Controlled Organization of Silver Nanoparticles into Network Assemblies by Tuning pH Values

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

(Received November 20, 2006; CL-061368)

We demonstrate the pH-induced assembly of 2-mercaptosuccinic acid-functionalized silver nanoparticles (MSA–Ag NPs) in the absence of hard or soft template. Two-dimensional (2D) and three-dimensional (3D) networks of silver NPs were achieved by tuning pH of the medium. The assembly process was monitored using atomic forces microscopy. The key factor affects the formation of network of silver NPs may be intermolecular hydrogen bonding between two carboxylic acid groups of MSA on two adjacent silver NPs.

The assembly of metal nanoparticles (NPs) into defined architectures has attracted much attention, because such metal NPs assemblies have optical and electrical characteristics that are different from individual particles,[1] and more complex nanostructures are in demand (e.g., nanowires, nanotubes, 2D and 3D nanoparticle assemblies). Several approaches, such as electrostatic,[2,3] covalent,[4,5] van der Waals forces,[6,7] and hydrophobic interactions[8] have been mostly utilized to prepare such nanostructured materials with various architectures. Most of these methods employed chemical or structural templates.[9–12] Recently, there has a great deal of interests to develop templateless low-temperature wet-chemical approaches to assemble nanoscale building blocks into larger scale structures.[13] Here, we investigated the assembly of 2-mercaptosuccinic acid-functionized silver NPs controlled by tuning pH values of solution. By controlling the pH values of the solution, various dimensional networks of silver NPs can be obtained. The nature of assembly is hydrogen bonding between 2-mercaptosuccinic acid (MSA) molecules, which process two free –COONa (COOH) groups and one –SH group which interacts with silver NPs surface. The –COONa groups can be acidified below its pK_a value and usually form intermolecular hydrogen bonds.[14]

Ten milliliters of 0.25 mM $AgNO_3$ solution (A. R., purchased from Beijing Chemical Co.) was at first mixed with 1 mL of 2-mercaptosuccinic acid (97%, MSA) and stirred for about 10 min to give a homogenous transparent solution. A freshly prepared 10 mM aqueous $NaBH_4$ solution (about 0.5 mL) was then added dropwise under vigorous stirring. The solution turned yellow-brown immediately and remained transparent. The pH value of the solution is at the range of 6–7. Then, standard HCl solution was added to adjust the pH value. UV–vis spectra were collected using a Cary 500 UV–vis NTR spectrometer (Varian). Tapping mode atomic force microscopy (AFM) imaging was performed on a Digital Instrument Multimode AFM controlled by a Nanoscope IIIA (DI, Santa Barbara, CA) equipped with an E scanner. Scan rate is 1–1.5 Hz.

The preparation of silver NPs was conducted by direct chemical reduction of silver nitrate in the presence of MSA by $NaBH_4$. A representative spectrum of MSA-capped silver NPs possessed a strong plasmon resonance peak at 410 nm, as shown in Figure 1a. The final pH of the obtained silver colloids is 6–7. The pK_{a1} and pK_{a2} values of MSA are 4.19 and 5.64, respectively.[15] And the silver NPs are actually stabilized through the interaction of –SH groups of MSA with silver atoms, leaving free –COONa (COOH) groups on the surface. Under pH 6–7, the –COONa other than –COOH groups exist on the surface of silver nanoparticles, so dispersed silver NPs will be formed by the strong repulsion between negatively charged carboxylate ions. Figure 2a shows the AFM image of well-dispersed silver nanoparticles. The dimension of the particles was measured according to the height but not width because the AFM tip radius will affect the measurements. A statistical histogram showed that the mean diameter of the silver NPs was about 8 nm, as shown in Figure 2b.

