Superlattice of Ag Nanoparticles Prepared by New One-Step Synthetic Method in Aqueous Phase

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Received May 29, 2007
Revised Manuscript Received September 3, 2007

Two- and three-dimensionally ordered arrays of nanoparticles comprise one of the most fascinating classes of nanomaterials. The tremendous interest in superlattices is also driven by their already established or envisioned applications in various fields, where optical, electronic transport, and magnetic properties change with nanoparticle organization.[1] The crystallography of self-assembled superlattice materials can be strongly affected by the geometrical shape of the nanoparticles, because the interaction between adjacent nanoparticles is believed to be a weak van der Waals interaction so that the packing is determined, to a large extent, by the geometrical configuration.[2−3] To obtain a superlattice, many approaches have been used.[2−10] However, their works have been performed in organic solvents, and postprocedures are used to reduce the size distribution. Narrow size distribution of nanoparticles is a necessary condition in making 2D and 3D superlattice structures, so that postprocedures are needed to reduce size distribution. Size-selected precipitation[3,5−7] and digestive ripening[4e,8] processes were used because the polydispersity in particle size hindered the fabrication of such well-defined superlattice structures. In previous other works, to obtain a superlattice, researchers redissolved nanoparticles in various nonpolar organic solvents such as hexane,[5a,6a] dodecane,[9a] heptane,[9b] toluene,[2,7] etc. The redissolved metal colloidal solution was placed onto a carbon-coated copper grid or supporting materials and then the grid or supporters were slowly dried in a dust-free area for several hours.[2,5−10] Two- and three-dimensional superlattices of Ag nanoparticles have been studied by many groups. Wang et al. used an aerosol technique with dodecanethiol to obtain 2D and 3D superlattice structured by slowly evaporating toluene solvent.[2b] Korgel et al. used phase transfer with dodecanethiol, size-selected precipitation, and drop-casting methods to obtain 3D superlattice structure by slow evaporation of organic solvents.[3] Pileni et al. prepared Ag nanoparticles in AOT reverse micelles and then obtained narrow size distributed Ag nanoparticles by a size-selected precipitation method. They also prepared 2D and 3D superlattice structures of Ag nanoparticles by dipping a TEM copper grid into Ag colloidal solution and taking it out to evaporate organic solvent.[6b] Water has a large heat capacity and high thermal conductivity, which contribute to thermal regulation and prevent local temperature fluctuations, thus allowing us to be able to easily control temperature. Also, water is a nontoxic and efficient solvent for polar and ionic compounds and salts, which contributed to the richness of the ionic interaction for high yield because of its polarity, high dielectric constant, and small size.[11] Despite the advantages of using water as solvent, only Kimura et al. reported a 3D superlattice of Ag nanoparticles synthesized with mercaptosuccinic acid in water, but in order to obtain a 3D superlattice, we used the ripening procedure to reduce the size distribution for 12 weeks.[4e] In this study, we introduce, for the first time, a one-step synthetic method for obtaining a superlattice of Ag nanoparticles in the aqueous phase for several hours. In the presence of the mixture of two capping molecules, sodium oleate and aromatic carboxylic acid, superlattices of Ag nanoparticles are easily obtained without any postprocedures or redissolving Ag colloidal solution into any other solvents. Moreover, regard-

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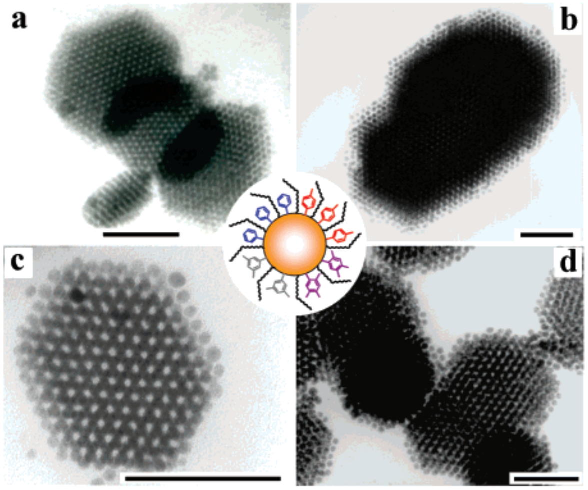

Figure 1. TEM images and schematic drawing of Ag nanoparticles capped with the mixture of two capping molecules, sodium oleate and aromatic carboxylic acid; (a) benzoic acid (blue), (b) 1,4-benzenedicarboxylic acid (red), (c) 1,3,5-benzenetricarboxylic acid (gray), and (d) 1,2,4,5-benzenetetracarboxylic acid (violet). All scale bars represent 97 nm.

less of condition of solvent evaporation time and concentration of Ag colloidal solution, 3D superlattice structures of Ag nanoparticles are easily obtained.

The Ag colloidal solution capped with the mixture of two capping molecules, sodium oleate and aromatic carboxylic acid, has a strong tendency to self-organize into a 3D superlattice because of their narrow particle size distribution and the uniform spherical shape. Spontaneous self-assembly is observed when colloidal solutions are spread onto a copper grid with subsequent drying of solvent.

