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# Interface Reaction for the Self-Assembly of Silver Nanocrystals under Microwave-Assisted Solvothermal Conditions

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We propose a one-step interface reaction for the direct synthesis of hexagonally arranged spherical silver nanoparticles under microwave-assisted solvothermal conditions without the requirement of the presynthesis of uniform silver nanoparticles or special precursors and the technique of size-selective precipitation. The ratio between ethylene glycol and dodecylthiol shows its effect on the nucleation and growth of silver and thus the morphology and arrangement of the obtained nanoparticles. At a low volume ratio, nanoparticles with a rectangular shape arranged in orthogonal arrays could be observed. This simple method has its generality, and by easily substituting thiourea aqueous solution for ethylene glycol, silver sulfide superlattices of nanoparticles could be synthesized.

## Introduction

Fine metal particles in the nanometer range have attracted considerable interest and have found numerous applications in various fields such as catalysis; optical, microelectronic, and magnetic devices; and biological diagnostic probes due to their conspicuous physical−chemical properties that differ markedly from those of bulk materials.[1−4] Especially for noble metal nanoparticles such as silver (Ag), the interest is mostly focused on their catalytic applications because these nanoparticles can serve as a bridge between homogeneous and heterogeneous catalysis and bring new opportunities for catalysis.[5,6] Until now, various methods have been utilized for the preparation of silver nanoparticles, such as chemical reduction using a series of chemical reductants including $NaBH_4$, $N_2H_4$, $NH_2OH$, ethanol, ethylene glycol, and *N*,*N*-dimethylformamide (DMF),[7−11] aerosol technique,[12] electrochemical or sonochemical deposition,[13,14] photochemical reduction,[15] and laser irradiation techniques.[16] Because most physical and chemical properties of these particles are sensitively dependent on their size and shape, how to become nonagglomerated uniform particles with a controlled mean size and a narrow size distribution could be crucial for their use as advanced materials in high technology or as model materials in fundamental studies.[17] Many physical, chemical, and electrochemical methods have been employed to obtain the metal nanoparticles with uniform size, such as the $NaBH_4$ reduction approach resulting in the thiol-capped 1.8−3.5 nm diameter silver nanoparticles and alcohol reduction of fatty acid silver salts under microwave irradiation.[8,18−21] However, these methods require a technique of size-selective precipitation or a presynthesis of precursors.

On the other hand, the assembly of uniform nanoparticles into well-defined two- and three-dimensional (2-D and 3-D) superlattices has attracted much attention because they are critically important to chemical, optical, magnetic, and electronic nanodevices and would bring possibilities to brand-new properties and applications that result from the spatial orientation and arrangement of the nanocrystals,[22−25] which was recently confirmed by the findings that the physical properties of 2-D and/or 3-D silver,[26] cobalt,[27] and ferrite[28]

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superlattices are different from those of isolated nanoparticles. As we know, the self-assembly of nanoparticles usually requires hard sphere repulsion, a controlled size distribution, and an inherent van der Waals attraction between the particles and the dispersion forces.[29] Several approaches, such as self-assembly,[30] Langmuir−Blodgett (LB) techniques,[8] and the electrophoretic deposition method[31] have been used to obtain self-organized lattices of metal, oxide, and chalcogenide nanoparticles including silver,[12,32] gold,[33] cobalt,[34] indium,[35] $\alpha$-$Fe_2O_3$,[36]cobalt oxide,[37] $BaTiO_3$,[38] CdS,[39] CdSe,[40] and $Ag_2S$[41] nanoparticle arrays. For the assembly of uniform Ag nanocrystals, the presynthesis of uniform nanoparticles or precursors is usually required followed by the organization process by surfactants or ligands. The development of a simple and direct method for the fabrication of such crystals is a major challenge for future research.

