Self-assembled Gold Nanoparticle Chains in Presence of Silver Ions

Lanlan Sun, Yonghai Song, Gang Wei, Li Wang, Cunlan Guo, Yujing Sun, and Zhuang Li*
State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry,
Graduate School of the Chinese Academy of Sciences, Chinese Academy of Sciences,
Changchun 130022, P. R. China

(Received August 29, 2006; CL-060983)

A simple method has been developed to assemble gold nanoparticles to generate 1D assemblies by the assistance of silver ions. The lengths of nanoparticle chains can be controlled by adjusting the content of silver ions in the system. The assembly procedure of gold nanoparticles chains requires no template. The gold nanoparticle chains were characterized using TEM and XPS techniques.

Assembling nanoparticles (NPs) into one-, two-, and three-dimensional nanostructures has attracted much attention in recent years.[1–11] As an important noble metal, gold NPs have been assembled into different superstructures,[2,3,5,6,11] because of their wide applications in electronic, optical, and sensor, etc.[12] Among these assembly methods, templating techniques are mostly used, in which the templates include DNA, protein, viruses, and other predesigned nanostructures.[1,5,8,9] For further study in this area, assembling gold NPs into 1D nanostructures by template-free wet-chemical approaches is highly desirable. Recently, Zeng and Zhang[13] have described a template-free method to construct parallel 1D assembly of gold NPs by the assistance of organic surfactants, and the length of NPs chains and their interchain space can be controlled by adjusting content of the surfactant, the size of metal particles, and the amount of solvent for dispersion. Here, we report a simple, template-free approach to prepare gold NPs chains by introducing silver ions into the reactants. By controlling the content of silver ions, the length of gold NPs chains can be further controlled.

Ten mL of 0.25 mM aqueous $HAuCl_4$ (A. R., purchased from Beijing Chemical Co.) solution was mixed with 1 mM (0.1, 0.5, 1.0, and 2.5 mL) aqueous (A. R., purchased from Beijing Chemical Co.) $AgNO_3$ solution. To this mixed solution, 0.25 mL of 1 mM aqueous 2-mercaptosuccinic acid (MSA, purchased from Aldrich) solution was added all at once, followed by heating at 100 °C for about 10 min. The solution developed a gray-green color. Subsequently, the heater was removed and the solution was left undisturbed at air for at least 1 h. The morphology of reaction products was observed by TEM images taken at 100 kV using a JEOL-1000 TEM. For all TEM observations, the sample was diluted four fold with ultrapure water, and a droplet of this sample solution was placed on a carbon-coated copper grid and let the solution evaporated at room temperature. The X-ray photoelectron spectra were collected on an ESCA Lab MK II X-ray photoelectron spectrometer (VG. Co., U.K.). Figure 1 presented typical TEM images of gold NP chains prepared in the presence of 1 mM $AgNO_3$ with the volume of 0.1, 0.5, 1.0, and 2.5 mL, respectively. These images displayed nanochains with lengths changing from several tens nanometers to several micrometers. Figure 1a shows the result of a growth process with 0.1 mL of $AgNO_3$, showing short nanochains consisting of a few NPs, the bottle necks between the adjacent particles are visible. The results indicate the formation of nanochains, and some of the chains have reached several tens nanometers. Figure 1b shows the results of the sample with 1 mM $AgNO_3$ with volume of 0.5 mL, where nanochains of several hundreds nanometers were observed, and there still exists short nanochains with several tens nanometers length in the samples. Figure 1c shows the results of the growth process with 1 mM $AgNO_3$ with volume of 1.0 mL, the length of nanochains further increased to several micrometers. Figure 1d suggests that the nanochains get longer than nanochains in Figure 1c. From these results, it can be concluded that the lengths of gold nanochains can be controlled by varying the volume of $AgNO_3$. The crystallographic structure of the Au nanochains is verified with the electron diffraction pattern investigated in Figure 2. The nanochains obtained are polycrystalline. In other words, the nanochains consist of individual different crystallites having different crystalline orientation. The XPS results of these nanochains obtained with different silver content are shown in Figure 3, which indicates that the gold is in its zerovalent states. Binding energies of Au (4f) electrons were determined and compared with those of bulk gold samples. According to above results a hypothesis was proposed to explain why the $AgNO_3$ volume changes the lengths of the nanochains. As the $AuCl_4^-$ is partly hydrolyzed through the following reaction:[14,15]

