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Investigation of passivated silver nanoparticles

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Abstract

Two-dimension self-assembly superlattices of passivated silver nanoparticles were formed on amorphous carbon films. Transmission electron microscopy (TEM) of the silver nanoparticles indicates that the particle formation involves a dynamic process. In X-ray photoelectron spectroscopy (XPS) spectra, the Ag3d_{5/2} value decreases first from 368.3 to 367.95 eV, and then to 367.65 eV during the formation, which indicates that the 1-nonanethiol is just physically adsorbed on the surface of the nanoparticles at the beginning of the reaction. Subsequently, the chemical bond was formed between the Ag atoms and S ions, which further demonstrated that the large particles were decomposed into smaller ones in the middle of the particle formation process. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Nanometer size crystals, nanocrystals (NCs), display many properties, which are both quantitatively and qualitatively different from their respective bulk materials and from the discrete atomic or molecular species from which they are derived. In the past few years, much interest has been focused on the size control of nanoparticles and the self-assembly into two-dimensional (2D) and three-dimensional (3D) superlattice structures [1–18]. Using colloidal metal or semiconductor nanoparticles as building blocks to construct ordered mesoscopic structural materials will provide the possibility of detecting the collective physical properties of the ensemble, and further explore size-tunable optical and electronic properties of the NCs in devices such as single electron transis-

tor, etc. In order to prepare the small particles at nanometer-scale and obtain the ordered 2D or 3D structure, capped organic molecules such as alkylthiol are necessary for preventing the nanoparticles from irreversible aggregation in a solvent, making the particles soluble in given solvents and forming the self-assembly superlattice structure. Therefore, the information about the properties of organic molecules capped at the surface of the nanoparticles is of interest. In addition, tight size distribution is also necessarily required for the superlattice formation. Thus, the study on the formation process of nanoparticles is helpful for understanding the particle growth and controlling the size distribution. Recently, several literatures have paid attention to the investigation of the formation of the passivated nanoparticles [4,19,20]. In the Letter, using the self-assembly method, two-dimensional superlattice was formed on the carbon films coated on transmission electron microscopy (TEM) copper grids. Then, the formation of the 1-nonanethiol protected silver

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nanoparticles prepared in the liquid–liquid two-phase system was analyzed with TEM. The results showed that the formation of the silver nanoparticle is a dynamic process, i.e. initially larger particles were quickly formed, followed by decomposition into smaller and more stable particles. In order to give a rational explanation about this formation process, X-ray photoelectron spectroscopy (XPS) was used to examine the bonding structure between the S atoms of 1-nonanethiol and Ag during the formation of silver nanoparticles protected by 1-nonanethiol.

2. Experiment

Silver nitrate (AgNO_3) and sodium borohydride (NaBH_4) were obtained from Acros Chemical, Tetra-n-octylammonium ($(\text{C}_8\text{H}_{17})_4\text{NBr}$) from Tokyo Chemical, 1-nonanethiol ($\text{CH}_3(\text{CH}_2)_8\text{SH}$) and other reagents were supplied by the Aldrich Chemical. All the reagents were used as-received, without further purification and all the water deionized.

Silver nanoparticles were prepared according to [21]. Thirty milliliters of an aqueous silver ion solution (0.03 M AgNO_3) was mixed with 20 ml of a chloroformic solution of phase transfer catalyst (0.20 M $(\text{C}_8\text{H}_{17})_4\text{NBr}$) and stirred vigorously for 1 h. The French gray organic phase was subsequently collected and suitable volume of 1-nonanethiol was added according to the nanoparticles size wanted. After the nonanethiol/ Ag^+ solution was stirred for 15 min, 24 ml of fresh aqueous sodium borohydride (0.43 M NaBH_4) solution used as the reducing agent was injected, and the system color became sable immediately. The reaction mixture was stirred for over 4 h before the organic/nanocrystal rich phase was collected. The dispersion was washed three times with ethanol to remove the phase transfer catalyst, excess 1-nonanethiol, and reaction by-products.

TEM images were obtained from a JEM 200CX operating at 200 kV by dropping the solution on the carbon film-coated copper grids. XPS were measured on the ESCA LAB5 X-ray photoelectron spectrometer with monochromated Mg X-ray at 10 kV.

