Preparation and Catalytic Activity of Two-dimensionally Networked Gold Nanowires

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Two-dimensionally (2-D) networked gold nanowires have been prepared by a simple chemical reduction method using glycerol as capping agents. It was found that 2-D gold nanowires were more active than spherical gold nanoparticles on hydrogen generation from sodium borohydride solution.

Since the optical, electric, catalytic, and magnetic properties of metal nanocrystals were considered to extensively depend on their shapes,[1] the fabricated nanocrystals with novel structures and shapes have attracted a great deal of attention. Recently, the preparation of 2-D networked gold nanowires has been actively studied because of its potential applications in the catalysis, optoelectronics, and nanoscale electronic devices. Many methods were used for the preparation of this specially shaped gold nanowires, such as wet chemical synthesis,[2] irradiation of an intense pulsed laser on Au nanoparticles in surfactant solution,[3] nanoparticle deposition within the porous template membrane,[4] laser ablation technique,[5] electrodeposition,[6] and electrochemical methods.[7] Although these methods have succeeded in preparation of uniform gold nanowires, the morphological effects on its chemical and physical properties were less reported. Therefore, more efforts should be done to investigate both the shape-controlled preparation of gold nanowires and the shape effects on its properties.

In this letter, a simple chemical reduction method for preparation of uniform and stable networked Au nanowires was reported. In addition, we found that the variation of the capping agents resulted in significant changes in the shape of the gold nanoproducts. The catalytic properties of shape-controlled gold nanocrystals for hydrogen generation reaction from sodium borohydride solution have also been studied. The networked gold nanowires showed higher activity than that of the spherical gold nanoparticle.

In a typical synthesis, 6 mL of glycerol was added to 25 mL of $HAuCl_4$ diluted solution (4×10^{-5} M) at 60 °C in a temperature-controlled water bath. Under strongly stirring, 0.2 mL of 0.05 M $NaBH_4$ solution (fresh prepared) was added rapidly, then the reaction mixture was kept still at 60 °C for 2 h. For comparison, spherical gold nanoparticles were prepared under the same condition but without glycerol. In all catalytic activity of experiments, 5 wt % $NaBH_4$ + 5 wt % NaOH solution was added to the sealed flask and given amount of catalyst, then the reaction was started while the solution was stirred vigorously. The volume of hydrogen gas evolved was measured by a gas chromatograph system equipped with a TCD detector.

The UV–vis absorption spectra of colloidal gold nanowires at different reaction time were shown in Figure 1A. Upon the addition of $NaBH_4$ solution, the initially light yellow solution became black, indicating the reduction of $AuCl_4^-$. As the reaction time increased, the strength of two absorptions at 528 and 970 nm increased. When the solutions turned to blue after 60 min, the color and UV spectrums remained constant even

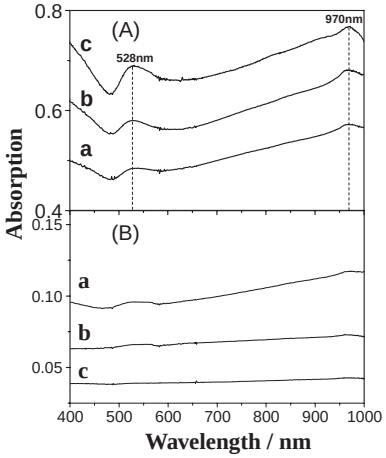

Figure 1. UV–vis absorption spectra of the synthesis solutions at different reaction time. (A) Networked gold nanowires, (B) spherical gold nanoparticles (a) 5 min; (b) 30 min; (c) 60 min.

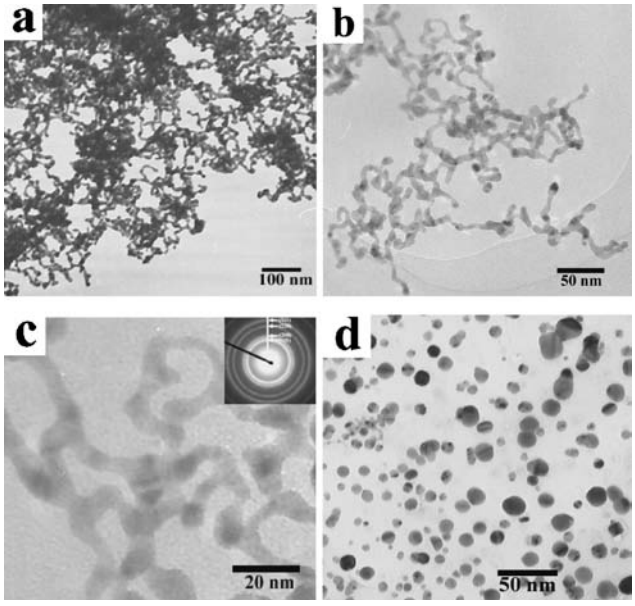

Figure 2. Representative TEM micrographs and diffraction pattern obtained from gold nanowires networks: (a) LRTEM of networked gold nanowires, (b) and (c) a higher magnification view and a selected-area electron diffraction pattern, and (d) spherical gold nanoparticles prepared without glycerol.