As a heating method, microwave irradiation has found a number of applications in chemistry since 1986 and recently shown a very rapid growth in its application in material science due to its unique reaction effects such as rapid volumetric heating and the consequent dramatic increase in reaction rates, etc.[42] As a quick, simple, and energy efficient heating method, the microwave irradiation was combined with many conventional methods such as a traditional hydrothermal method[43] in 1992 and a solvothermal process[10,44] recently and has been widely used in many fields such as molecular sieve and inorganic complex preparations,[45] organic reactions,[46] and catalysis[47] and lately extended to the synthesis of nanocrystalline particles.[48] Several kinds of nanocrystallites including Ag,[10] CdS,[49] CdSe,[50] $Bi_2S_3$,[51] and $CeO_2$[52] have been synthesized. Our group has reported a microwave-polyol process for the synthesis of unassembled silver nanoparticles[53] and an ethylenediamine-assisted microwave-heated approach for the synthesis of 1-D nanomaterials.[54]

In this paper, we report a general and one-step interface reaction for the synthesis and assembly of monodispersed silver nanoparticles by a simple microwave irradiation approach. In the process, dodecylthiol was used as a structure-directing agent, and simple compounds such as $AgNO_3$ and ethylene glycol as reactants were used directly. Toluene is added to form an interface between toluene and ethylene glycol. The presynthesis of the initial silver nanoparticles or precursor and the technique of size-selective precipitation are not required. By adjusting the ratio between reactants, rectangular nanocrystals that arranged into orthogonal superlattices could be observed. This method shows its applicability in the direct synthesis and assembly of $Ag_2S$ nanoparticles by simply changing ethylene glycol with the thiourea aqueous solution.

## Experimental Procedures

**Materials.** Silver nitrate was purchased from Alfa Aesar, a Johnson Matthey Company. Ethylene glycol and thiourea were from Sigma-Aldrich Inc. Toluene was from J. T. Baker chemical company, and dodecylthiol was from Research Chemicals Ltd.

**Synthetic Processes**. For the synthesis of silver nanoparticles, there was no need to exclude air or ventilate inactive gases. All manipulations were operated in fume hood. In the typical procedure, 0.15 g of $AgNO_3$ was added into a Teflon vessel of a double-walled digestion vessel. The double-walled digestion vessels have an inner liner and cover made up of Teflon PFA and an outer high-strength shell of Ultem polyetherimide. Then 10 mL of toluene and appropriate amounts of ethylene glycol (EG) and dodecylthiol (thiol) were added into the vessel in order. After being sealed, the vessel was treated at 160∼170 °C for 3 h using a microwave digestion system, MARS-5 (CEM Corp.). After being cooled to room temperature, the product was collected, and a thin layer of black product formed between the polar and the nonpolar solvents.

The procedure for the synthesis of silver sulfide nanoparticles was quite similar to that for silver. A total of 0.15 g of $AgNO_3$ was added in a Teflon vessel of a double-walled digestion vessel. Then 2 mL of toluene, 1 mL of dodecylthiol, and 10 mL of distilled water was put into the vessel in order, followed by adding 0.1 g of

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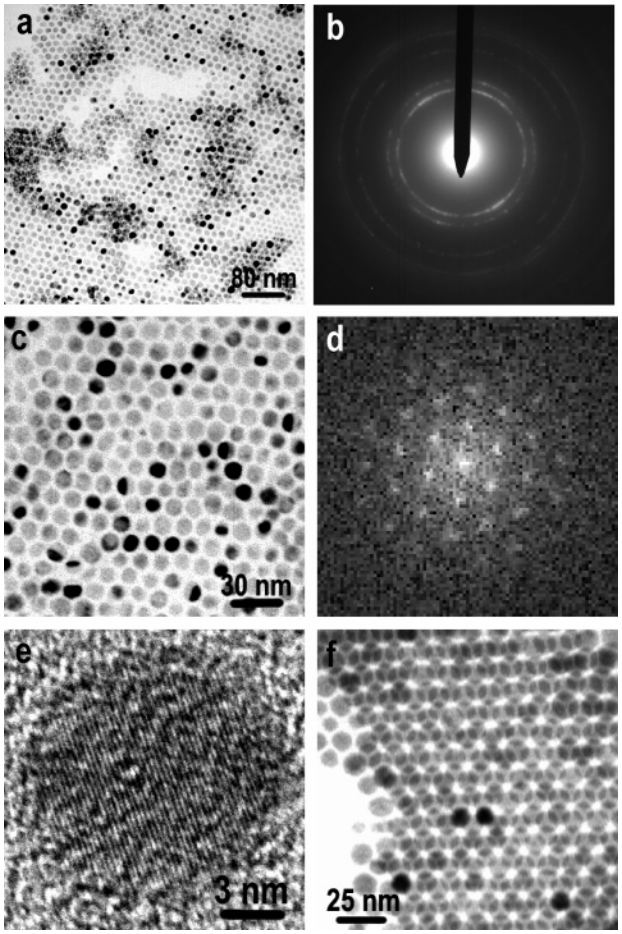

**Figure 1.** TEM images, SAED pattern, Fourier transform power spectrum, and HRTEM image of the synthesized silver sample.

thiourea. After being sealed, the vessel was treated at 160∼170 °C for 3 h using the microwave digestion system, MARS-5 (CEM Corp.). After being cooled to room temperature, the product was collected, and a thin layer of black product formed between the polar and the nonpolar solvents.

