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Silver Nanodisk: Synthesis, Characterization and Self-Assembly

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ABSTRACT

A new form of silver nanostructured materials, a silver nanodisk, is generated by a solution-phase approach. In this method, two main steps are applied: the first is the generation of the truncated triangular silver nanoplates, which are obtained by seed-mediated growth of silver particles using cetyltrimethylammonium bromide (CTAB) as the soft templates. The second is the mild aging of the above triangular silver nanoplate solution at 40 °C to get the desired silver nanodisks. Transmission electron microscopy and atomic force microscopy studies show that the nanodisk has a thickness of the order of 20 - 30 nm, and a diameter around 60 nm. X-ray and electron diffraction analysis reveal that the nanodisk is single crystal and with its basal plane as (111) lattice plane. These nanodisks display a strong surface plasmon absorption band at 475 nm; this band can be continuously tuned within 420 nm to 560 nm through adjusting the aging time. The formation of self-assembled monolayer of CTAB on the basal plane is suggested to account for both the anisotropic growth from triangular nanoplates to nanodisks, and the formation of large-scale necklace-like structures.

INTRODUCTION

Due to the strong surface plasmon resonant absorption band, silver nanoparticles have attracted wide attention. More interestingly, this surface plasmon band are shape sensitive. For example, Schultz et al [1] have shown that triangular particles can display the peak plasmon resonance wavelength mainly in the range of 600 – 700 nm while that of pentagons in the range of 500 – 560 nm. Mirkin et al [2] have also succeeded in the preparation of triangular nanoprisms which displayed a strong in-plane dipole plasmon resonance at 670 nm. These shape sensitive optical properties render silver hot materials for application in optics [1] surface enhanced Raman spectroscopy (SERS) [3], biological label and diagnosis [4].

Shaped silver nanostructures have been observed or synthesized using various chemical approaches. These include spherical particles [5] tetrahedral [6] cubic [7], triangular [8], pentagonal [1], hexagonal [9], decahedral [10], icosahedral, cuboctahedral [11], as well as nanorods and wires [12]. Also, dendritic nanostructures of silver have been generated [13]. Here, we wish to report a new kind of silver nanostructure, i.e., silver nanodisks, which are generated in large quantities using a solution-phase chemical approach. We found that the nanodisks display a strong surface plasmon band at around 475 nm. Furthermore, we can tune this band within 420 nm to 560 nm through a mild aging process. In addition, since the top surface of these nanodisks is covered with a self-assembled monolayer of long chain organic molecules, they provide an ideal model system that mimics the self-assembled monolayer on surface. Due to their nanoscale sizes, they are expected to be applicable as building blocks in the modern nanoelectronics.

EXPERIMENTAL DETAILS

Materials. NaBH_4 (98%), AgNO_3 (99.9%), sodium citrate (99%), CTAB (99%), NaOH (99.996%), L-ascorbic acid (99%), are all from Alfa Aesar and used as received.

Ag seeds formation. 0.6 mL of 10 mM NaBH_4 was rapidly injected into the stirring mixture containing 0.5 mL of 10 mM AgNO_3 and 20 mL of 1.25 mM sodium citrate. The resultant solution was slowly stirred for 3 min and aged for 2 h before use. The particle sizes are 15 ± 6 nm.

Ag nanodisk formation. A particle growth solution was prepared: 2.5 mL of 10 mM AgNO_3 , 5 mL of 100 mM L-ascorbic acid 73 mL of 0.1 M CTAB and 2.5 mL of silver seeds. To this solution, 1 mL of 1M NaOH was rapidly added. With gently shaking, the color of the solution changed from light yellow to brown, red and finally to green within 5 min. With further 4 days of aging at ambient condition (20 °C), the final nanodisks are obtained by aging of the triangular silver nanoplate solution at 40 °C for 4 hours.