When TEM grids of Ag colloidal solutions without dilution and those with 5× and 20× dilutions with water were dried in the irradiation of an IR lamp for a few minutes, almost perfect hexagonal and distorted hexagonal 3D superlattice structures were obtained. Even when as-prepared Ag colloidal solution was slowly dried in a dust-free area for several hours, 3D structures were obtained. From these results, regardless of the condition of solvent evaporation time and the concentration of colloidal solution, self-organized 3D superlattice structures are observed. Water is antisolvent with regard to oleic hydrocarbon chain (surfactant) so that Ag nanoparticles had low dispersibility and short-range-ordered superlattice structures (see the Supporting Information, Figure S1).[3b,4f,8b]

The mixture of two capping molecules acts as double capping layer, short length capping layer (aromatic carboxylic acid), and long length capping layer (sodium oleate), which allowed the particles to grow steadily while protecting them from aggregation and oxidation (Figure 1). Sodium oleate, when used alone, is an excellent stabilizing agent, but it has steric hinderence (cis-form) and is irrequarly capped on the surface of nanoparticle so that Ag nanoparticles have large size distribution and nonuniform shape. When only aromatic carboxylic acid was used, Ag nanoparticles with no definite shape and large size distribution are obtained.[4a,5b,12] In the optimum amounts of the mixture of two capping molecules, a superlattice is obtained and the mean diameter and size

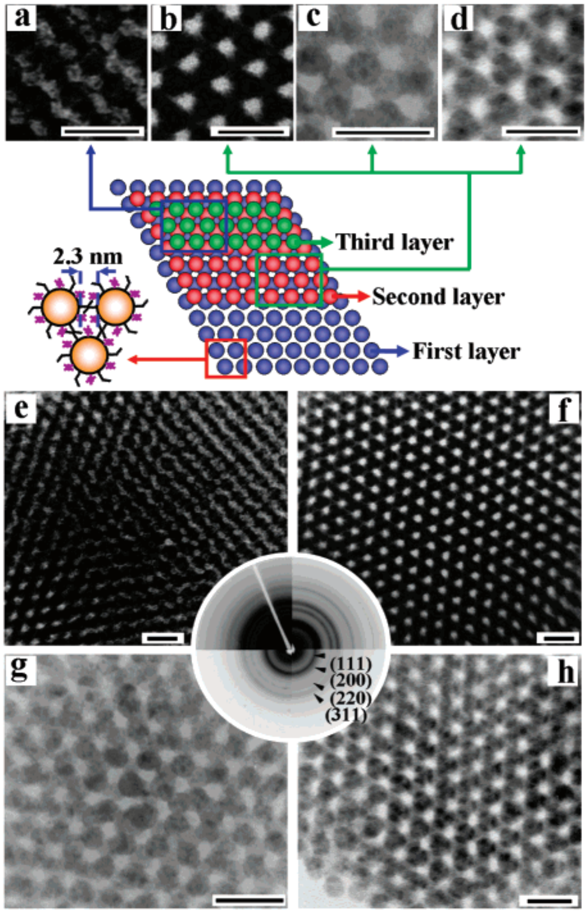

Figure 2. High-resolution TEM images and ED patterns of Ag nanoparticles capped with the mixture of two capping molecules, sodium oleate and aromatic carboxylic acid; (a and e) benzoic acid, (b and f) 1,4-benzenedicarboxylic acid, (c and g) 1,3,5-benzenetricarboxylic acid, and (d and h) 1,2,4,5-benzenetetracarboxylic acid. Schematic representation of Ag interparticles capped with the mixture of two capping molecules, view of the topology of one, two, and three layers of Ag nanoparticles capped with the mixture of two capping molecules are shown. All scale bars represent 20 nm.

distribution of Ag nanoparticles are smaller than those prepared by sodium oleate alone because of the double capping layer. As the molar ratio of aromatic carboxylic acid to sodium oleate is increased, the shape and size distribution of Ag nanoparticles are similar to those prepared by aromatic carboxylic acid alone because the reactivity of aromatic carboxylic acid to metal is greater than those of sodium oleate, and Ag nanoparticles are capped with only a short length capping layer (see the Supporting Information, Figure S2). Carboxylic anions $(-\mathrm{COO}^-)$ of sodium oleate and aromatic carboxylic acid can covalently link to Ag, forming Ag carboxylate $(-\mathrm{COO-Ag})$, and the tails of sodium oleate have hydrophobic and van der Waals interaction between hydrocarbon alkyl chains (see the Supporting Information, Figure S3).[5b,13] In particular, the interparticle distance is very even. Here, as in most cases, adjacent silver nanoparticles were separated by a distance of about 2.3 nm from TEM images in Figure 2.[12,14] Assuming that the alkyl chains in sodium oleate are fully extended and all-trans, the chain length from the carboxylate carbon atom to the terminal methyl group should be about 24.507 Å: 20.048 Å (1.253 Å per C−C × 16) plus 1.113 Å (bond length of C−H), 2.009 Å (distance between C−H in COOH), and 1.337 Å (bond