**X-ray Diffraction Measurements.** The precipitates were deposited on slides and dried at room temperature for X-ray diffraction characterization using a Scintag diffractometer operated at 35 kV voltage and 30 mA current with Cu$K_\alpha$ radiation.

**Transmission Electron Microscopy Measurements.** The morphology, crystallinity, size, and organization behavior of silver nanocrystals were determined by transmission electron microscopy (TEM), accompanied by selected area electron diffraction (SAED), carried out on a Philips 420 transmission electron microscope (TEM) operated at 120 kV and a JEOL-20l0F high-resolution transmission electron microscope (HRTEM) operated at 200 kV. A small amount of the black sample was dispersed in toluene, and then a drop of this solution was deposited on an amorphous carbon film on 300 mesh Cu grid for TEM observation directly without the technique of size-selective precipitation.

## Results and Discussion

The TEM image of the as-prepared sample (Figure 1) shows that the sample consists of hexagonal-like ordered superstructures of monodispersed silver nanoparticles. Figure 1a displays a wide-field TEM image, clearly confirming that the 2-D hexagonal superlattices are the typical morphology of the as-prepared silver sample. The SAED pattern of this sample (Figure 1b) exhibits polycrystalline diffraction rings, which can be indexed to cubic-phase metal silver, indicating that these nanoparticles are crystalline metal silver. A magnified TEM image of the silver sample (Figure 1c) displays clearly that these nanoparticles are monodispersed spherical nanoparticles with an average diameter of ∼10 nm, and the interparticle spacings are calculated to be about 2 nm. Its Fourier transform power spectrum (Figure 1d) displays ordered hexagonal-like spot arrays, further confirming that the formed silver superlattices have hexagonal structures. The high-resolution TEM image (Figure 1e) exhibits clear lattice planes in a particle, which confirms that these ordered nanoparticles are single crystals and have high crystallinity, in agreement with the SAED pattern. In our sample, some structures with 3-D arrangement can also be found. Figure 1f shows a TEM image of two/three layers of superlattices. It can be seen that the upper layer is also hexagonally arranged, and these spherical nanoparticles are laid on the interspaces of the hexagonally arranged nanoparticles of the lower layer.

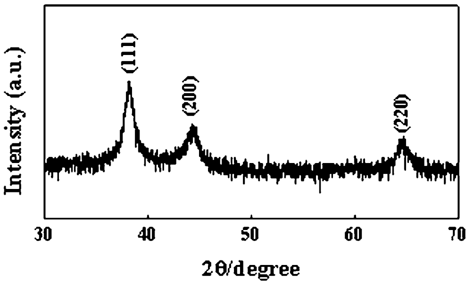

**Figure 2.** XRD pattern of the synthesized silver sample.

**Scheme 1. Possible Mechanism of the Interface Reaction for the Synthesis of Silver Superlattices of Uniform Nanoparticles**

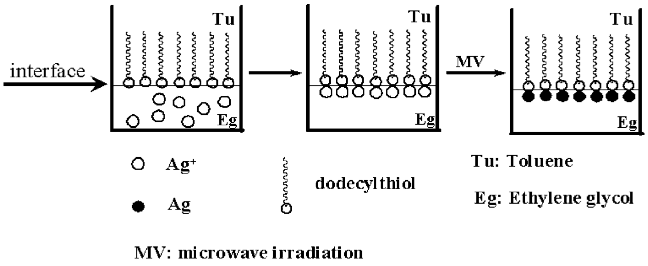

Figure 2 shows the powder XRD pattern of the obtained product. The diffraction peaks are quite similar to those of bulk metal silver, which can be indexed as the cubic structure of silver with lattice constants of $a = 4.07$ Å. This result is consistent with the JCPDS file of silver (JCPDS 4-783). No impurity peaks were observed, indicating the high purity of the final product. The XRD characterization results are in good agreement with TEM observation results.

