Direct Chemical Synthesis of Gold Nanowires with 2-D Network Structure and Relationship between the Presence of Gold Ions and Shape Stability of Gold Nanowires

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Gold nanowires with a 2-D network structure were synthesized by a direct chemical synthesis method; the shape stability of gold nanowires was closely related to the presence of gold ions in the solution phase, without which the nanowires broke, and larger nanoparticles were formed.

The synthesis of metal nanowires has attracted a great deal of attention because of their unusual roles in the fabrication of nanoscale electronic devices[1] and investigation of quantized conductance and localization effects.[2] A lot of works have been done for the preparation of metal nanowires using various methods such as electrochemical[3] and photochemical[4] reduction in aqueous surfactant media, templating from porous alumina,[5] polycarbonate membrane[6] or carbon nanotube,[7] wet chemical synthesis based on a seed-mediated growth mechanism,[8] and solution-phase method based on capping reagents.[9] Although these methods have succeeded in synthesizing monodisperse uniform nanowires, some problems remain, for example, removal of surfactant, process complexity, or the search for a suitable capping agent. The formation mechanism is not yet fully understood. Therefore, it will be a significant challenge to simplify the synthesis route and clarify the growth mechanism of the anisotropic metal nanoparticles.

Here, we report the synthesis of gold nanowires with 2-D network structure using a simple chemical reduction method with a low concentration of reducing agent. The reaction system contains the gold precursor and reducing agent only. In addition, it was found that the gold ions played an important role in stabilizing the shape of gold nanowires in the formation process.

The experimental method was a modification of conventional citrate reduction of $AuCl_4^-$ in water developed by Frens (1973).[10] In a typical synthesis, aqueous solution of sodium tetrachloroaurate ($NaAuCl_4 \cdot 2H_2O$, 0.25 mM) was stirred in a temperature-controlled oil bath until the solution was warmed to 80 °C. Then a controlled amount of trisodium citrate was added rapidly into this solution. After the initiation of the reaction, the solution was taken out at specific time intervals for UV–vis spectroscopy and TEM observation. To monitor the concentration of gold ions during the reaction, 3 µL 48% HBr acid was injected into the 5-mL aliquots taken from the reaction flask, followed by centrifugation for 15 min at 6000 rpm. The supernatant layer was used to measure the UV–vis absorbance. Then, the concentration of gold ions was calculated from the peak absorbance at 381 nm. The initial molar concentration ratio of citrate/$NaAuCl_4$ (denoted as R) was controlled at 0.4 and 0.3, respectively.

Figure 1 shows the UV–vis absorption spectra taken from solutions at different reaction stages for R = 0.4 and R = 0.3. Upon the addition of sodium citrate, the initially light yellow solution became colorless, indicating the reduction of $AuCl_4^-$. It should be noted that when the solution turned blue, an almost flat absorbance curve with a board peak was observed from 500 to 900 nm, for example, at 6 and 20 min in Figure 1A, and 10 and 180 min in Figure 1B. When the solution color turned to wine red, the UV–vis spectrum exhibited a narrow peak at about 547 nm after 40 min at R = 0.4. Thereafter, this wine red color and UV spectrum remained constant over time, indicating the formation of stable gold nanoparticles. However, at R = 0.3, the flat adsorption pattern (Figure 1B) lasted until 180 min which corresponded to the blue solution.

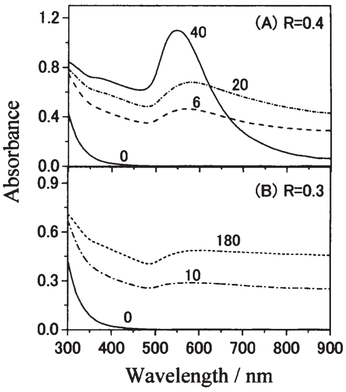

Figure 1. UV–vis absorption spectra of the reaction solutions at different reaction stages: (A) R = 0.4, reaction time of 0, 6, 20, 40 min; (B) R = 0.3, reaction time of 0, 10, 180 min. Temperature 80 °C.