3. Results and discussion

Fig. 1 is a typical TEM image of the 1-nonanethiol capped silver nanoparticles 2D superlattices. In Fig. 1, the inset picture in the upper-left hand is the 2D Fourier transform power spectrum of the zoom area, which confirms the hexagonal close-packed (hcp) structure. From the down-left insert histogram of the size distribution, we can find that the standard deviation of the size distribution is about 0.23. The further observation as shown in Fig. 1 demonstrates that the mean diameter of the nanoparticles is 4.2 nm, and the average spacing between neighboring particles is 1.5 nm. The domains are usually separated by domain boundaries resulted from the rate of solvent evaporation and the rough morphology and the defects on the surface of the substrate.

As mentioned above, the study of the formation of nanoparticles is helpful to understand the particle growth and control the size distribution of the particles. In fact, as mentioned in Section 2, the color change showed the size change process of the nanoparticles during the reaction. Upon dropping sodium borohydride solution into the nonanethiol/ Ag^+ mixture, the color of the solution changed quickly from French gray to sable or black in a few seconds, which indicates the for-

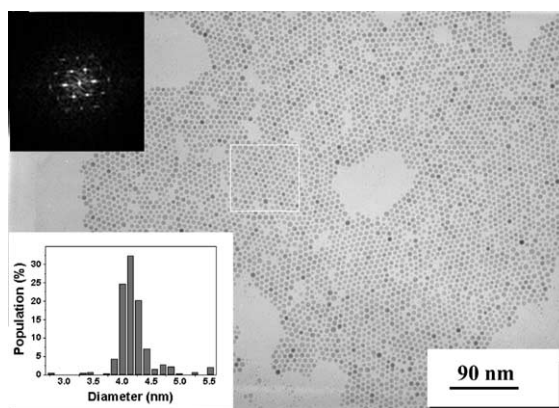


Fig. 1. TEM image of a two-dimensional silver nanoparticle superlattice, the inset histogram of the nanoparticles (low-left), and the 2D Fourier transform power spectrum of the zoomed image (up-left).

mation of silver particles [19]. However, the color gradually changed to orange when the mixture was stirred for a longer time at room temperature, suggesting that the initially produced particles were not stable and were decomposed back to smaller ones. The formation process of the 1-nonanethiol protected silver nanoparticles was investigated by TEM. At different reaction times, the synthetic solutions were put on the carbon film-coated TEM copper grids. Fig. 2 showed the TEM micrographs of the nonanethiol-capped silver particles at different reaction times. It has been found that the particles were quite big in the range of 4.4 ± 1.3 nm, and the size distribution was broad at the initial time of 15 min. However, at the reaction time of 30 min, the particle size strongly decreased to 2.1 ± 0.5 nm. With the time of 1 h, the size of the particles increased to 3.2 ± 0.5 nm,

when the particle was more uniform than that at the initial time of 15 min. These results show that the formation of the silver nanoparticle capped by 1-nonanethiol is as follows. Larger particles are formed at the beginning of the reaction, then the larger particles are decomposed into smaller ones, and finally the nanoparticle became larger again. However, in this formation process, what is the mechanism for the larger particles decomposing into the smaller one? Why do the larger particles break into smaller ones?

In order to make clear the formation mechanism of the silver nanoparticle, we investigated the interaction between the S atoms of 1-nonanethiol and the Ag atoms during the formation of 1-nonanethiol protected silver nanoparticles with XPS. The $S2p_{3/2}$, and $Ag3d_{5/2}$ peaks of the 1-nonanethiol-capped silver nanoparticles at different re-