Figure 1b is the UV–vis absorption spectrum of the silver nanoparticle solutions at pH 5, which shows a red shift comparing with the spectrum of the silver nanoparticles. The red shift of the spectrum is attributed to the aggregation of silver nanoparticles. And Figure 3a shows the AFM micrograph of the assembly of MSA-capped silver NPs at pH 5. The AFM image reveals that

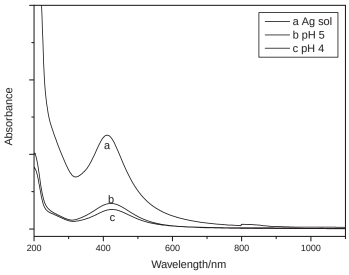

Figure 1. UV–vis spectra of 2-mercaptosuccinic acid-modified silver nanoparticle solutions with different pH: (a) 6–7; (b) 5; (c) 4.

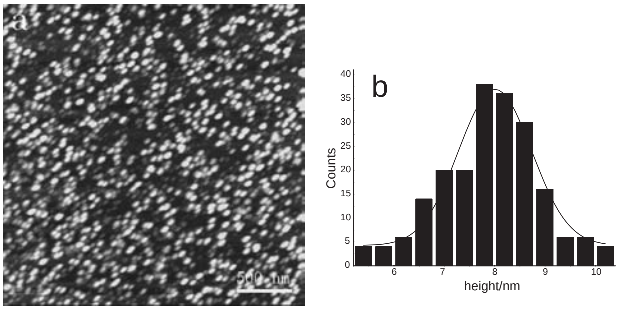

Figure 2. (a) AFM image of 2-mercaptosuccinic acid-modified silver nanoparticles. (b) Statistical histogram of diameter of silver nanoparticles by section analysis of AFM.

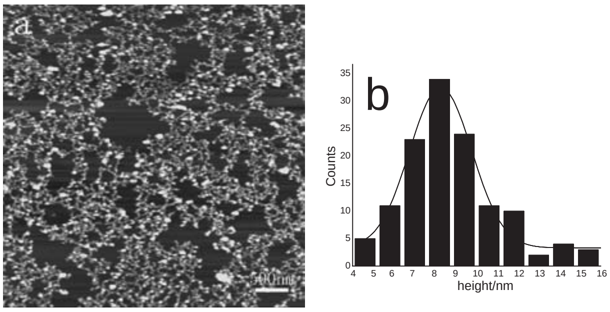

Figure 3. (a) AFM micrographs of the assembly of MSA-capped silver NPs at pH 5. (b) Statistical histogram of diameter of networks of silver NPs at pH 5.

at pH 5, the assembly is leading to the formation of mainly 2D architectures, which agrees well with the UV–vis absorption results. The silver NPs are interlinked together to form a network of silver NPs as large as 5 μm^2, and a statistical analysis reveals that the mean diameter of chains in networks was about 8 nm (Figure 3b), which is consistent with the diameter of single silver NPs. From these AFM images, it also suggests that some single silver NPs "glue" to the networks so that results in obvious height increase in some place of the networks. Section analysis of these places shows that the height is about 16 nm, which is in close agreement with the sum of diameter of two single silver NPs. At pH 5, which is just between pK_{a1} (4.19) and pK_{a2} (5.64), so one of –COONa groups is acidified to the –COOH group and forms intermolecular hydrogen bonds. The hydrogen bonding between –COOH groups of MSA molecules brings the silver NPs into close adjacent and result in a network architectures. The networks of silver NPs are extremely stable, and it will not cause the movement of the networks on the substrates, even if scanned this sample for many times, which indicates a strong cross-linking interaction rather than random arrangement. Because only one of the –COONa groups is protonized, the hydrogen-bonding interaction is limited. Therefore, the chains in the networks are mostly composed of one nanoparticles as shown in AFM image (Figure 3a).