In the synthetic system, dodecylthiol is the assisting agent for the assembly of silver nanoparticles. Ethylene glycol and toluene are immiscible and form two layers with an interface when they are mixed. Dodecylthiol could be dissolved in toluene with polar groups toward polar solvent, in this case ethylene glycol. The thiol group of dodecylthiol reacted with silver ions at the interface to form an inorganic−organic complex, which was reduced to elemental silver by ethylene glycol under microwave solvothermal conditions. After the

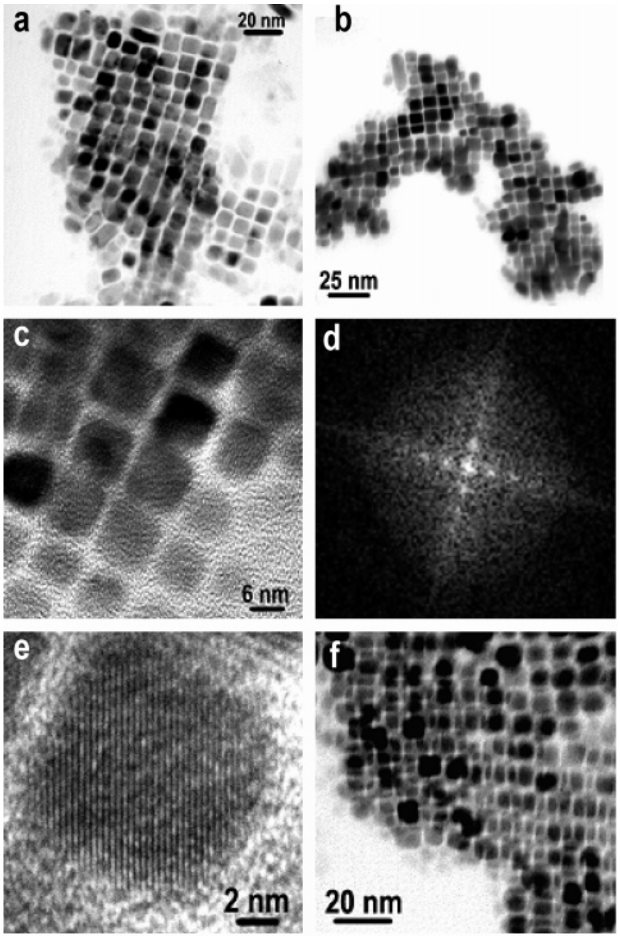

**Figure 3.** TEM images, Fourier transform power spectrum, and HRTEM image of the sample prepared at low ratio between ethylene glycol and dodecylthiol.

reaction, a black thin layer was found at the interface, which is detected to be elemental silver nanoparticles, and the formed silver nanoparticles are automatically compact-packed to form ordered superstructures at the interface. This possible synthetic process has been summarized in Scheme 1. Fourier transform infrared (FTIR) spectra (not shown) of the upper and bottom solutions of our sample show strong peaks that come from toluene (the upper layer) and ethylene glycol (the bottom layer), respectively. And the FTIR spectrum (not shown) of the solid particles (the interface) shows the peaks coming from dodecylthiol, indicating that there are surfactants coating the nanopartilces and making the nanoparticles stable. All of these suggest that there is little dodecylthiol remaining in the solution, and almost all of them are in the interface of the two solutions to react with the silver reactant to form ordered nanoparticles, which are consistent with the possible interface reaction mechanism.

There are strong interactions between silver ions and dodecylthiol, which might form a complicated inorganic–organic intermediate. The ratio between ethylene glycol and dodecylthiol (EG/thiol) will affect the reducing rate and then the morphology of the intermediate compounds, which might direct the shape of the final product. The uniform and self-assembled spherical silver nanoparticles can be synthesized at a relatively large range such as EG/thiol volume ratios of 3:1 by keeping the amount of dodecylthiol at 2 mL or EG/thiol volume ratios of 4:1 by keeping the amount of dodecylthiol at 1 mL. And by decreasing the EG/thiol ratio to 1.5, rectangular nanoparticles, which are assembled orderly, could be found in the product. Figure 3a,b shows the TEM images of the sample prepared at a low ratio of EG/thiol. It can be seen that these nanoparticles have a rectangular shape and are assembled to form an ordered structure. The TEM image with high magnification of this sample (Figure 3c) displays clearly that these nanoparticles are monodispersed rectangular nanoparticles with diameters ranging from 6 to 10 nm. The Fourier transform power spectrum (Figure 3d) of the particle arrays in Figure 3a displays ordered orthogonal-like spot arrays, further confirming the formation of the orthogonal superstructures. The high-resolution TEM image (Figure 3e) confirms that these ordered nanoparticles are single crystals and have a high crystallinity. In this sample, 3-D arranged structures could also be found. Figure 3f shows a TEM image of two layers of superlattices. The upper layer is also orthogonally arranged, and these rectangular nanoparticles are laid on the interspaces of the orthogonally arranged nanoparticles of the lower layer.