Instrumentation. A Hitachi H-7000 transmission electron microscope (TEM), operated at 100 kV was used to observe the images. The specimens were prepared by dropping the solution (centrifuged at 3000g for 10 min to remove the surfactant) on the copper grids covered with Formvar and amorphous carbon, and let dry in air. Atomic force microscopic (AFM) studies are conducted with a Topometrix TM 2010, operated with non-contact mode. The sample is prepared by dropping the solution on a silicon wafer and dry in air. UV-Vis absorption spectra were obtained on a Perkin-Elmer Lambda 900 spectrophotometer. Oriented particulate monolayer X-ray diffraction (OPML-XRD) was used to determine the Miller indices of the basal plane of the nanoplates, performed on a Scintag DXS 2000 diffractometer with the X-ray generator ($\text{Cu K}\alpha$ radiation, $\lambda = 0.15418$ nm) operated at 40 kV and 30 mA. The samples were prepared by dispersing the nanoplates into 3% gelatin (at 40 °C) on a glass plate, spreading the solution evenly with a glass stick, and let dry naturally in air.

RESULTS AND DISCUSSION

Figure 1a shows the TEM image of the obtained silver nanodisks lying flat on the substrate. Most of the particles show clear outlines of round circles. The mean diameter and standard

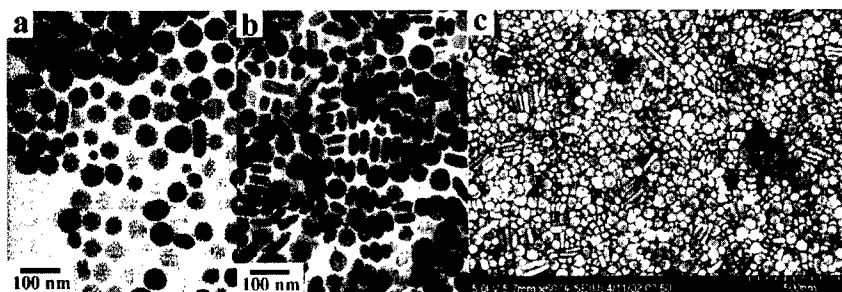


Figure 1. TEM (a and b) and SEM (c) images of the silver nanodisks. The particles in (a) lie flat on the substrates, while those in (b) stack together.

deviation of the particles are 59 ± 10 nm. The thickness of these particles are obtained by observing the closely packed particles, as shown in Figure 1b, the thickness is estimated their as 26 ± 3.4 nm. This further demonstrates the plate-like nature of these particles. Observed from the side view, these nanoplates are round in edges and also look like rods; the aspect ratios of these images are between 2 and 3, which are consistent with the value of 2.3 obtained with average disk diameter divided by their thickness. Note that there are still gaps between the packed neighboring nanodisks with an average distance of 3 - 3.6 nm, since the average molecular length of the C_{16} chain is about 1.8 - 1.9 nm [14], this gap distance is almost double the length of the CTAB long alkyl chain. It suggests that the basal plane of each nanodisk may be covered with a monolayer of CTAB molecules, most likely, with its CH_3-N^+ headgroup bound to the silver surface, and its long alkyl hydrophobic chain toward outside. It is the strong hydrophobic interactions between long alkyl chains on neighboring plates that cause the stacking of the nanodisks. The similar double alkyl layer structures for CTAB have already been suggested on Au nanorod surface [15].

Structure information is obtained with electron diffraction and oriented particulate monolayer X-ray diffraction (OPML-XRD) analysis. Electron diffraction of individual silver nanodisk gives spot points with a hexagonal arrangement indicating that the particle is a single crystal. The XRD patterns for the flat-lying nanodisks with their basal plane parallel to the substrate only show an overwhelmingly intensive diffraction peak at $2\theta = 38.05$, which is from the (111) lattice plane of face-centered cubic (fcc) silver. This clearly demonstrates that the particles are made of pure silver and their basal plane, i.e., the top crystal plane, should be the (111) plane.