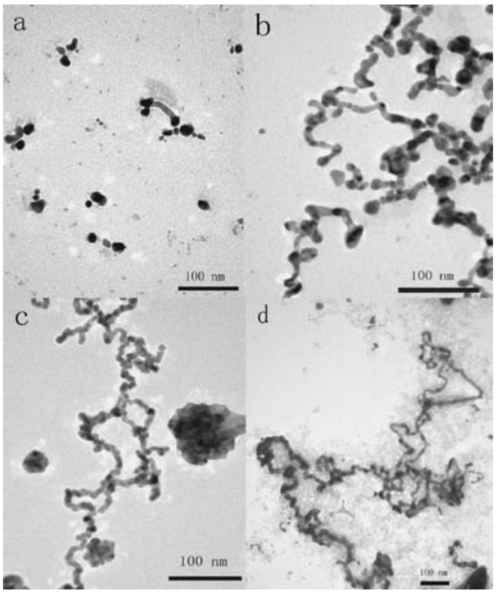

Figure 1. TEM images of gold nanoparticle chains prepared with 1 mM $AgNO_3$: (a) 0.1, (b) 0.5, (c) 1.0, and (d) 2.5 mL.

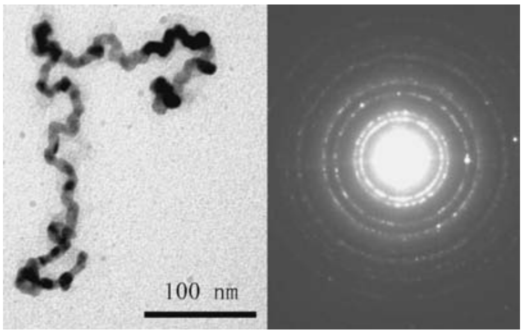

Figure 2. TEM image and its electron diffraction pattern of gold nanoparticle chains prepared with 2.5 mL of 1 mM $AgNO_3$.

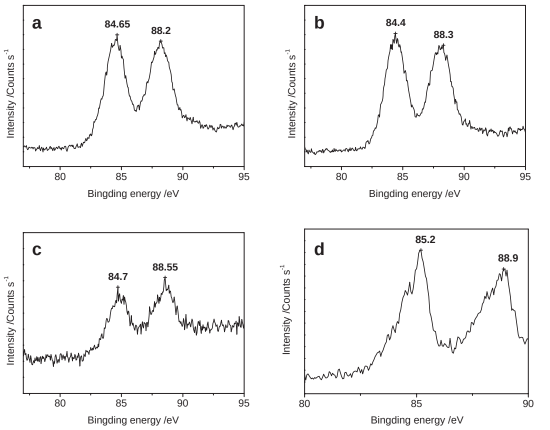

Figure 3. The XPS spectra of gold nanowires prepared with $AgNO_3$: (a) 0.1, (b) 0.5, (c) 1.0, and (d) 2.5 mL.