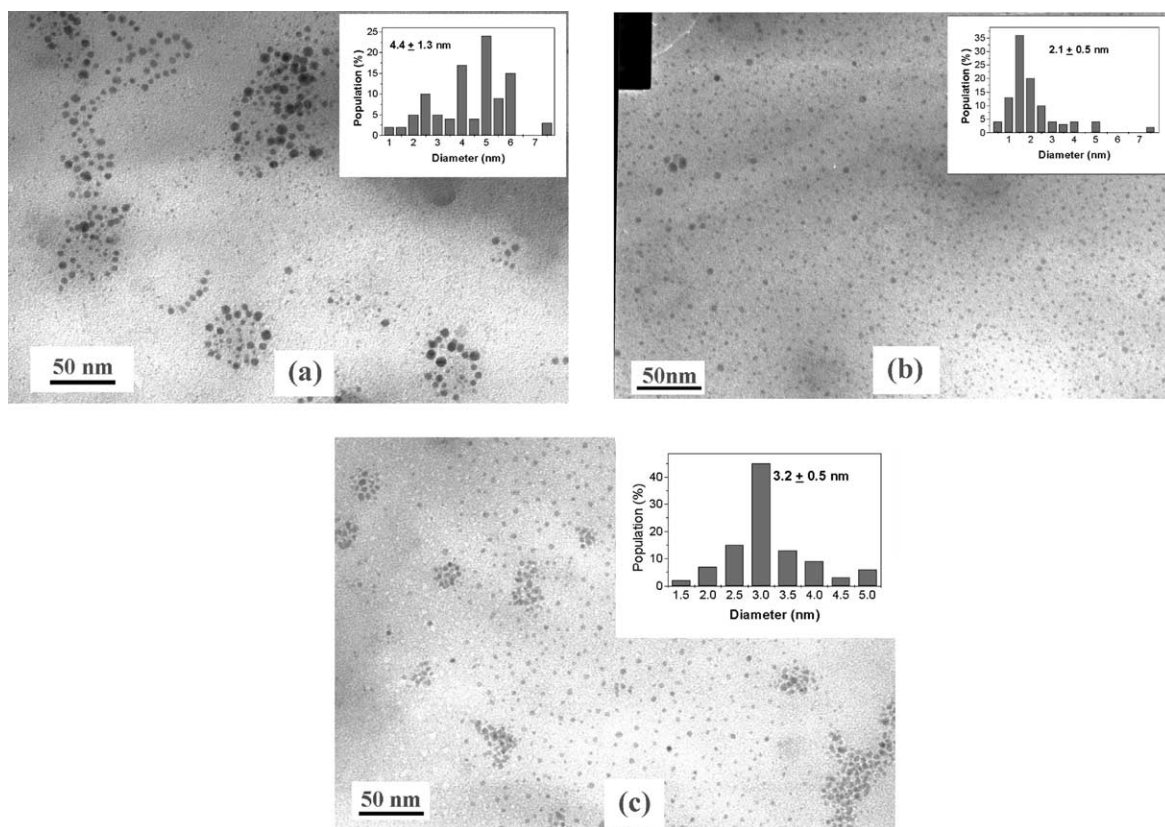


Fig. 2. TEM images of silver nanoparticles at different reaction times: (a) 15 min; (b) 30 min and (c) 60 min, and the corresponding size histograms inserted.

action times during the particle formation were measured. Fig. 3a is the XPS spectrum of the capped silver nanoparticle at a reaction time of 15 min. As shown in Fig. 3a, in all XPS spectra of the measured samples, no oxygen, chlorine and bromine were detected. Fig. 3b is the XPS spectrum of the Ag3d_{3/2} and Ag3d_{5/2} at the time of 15 min, which shows that the valence state of silver element is Ag⁰. All the values of the Ag3d_{5/2} and the S2p_{3/2} of the passivated silver nanoparticle at different reaction times are listed in Table 1. Comparing the S2p_{3/2} binding energies of 1-nonanethiol and the Ag3d_{5/2} of the silver atoms, we can see that there is no obvious difference between