The formation process was studied by combined TEM and absorption methods. Immediately after the addition of NaOH, sampling was conducted by taking small aliquot which is quenched by HCl solution, the TEM photos of the samples taken at 30s, 90s and 300s are shown in Figure 2. One can see that at 30s, the most of the particles are small and spherical; the triangular particles formed at about 90s, and continue to grow at 300s. This process can be clearly seen from the absorption spectra shown in Figure 3. At 30s, the spectrum displays two peaks, one at 430 nm; another at around 520 nm, the former is due to the formation of spherical particles, the latter to the triangular shaped one. As the time increased, the latter peak shifted to longer wavelength, indicating the formation of triangular particles. Noted that the intensity of the 430 nm peaks increased during this time, this shows that spherical particles may produce continuously.

After aging for 4 days at room temperature, we found that the 430 nm peak decreased in

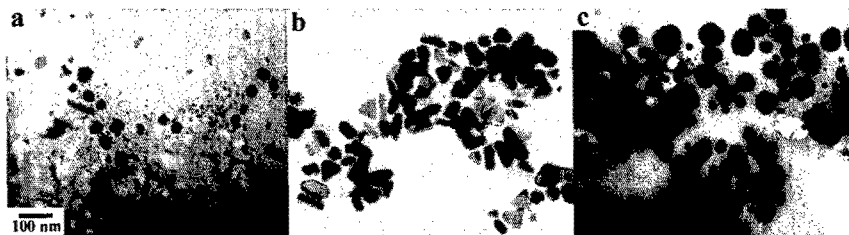


Figure 2. TEM images of the silver particles obtained at 30s (a), 90s (b) and 300s (c) after adding NaOH solution. The scale bar in (a) applies to all images.

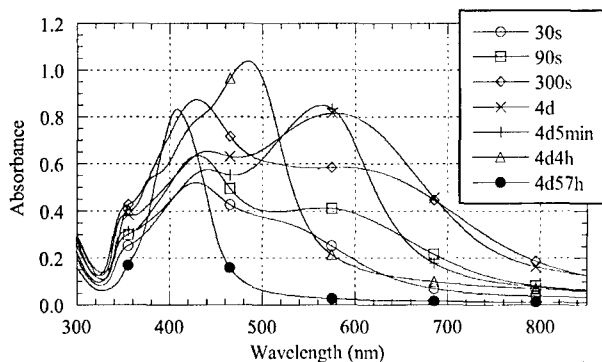


Figure 3. Absorption spectra of the samples at 30s, 90s, and 300s after the addition of NaOH solution. And that after 4 days of aging at 20 °C, then aged at 40 °C for 5 min, 4 h, and 57 h.

intensity at the expense of that of the long wavelength peak (Figure 3), implying that spherical particles continuously grow to triangular particles. The aging process at 40 °C is found to exert a strong influence on the shape transformation of the silver particles. As the aging time increased from 5 min to 4 h (Figure 4a and b), the particle shape changed from triangular to circles. On the other hand, the particle thickness is essentially unchanged (24 ± 8 nm at 5 min vs. 26 ± 3.4 nm at 4 h), similar OPML-XRD patterns are observed for the not aged, 5 min and 4 h aged samples, implying that the (111) basal plane is not altered during this aging process. This shows that the isotropic growth of silver mainly occurred within the basal plane.

It is reasonable to suggest that CTAB molecules play a critical role in this isotropic growth. Well-defined SAM layer of CTAB on the (111) plane should prevent this plane from further growth, leading to the rounding of the triangular particles.

Interestingly, after long time (e.g. 57 h) of aging, as shown in Figure 4c, the particles shrank in size to 44 ± 8 nm and changed to spherical in shape. Since this size is larger than the thickness of the nanodisks, particle growth normal to the basal plane should occur due to desorption or destruction of the CTAB self-assembled monolayers. Similar aging effects are also reported for the gold nanorod [16]. On the other hand, particle dissolution is also found for the basal plane. This phenomenon is more apparent when aging is carried out at a higher temperature, such as 80 or 95 °C. In some cases, particles are completely dissolved, giving a colorless transparent solution.