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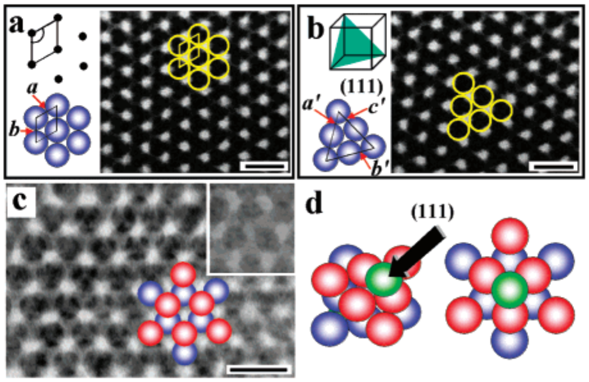

Figure 3. Schematic drawing and dimensions and angles of 2D and 3D superlattice. (a) 2D hexagonal lattice and (b) 3D-face centered cubic lattice. (c) Drawing of two FCC (111) layers on TEM image. (d) View of the 111 plane in FCC, corresponding to the inserted image of (c). All scale bars represent 20 nm.

length of $C{=}C$); the $C-C$ bond length in $-OOC-CH_2-$ is known to be the same as that in $-CH_2-CH_2-$ and $-CH_2-CH_3$.[12,14] Taking into account that the oleate chain is cis-form, the total chain length is shorter than the calculated chain length. The interparticle distance of all products is measured as about 2.3 nm and is the interpenetration distance of the oleate chains, not aromatic carboxylic acid (schematic drawing in Figure 2).

Highly magnified TEM images of the superlattice are shown in Figure 2. Three-dimensional superlattice structures could be followed by either hexagonal close packing (HCP) or face-centered cubic (FCC) structure. In this case, HCP or FCC structures are determined by the location of Ag nanoparticles in the third layer. When a Ag nanoparticle is located on the hexagonal hole made by six Ag nanoparticles in the first and second layers, FCC structure is observed because FCC has the sequence of ABCABC and the hole is capped. The facts observed in images a and e in Figure 2 and the inset image of Figure 3 c exclude the possibility of HCP structure, which has a sequence of ABAB and an opened hexagonal hole; it can be concluded that these 3D superlattices have FCC structures. ED patterns of all products are identical to each other. In ED analysis, four patterns corresponding to (111), (200), (220), and (311) planes of silver are observed, and the same patterns are observed in XRD spectra. The XRD data confirm the tendency of nanoparticles to form organized superlattice structures (see the Supporting Information, Figure S4).[4d,7b,15]

A schematic drawing of the 2D hexagonal lattice pattern on the TEM image is shown in Figure 3a. Dimensions (a = 11.6 nm and b = 11.6 nm) and angle (γ = 120°) of the layer in the TEM image are equal to those of 2D hexagonal lattice rules; dimensions ($a = b$) and angle (γ = 120°). Figure 3 b shows the FCC (111) surface plane and a schematic drawing of the FCC (111) surface pattern on the TEM image. These surface layers actually correspond to one of the close-packed layers on which the FCC structure is based. The FCC (111) surface plane has special dimensions ($a' = b' = c'$). The distance of a' ($a\sqrt{2}$) is measured as about 23.2 nm, and a is calculated as about 16.4 nm. (see the Supporting Information, Figure S5). Yellow shells on the TEM image are representative drawing of capping layers. The thickness of two yellow shells is equal to the interparticle distance between Ag nanoparticles. Figure 3c and the inserted image show TEM images of two and three FCC (111) layers, respectively. In the first layer and the second layer, each Ag nanoparticle of 9.3 nm is surrounded by a hexagon formed by six neighbor Ag nanoparticles with 2.3 nm interparticle distance, and the inset image of Figure 3c corresponds to the FCC (111) crystal structure of atoms (Figure 3d).

In this study, a colloidal synthesis of Ag nanoparticles in the aqueous phase was developed for the same diameter with narrow particle size distribution. In the mixture of two capping molecules, a superlattice of Ag nanoparticles is easily obtained without any postprocedure because of the double capping layer. This new one-step hydrothermal synthetic method for preparing superlattice reduces time-consuming and multistep synthetic works.

Acknowledgment. We acknowledge the Nano R&D Program (Korea Science & Engineering Foundation, Grant 2007-02628) and Thefaceshopkorea Co., Ltd., for their financial support. Y.H.K. thanks the financial support by the Brain Korea 21 project in 2007. Also, we are thankful to Dr. Sun Bae Kang and Dr. Ho Jung Ryoo at the Cooperative Lab, Center of Pukyong National University, for assisting in the TEM and XRD measurements, respectively.

Supporting Information Available: Experimental details, TEM images of Ag nanoparticles and superlattice, XRD patterns, FT-IR spectra, and 3D FCC superlattice patterns (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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