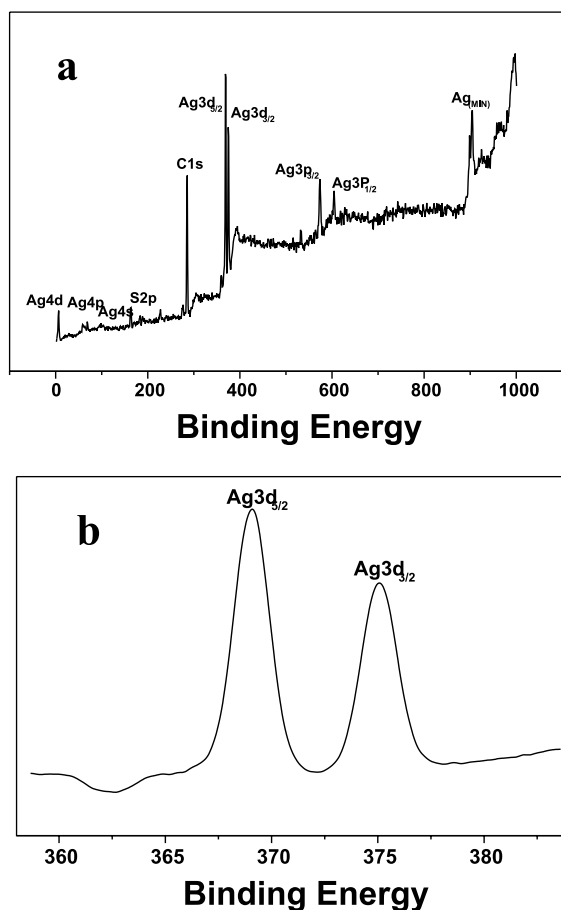


Fig. 3. XPS spectra of the 1-nonanethiol-capped silver nanoparticles (a) and Ag3d of the silver nanoparticles (b) at the reaction time of 15 min.

Table 1

Binding energies of S2p_{3/2} and Ag3d_{5/2} orbitals of the 1-nonanethiol and 1-nonanethiol protected silver nanoparticles at different reaction times

Different reaction time samples	Binding energy (eV)	
	Ag3d _{5/2}	S2p _{3/2}
Free 1-nonanethiol		161.98
15 min	368.3	162.13
30 min	367.95	162.03
60 min	367.65	161.98

the S2p_{3/2} of the 1-nonanethiol capped on silver nanoparticles and that of the free 1-nonanethiol during reaction. The reason why the values of S2p_{3/2} binding energy do not change is due to the stable valence state of the S during the formation of passivated silver nanoparticles. However the Ag3d_{5/2} peak shifts to lower binding energy. In Table 1, the value of the Ag3d_{5/2} of the silver nanoparticles is equal to that of the silver atoms at the beginning of the reaction (15 min). Then the value shifts to the lower binding energy, -0.35 eV at 30 min, -0.65 eV at 60 min, which is the binding energy of the sulfide of the silver. These results indicate that the 1-nonanethiol is just adsorbed physically on the surface of the silver nanoparticles, and no chemical bond has formed between the silver atoms and the S ions of the 1-nonanethiol at the beginning of the reaction. With the reaction going on, the chemical bond can be formed between the silver atoms and S ions of the 1-nonanethiol. Consequently, the formation process of the 1-nonanethiol passivated silver nanoparticles can be summarized as follows. At the beginning of the reaction, the Ag ions are reduced to Ag atoms and the Ag atom nuclei rapidly form small nanoparticles, there is less capping agent adsorbed physically on the surface of the nanoparticles. The formed small nanoparticles will aggregate to become larger nanoparticles due to the high density and the higher surface energy of the small nanoparticles at the beginning of the reaction. But the formed large particles are not stable and will be broken into small parts due to the fact that the 1-nonanethiol prevalingly links the surface of the silver nanoparticles chemically. This reaction will be going on and more silver ions are reduced to the silver atoms. The particle size stops

decreasing, and start to increase at a certain reaction time, and finally becomes stable.

4. Conclusions

We have investigated the formation of the silver nanoparticles protected by the 1-nonanethiol with TEM and XPS. The TEM results shows that the formation of the passivated silver nanoparticles is a dynamic process, where larger particles were quickly formed at the initial stage, followed by decomposition into smaller ones, then formed the larger particles again, and finally stable particles were formed. The XPS results show that the 1-nonanethiol is adsorbed on the surface of the nanoparticles physically at the beginning of the reaction, when the formed particles are not stable. The 1-nonanethiol prevalingly links the surface of the silver nanoparticles chemically, which makes the formed larger particles decompose into smaller ones. These results are helpful for understanding the whole process of the particle formation and controlling the size distribution of the particles for the further application to nanodevices.

Acknowledgements

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