$$AuCl_4^- + H_2O \rightleftharpoons AuCl_3OH^- + H^+ + Cl^- \qquad (1)$$

The equilibrium constant for the reaction (298 K) was reported to be $2.4 \times 10^{-6}\,M^2$ in aqueous solutions.[15] The equilibrium principle shows that in the presence of Ag^+ ions, the concentration of Cl^- ions decreased and the concentration of H^+ ions increased. Therefore, there may be two possible interpretations about the influence of silver ions. It is well known that Cl^- ions always incline to adsorb to gold surface, accordingly may prevent NPs to come close. The presence of silver ions decreases the concentration of Cl^- ions through the formation of AgCl, thus preventing the adsorption of Cl^- onto the gold NPs, which eventually results in the prolongation of NP chains. Jana et al. have reported that the nanorods prepared would convert to nanocrystals at the absence of silver ions.[16] El-Sayed and Nikoobakht have proposed that silver ions could assist in the template elongation by pairing with Br^- ions of CTAB.[17] For another factor to influence the length of NPs chains, pH should be taken into account. In this paper, the low pH of the solution will make most carboxyl group of the MSA existing in the form of –COOH rather than $–COO^-$. As carboxyl group is outside the MSA-capped NPs, and the repulsion between the $–COO^-$ is stronger than that of –COOH because that the electric repulsion exists between $–COO^-$ ions. Hence, under low pH, the repulsion between gold NPS is lower than high pH. Accordingly, the content of Ag^+ ions has an influence on the assembly of gold NPs. To further understand the effect of silver ions on the assembly of nanochains, we performed a control experiment in the absence of $AgNO_3$, and main products were nanoclusters (shown in Figure 4). And the average diameter of the nanoparticles are about 7–8 nm. The control experiment further confirms that the silver ions could affect the assembly of nanochains by adjusting the concentration of Cl^-.

Figure 4. TEM image of gold NPs prepared in the absence of $AgNO_3$.

We have demonstrated a one-step, template-free solution method to assemble gold NPs into chains. The lengths of gold NP chains can be controlled by introducing different contents of silver ions, as the silver ions may change the Cl^- ions concentration and pH in the system. Moreover, the method is expected to extend the field of controlling the assembly of NP chains.

This work was supported by the National Natural Science Foundation of China.

References

1 S. H. Park, R. Barish, H. Y. Li, J. H. Reif, G. Finkelstein, H. Yan, T. H. LaBean, *Nano Lett.* **2005**, *5*, 693.

2 A. D. Bates, B. P. Callent, J. M. Cooper, M. Cosstick, C. Geary, A. Glidle, L. Jaeger, J. L. Pearson, M. Proupin-Perez, C. G. Xu, D. R. S. Cumming, *Nano Lett.* **2006**, *6*, 445.

3 R. P. Liang, H. D. Qiu, P. X. Cai, *Anal. Chim. Acta* **2005**, *534*, 223.

4 M. Qhobosheane, P. Zhang, W. H. Tan, *J. Nanosci. Nanotechnol.* **2004**, *4*, 635.

5 R. A. McMillan, C. D. Paavola, J. Howard, S. L. Chan, N. J. Zaluzec, J. D. Trent, *Nat. Mater.* **2002**, *1*, 247.

6 B. Nikoobakht, Z. L. Wang, M. A. El-Sayed, *J. Phys. Chem. B* **2000**, *104*, 8635.

7 Y. Lin, A. Boker, J. B. He, K. Sill, H. Q. Xiang, C. Abetz, X. F. Li, J. Wang, T. Emrick, S. Long, Q. Wang, A. Balazs, T. P. Russell, *Nature* **2005**, *434*, 55.

8 Y. Huang, C. Y. Chiang, S. K. Lee, Y. Gao, E. L. Hu, J. De Yoreo, A. M. Belcher, *Nano Lett.* **2005**, *5*, 1429.

9 M. N. Zhang, L. Su, L. Q. Mao, *Carbon* **2006**, *44*, 276.

10 Y. F. Liu, S. P. Wang, J. W. Lee, N. A. Kotov, *Chem. Mater.* **2005**, *17*, 4918.

11 A. N. Shipway, M. Lahav, R. Gabai, I. Willner, *Langmuir* **2000**, *16*, 8789.

12 A. N. Shipway, E. Katz, I. Willner, *ChemPhysChem* **2000**, *1*, 18.

13 Y. X. Zhang, H. C. Zeng, *J. Phys. Chem. B* **2006**, *110*, 16812.

14 L. I. Elding, A. B. Groning, *Acta Chem. Scand.* **1978**, *A32*, 867.

15 L. Carlsson, G. Lundgren, *Acta Chem. Scand.* **1967**, *21*, 819.

16 N. R. Jana, L. Gearheart, C. J. Murphy, *Adv. Mater.* **2001**, *13*, 1389.

17 B. Nikoobakht, M. El-Sayed, *Chem. Mater.* **2003**, *15*, 1957.