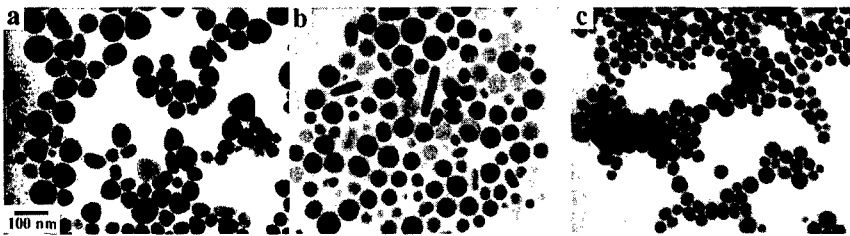


Figure 4. TEM images of the silver particles obtained after 5 min (a), 4 h (b) and 57 h (c) of aging at 40 °C. The scale bar in (a) applies to all images.

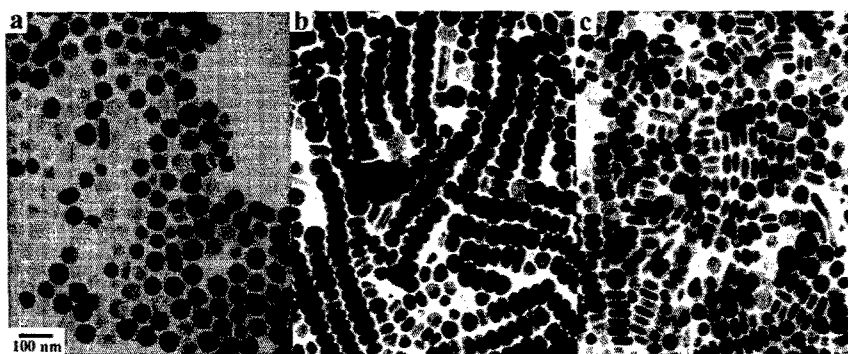


Figure 5. TEM images showing different self-assembled structures. (a), side by side. (b) shoulder to shoulder, and (c) head to head. The scale bar in (a) applies to all images.

The above shape changes are reflected in the absorption spectra (Figure 3). Before aging, truncated triangular particles display mainly three absorption peaks at 584 nm, 444 nm and 351 nm. According to the theoretical calculation of Schatz et al. [2], these peaks are assigned to in-plane dipole, out-of-plane dipole and quadrupole plasmon bands, respectively. When aging time changed from 5 min to 4 h, the first 584 nm peak quickly blue-shifted (see Figure 3), corresponding to the in-plane transformation of the triangles to circles. At the same time, the peak position of the two out-of-plane peaks are kept almost unchanged due to the constant thickness of the nanoplates. Continuous aging to 57 h finally give a single absorption band which belongs to the spherical particles.

The nanodisks are found to form different kind of large-area self-assembled nanostructures on the copper grid (Figure 5). From the optical microscopy, it is found that the aggregation occurs during the dry of the solvent. Also, two factors can be considered as prerequisites for generating these structures: one is the existence of the SAM layer on the basal plane of the nanodisks, which provides the hydrophobic interactions between neighboring particles. Another is the monodispersity of the nanodisks. One can see that nanodisks in the trains are similar in sizes. From Figure 5, at least three kinds of self-assembled structures can be defined; they are side by side (nanodisks sit at the same plane, forming associated structures), shoulder by shoulder (partial overlap) and head to head (close packing). These self-assembled structures provide an interesting example showing that nanodisks can be used as very useful building blocks in constructing devices in future nanoelectronics.

CONCLUSION

In summary, silver nanodisks have, for the first time, been generated in large quantities by a solution-phase approach. These particles have a thickness of 26 nm, and a diameter around 60 nm. They are single crystal and with their basal plane as (111) lattice plane. The formation of self-assembled monolayer of CTAB on the basal plane is likely to be very important not only in explaining the anisotropic growth from triangular nanoplates to nanodisks, but also the formation of large-area necklace-like structures. A strong surface plasmon absorption band at 475 nm is

found for these nanodisks. In addition, a simple mild aging method is provided to systematically control the surface plasmon band of silver particles within 420 nm to 560 nm.

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**Synthesis of
Nanostructured Materials II**