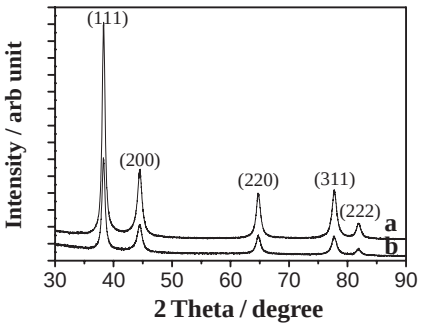

Figure 3. XRD patterns of networked gold nanowires: (a) networked gold nanoparticles, (b) spherical gold nanoparticles.

for months. However, in the case of preparation of spherical gold nanoparticles (Figure 1B), the plasmon band decreased gradually, and finally disappeared. It may be due to the aggregation of nanoparticles as indicated by increase in black flocculation parameter.

Figures 2a–2c showed typical TEM and SAED images of colloid gold nanowires. Clearly, these gold nanowires owned 2-D-networked structures and extended to a surface area of hundreds of nanometers. Its average diameter was approximately 5–10 nm as shown in a high-resolution TEM (HRTEM) image (Figure 2c). The electron diffraction (insert of the Figure 2c) showed scattering points corresponding to (111), (200), (220), and (311) reflections of gold crystalline facets, confirming that gold nanowires were comprised of many small face-centered cubic (fcc) nanocrystals. In contrast, Figure 2d showed TEM images of spherical gold nanoparticles prepared without glycerol. It can be seen that these gold nanoparticles have a broad size distribution, which corresponded to the flat peak in Figure 1B.

The X-ray diffraction (XRD) patterns of the spherical and networked gold nanoproducts were both shown in Figure 3, and the peaks were assigned to the diffraction of {111}, {200}, {220}, {311}, and {222} planes of fcc gold accordingly (PCPDF No. 04-0784), which was agreement with the electron diffraction of the colloidal gold nanocrystals. However, it should be noted that the networked gold nanowires owned higher diffraction intensity and narrower width of half peak height than spherical gold nanoparticles. The reason for this may be due to the extended surface of the two-dimensionally networked gold nanowires.

The effect of different capping agents on the morphology of Au nanocrystals was investigated and shown in Figure 4. It can be seen that Au nanoparticles with uniformly spherical shape and smaller size were obtained in the presence of 1,3-propylene glycol (Figure 4a). However, when 1,2-propylene glycol was used as a capping agent, the gold nanocrystals were consisted of anomalistic networked nanowires (Figure 4b). This result showed that the position and number of OH groups played an important role in the morphology of gold nanoproducts.

Finally, the catalytic behaviors of the prepared networked and spherical (prepared without glycerol) gold nanoproducts were explored using the hydrolysis of sodium borohydride liberating hydrogen gas as a probe. To the best of our knowledge, these colloidal gold nanocrystals were used, for the first time, as catalyst for this reaction. The comparison in the reactivity for the spherical gold nanoparticles (1.2 mg) and networked gold nanowires (1.2 mg) was shown in Figure 5. It can be seen that the

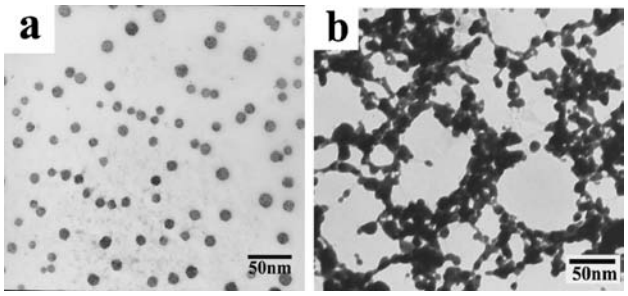

Figure 4. TEM images of Au nanoparticles: (a) prepared in the 1,3-propyleneglycol solution. (b) Prepared in the 1,2-propylene glycol solution.

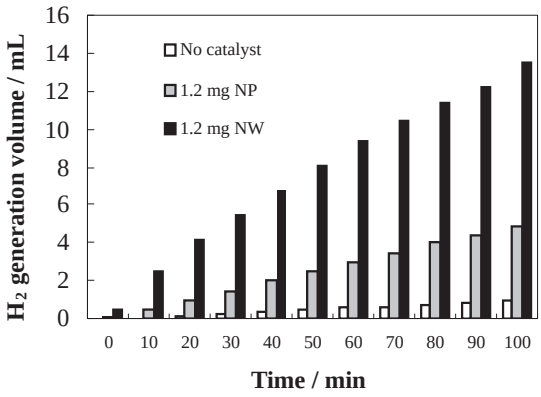

Figure 5. Hydrogen generation volume measured from 5 wt % $NaBH_4$ + 5 wt % NaOH solution over colloids gold catalysts at room temperature. NW: networked gold nanowires; NP: sphere gold nanoparticles.

catalytic activities were greatly dependent on the structural evolutions of colloidal gold catalysts. The networked gold nanowires showed higher activity than that of the spherical gold nanoparticle. During 100 min, the average hydrogen generation rate was calculated to be 1350, and 425 mL min^{-1} g^{-1} on networked gold nanowires and spherical gold nanoparticles, respectively, demonstrating the superior catalytic properties of the 2-D gold nanoarray material to spherical gold nanoparticles. The special 2-D networked structure and high surface area (nanowire: 6.09 m^2/g, nanoparticle: 3.41 m^2/g) of gold nanowires may result in high H_2 generation rate. The catalytic mechanism of hydrogen generation on colloidal gold nanocrystals with different shape is still under investigation.

In summary, a simple protocol for the preparation of uniform and stable 2-D networked gold nanowires has been developed. Moreover, we reported here the first successful application of colloidal Au nanocrystals toward the hydrogen-generation reaction from $NaBH_4$ solution and found that 2-D gold nanowires were more active than spherical gold nanoparticles.

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