Figure 2 shows typical transmission electron microscopy (TEM) images of samples prepared at R = 0.3 and R = 0.4 with various reaction times. Figure 2A clearly shows the formation of gold nanowires covering a 2-D space uniformly at R = 0.3 with 30 min reaction. Figure 2B shows that gold nanowires with such a 2-D network structure can also be formed at R = 0.4. The network structure of gold nanowires always corresponds to the flat UV absorbance pattern shown in Figure 1. Figure 2C is a high-resolution TEM image of one part of the gold nanowire showing a uniform diameter of approximately 11 nm. The electron diffraction of the gold nanowire (inset of the Figure 2C) shows scattering points corresponding to (111), (200), (220), and (311) of gold crystalline facets. These findings clearly indicate that gold nanowires are formed by tightly fused polycrystalline nanoparticles. In the case of R = 0.3, the shape of nanowires remained after 180 min of reaction. However, for R = 0.4, the nanowires broke and aggregated into nanoparticles (Figure 2D) of 50–60 nm after reaction of 40 min, which corresponded to the narrow peak in Figure 1A. There was no change in particle morphology observed after the larger particles were formed.

Time-resolved measurement of the concentration of gold

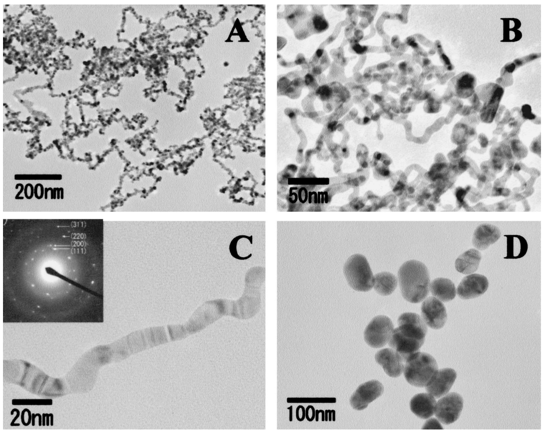

Figure 2. TEM images of gold nanowires taken from the reaction solution at different reaction stages: (A) R = 0.3, 30 min; (B) R = 0.4, 20 min; (C) HRTEM and ED, R = 0.4, 20 min; (D) R = 0.4, 40 min. The TEM samples were obtained by dropping the solutions onto carbon-coated copper grids placed on a filter paper for rapid removal of the liquid.

ions showed that the gold ions were completely reduced after 40 min when R was controlled at 0.4. However, the reduction reaction was much slower for R = 0.3 and a certain amount of gold ions remained in the solution after 180 min. The UV–vis spectra and TEM observations indicated that transformation from gold nanowires to particles always coincided with disappearence of the gold ions, indicating that gold ions played an important role in stabilizing the shape of gold nanowires during the formation process. In order to verify the decisive effect of gold ions on the shape stability, a TEM grid with as-synthesized nanowires was treated with H_2 gas at room temperature then observed again. Figure 3 shows that the beautiful nanowires (Figure 3A) broke after the H_2 treatment and larger particles were formed (Figure 3B). This result indicates that the gold ions capped on the surface of gold nanowires were reduced by H_2,[11] resulting in a breakdown of the nanowire shape.

The citrate reduction of $AuCl_4^-$ has been used for synthesis of gold nanoparticles.[10] The sodium citrate acts as both reducing agent and capping agent in the reaction. However, when the molar ratio of the sodium citrate/$NaAuCl_4$ was reduced to 0.4 or 0.3, the preliminary gold nanoparticles formed by the chemical reduction of $AuCl_4^-$ were considered to be thermodynamically unstable because of the insufficient capping of citrate. Furthermore, as presented in the study by Biggs et al., $AuCl_4^-$ can be adsorbed preferentially onto the gold surface even in the presence of excess citrate ions and initiate an attractive force between the gold surfaces.[12] Thus we can hypothesize that the formation of gold nanowires was initiated by the jump in of gold nanoparticles when they approached below 10 nm,[12] followed by deposition of newly-formed gold atoms onto the concave regions of the connected particles. Successively, the relatively excess of $AuCl_4^-$ adsorbed on the surface of nanowires maintaining their shapes. When the $AuCl_4^-$ had disappeared by the reactions, the nanowires broke and aggregated into thermodynamically stable gold nanoparticles. The formation mechanism of gold nanowires and its relation to the gold ions are still under investigation.

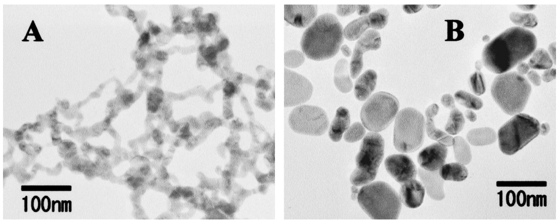

Figure 3. TEM images of as-synthesized gold nanowires (A) and after treatment with H_2 (B). The sample of A was prepared at R = 0.3 for 10 min. The TEM grid of B was obtained by putting the TEM grid A in the atmosphere of H_2 gas for 1 hour at room temperature.

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References and Notes

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