyses. Strong (111) peak shows that Au has a preferential growth direction along (111), and thus anisotropic gold nanostructures were formed.

As for the formation mechanism of single-crystalline gold nanorods, we preliminarily believe that the novel microemulsion is formed in the reaction system. It is reported dilute formamide in isooctane microemulsions gives rod-like aggregates.[20] We adjusted molar ratio of composition to form rod-like aggregates, which are used as template for the formation of Au nanorods. So molar ratio of CTAB/octane/butanol/formamide plays an important role in controlling the formation of Au nanorods. Solvothermal reduction method (high temperature and pressure and even the supercritical condition), on one hand, can increase the reduction ability of formamide and thus reach the suitable reaction rate. On the other hand, it facilitates the opening of droplets owing to a decrease in interfacial rigidity, enhanced interdroplet interaction, and rapid diffusion of Au from one droplet to another in the transient droplet dimers. The increased reaction time kept at 180 °C has led to size-increased nanorods, which is probably attributed to further and full growth of nanorods. The low temperature (130 °C, slightly higher than the boiling point of the solution: 125 °C) leads to the elongated spheric particles instead of nanorods. This is probably due to the weak interdroplet interaction, and slow diffusion of Au from one droplet to another in the transient droplet dimers.

In summary, single crystalline gold nanorods have been prepared by solvothermal reduction method in novel nonaqueous microemulsions. The novel solvothermal microemulsion system can provide a useful tool for preparation of other nanomaterials with different shapes, structures and crystallinity.

This work was financially supported by the Natural Science Foundation of Jiangsu Province (BK2002414).

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Published on the web (Advance View) April 22, 2005; DOI 10.1246/cl.2005.730