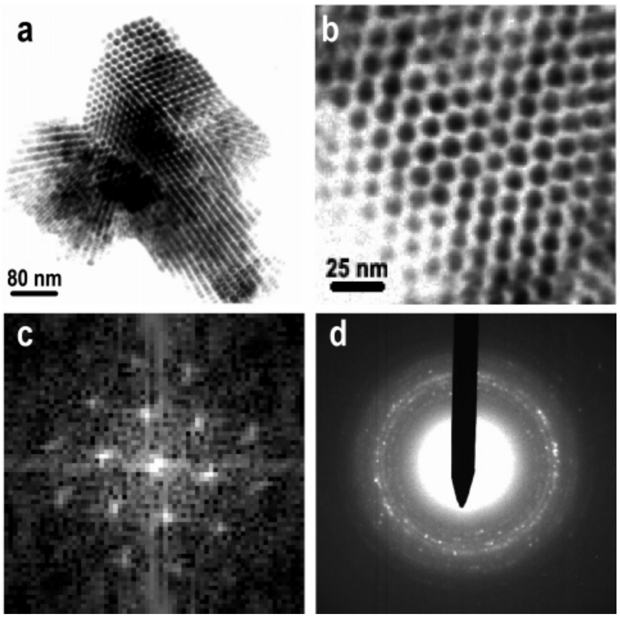

**Figure 4.** TEM images, SAED pattern, and Fourier transform power spectrum of the silver sulfide sample prepared with thiourea as sulfur source.

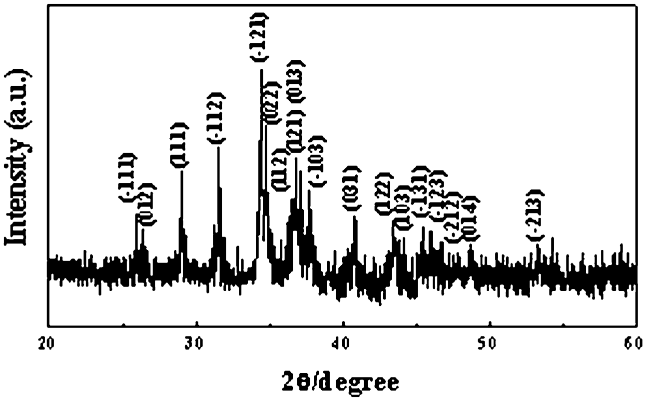

**Figure 5.** XRD pattern of the synthesized silver sulfide sample.

This method is not limited in the synthesis of elemental silver. It also can be extended to the synthesis of hexagonal $Ag_2S$ superlattices by just changing ethylene glycol to thiourea aqueous solution. The TEM image of the obtained silver sulfide sample (Figure 4a) clearly shows spherical and monodispersed nanoparticles that are assembled to form hexagonal superstructures. The TEM image with high magnification (Figure 4b) indicates that these nanoparticles are with average size of ∼8 nm, and the spacings between silver sulfide nanoparticles are calculated to be ∼1.5 nm. Its Fourier transform power spectrum (Figure 4c) displays ordered hexagonal-like spot arrays, further confirming that the formed silver sulfide superlattices have hexagonal structures. The SAED pattern of the silver sulfide sample (Figure 4d) indicates that these nanoparticles are crystalline silver sulfide, which is agreeable to the sample's XRD pattern (Figure 5). So, this method is easily extended to the formation of silver sulfide nanoparticle arrays.

## Conclusion

In this paper, we proposed an interface reaction for the one-step synthesis of hexagonally arranged silver spherical nanoparticles. At a low ratio between ethylene glycol and dodecylthiol, nanoparticles with a rectangular shape arranged in orthogonal arrays could be found. This method seems to be general in its approach and can be easily extended to the formation of silver sulfide superlattices by changing the ethylene glycol to a thiourea aqueous solution.

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