The optical spectrum of silver nanoparticle solutions at pH 4 is shown in Figure 1c. A continuous red shift can be seen comparing with Figure 1b due to the continuous aggregation of the silver nanoparticles. Figure 4a shows 3D silver NPs networks prepared at pH 4. Compared to the image in Figure 3a, the diameter of the network chains is increased, and a histogram analysis reveals the diameter of the network chains is about 16 nm (shown in Figure 4b) which is consistent with the sum of diameter of two silver NPs. From these images, it is clearly that no single nanoparticle exists on the surface of mica, which indicates the formation of extensive hydrogen bonding between the silver NPs. From above results, we can conclude that the assembly process is more controlled at pH 4 compared to that at higher pH values such as pH 5. According to the simplest interpretation, the change in pH value mainly influences the hydrogen-bond forming by tuning the protonation of the –COONa groups. At pH 4, which is lower than pK_{a1} (4.16), both of –COONa groups in a MSA molecule are protonized and result in extensive hydrogen-bonding interaction. Thus at lower pH, more hydrogen bonding between –COOH groups of MSA brings the silver NPs into more dense assembly and produce 3D networks of silver NPs.

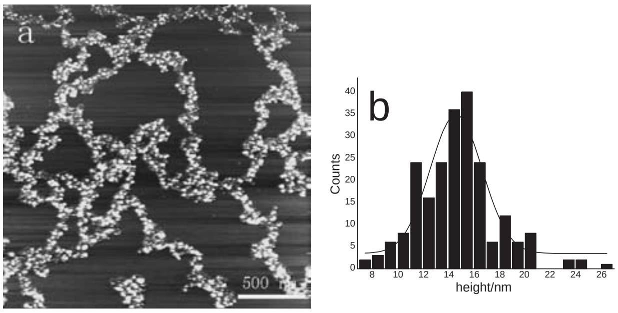

Figure 4. (a) AFM micrographs of the assembly of MSA-capped silver NPs at pH 4. (b) Statistical histogram of diameter of networks of silver NPs at pH 4.

We demonstrated a very simple method for assembling 2D and 3D silver networks through intermolecular hydrogen bonding between carboxylic groups of two adjacent surface bound MSA molecules. A key aspect on their assembly is to restrict the hydrogen-bonding formation by varying the pH of the medium. The networks have uniform diameter identical to that of one or two nanoparticles. Extending our technique to other material system would open up the possibility of preparation of large structures from nanoparticles, for applications such as self-supporting networks for devices, and porous nanofilters for composites.

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

References

1 D. Feldheim, *Electrochem. Soc. Interface* **2001**, *10*, 22.
2 M. G. Warner, J. E. Hutchison, *Nat. Mater.* **2003**, *2*, 272.
3 A. N. Shipway, M. Lahav, R. Gabai, I. Willner, *Langmuir* **2000**, *16*, 8789.
4 C. M. Niemeyer, B. Ceyhan, S. Gao, L. Chi, S. Peschel, U. Simon, *Colloid Polym. Sci.* **2001**, *279*, 68.
5 A. M. Kalsin, M. Fialkowski, M. Paszewski, S. K. Smoukov, K. J. M. Bishop, B. A. Grzybowski, *Science* **2006**, *312*, 420.
6 Z. L. Wang, *Adv. Mater.* **1998**, *10*, 13.
7 B. Kim, S. L. Tripp, A. Wei, *J. Am. Chem. Soc.* **2001**, *123*, 7955.
8 N. A. Kotov, *Nanostruct. Mater.* **1999**, *12*, 789.
9 M. F. Zhang, M. Drechsler, A. H. E. Muller, *Chem. Mater.* **2004**, *16*, 537.
10 S. Hoeppener, R. Maoz, S. R. Cohen, L. F. Chi, H. Fuchs, J. Sagiv, *Adv. Mater.* **2002**, *14*, 1036.
11 N. Chandrasekharan, P. V. Kamat, *Nano Lett.* **2001**, *1*, 67.
12 M. G. Warner, J. E. Hutchison, *Nat. Mater.* **2003**, *2*, 272.
13 Z. J. Zhong, J. Z. Luo, T. P. Ang, J. Highfield, J. Y. Lin, A. Gedanken, *J. Phys. Chem. B* **2004**, *108*, 18119.
14 J. Clayden, N. Greeves, S. Warren, P. Wothers, *Organic Chemistry*, Oxford, University Press, New York, **2001**.
15 L. G. Wade, Jr., *Organic Chemistry*, Prentice Hall, New York, **1987**, p. 987.