Photochemical Synthesis of Monodisperse Size-Controlled Silver Decahedral Nanoparticles and Their Remarkable Optical Properties

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Monodisperse decahedral silver nanoparticles have been synthesized with excellent shape selectivity (>99%) by novel photochemical transformation of aqueous silver nanoparticle precursors. The procedure employs intense white light and is very robust and reproducible. The precursor solution transforms from a mixture of shapes dominated by small silver platelets into the decahedra, driven by superior stability of decahedral seeds. The decahedra size can be varied by adjusting intensity and spectral properties of the irradiating light. Furthermore, the decahedra can be controllably photochemically regrown to larger sizes, while fully preserving the monodispersity. Silver decahedra exhibit remarkable optical properties featuring a bicolored appearance due to the interplay between plasmonic adsorption and scattering. The sharp plasmon resonances of silver decahedra were tunable from 455 to 570 nm through size variation. Finally, silver decahedra exhibited greatly superior enhancement of Raman scattering compared to other silver nanoparticles. Overall, our findings highlight the importance of pentagonal symmetry in metal nanoparticles and offer a powerful general approach to monodisperse shapes via selective regrowth of appropriately identified and stabilized intermediates.

Introduction

Control over nanoparticle morphologies is essential for the fundamental understanding and practical applications of their nanoscale properties.[1–3] Shape-selective preparation of metal nanoparticles[4,5] (MNPs) is crucial for realization of their full potential in catalysis,[6] plasmonics[7] and optical sensing.[8,9] Single-crystalline defect-free MNPs form Platonic shapes compatible with their lattice symmetries, such as tetrahedra, cubes, and octahedra.[4,5] Other MNP morphologies, such as right bipyramids and nanobeams,[10] originate from twin defects. Pentagonal cyclic twinning[11] (PT) is an important structural element of metal clusters,[12] as revealed by recent X-ray structure determination of Au_{102}.[13] Symmetric MNP shapes with PT include icosahedra,[14,15] pentagonal bipyramids,[16] decahedra,[17,18] and structurally related pentagonal wires.[10] The decahedron (pentagonal dipyramid, Johnson solid J_{13}) is the most compact PT shape with D_{5h} symmetry. Decahedral MNPs, mostly of coinage metals, have been described as a minor component in preparations by vapor condensation and in solution.[19] The structure of decahedral MNPs has been studied by high-resolution electron microscopy[20,21] and their thermodynamic stability has been elucidated by theoretical modeling.[11] Synthesis of gold decahedra has been reported with shape[17] and size[18] selectivity by $HAuCl_4$ reduction in DMF assisted by ultrasound. At the same time, while silver decahedra were postulated to be a key intermediate in the synthesis of rods[22] and wires,[10] their high-yield preparation has not been reported to date. Furthermore, attractive optical properties of the silver decahedral NPs can be expected based on superior plasmonic properties of silver compared to other coinage metals and literature reports on narrow plasmonic adsorption of gold bipyramids[16] and plasmon tuning and environmental sensitivity of gold decahedra.[18]

Herein we present a novel photochemical approach to shape-selective growth of monodisperse silver decahedral

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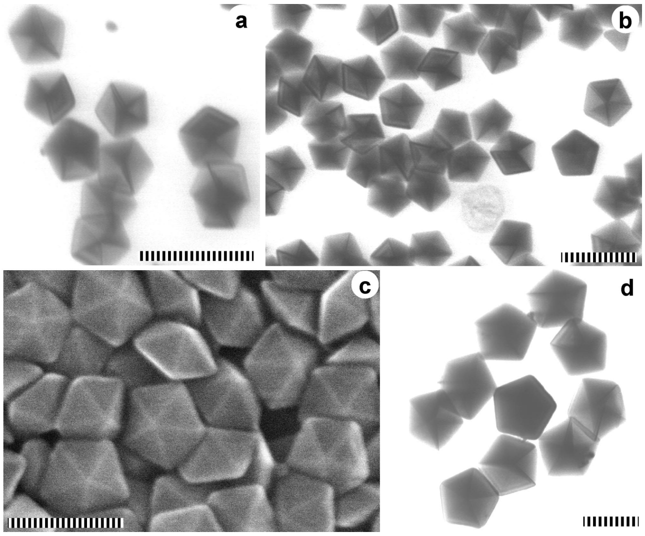

Figure 1. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of synthesized decahedral AgNPs with the largest dimension across the pentagonal rim of (**a**) 46 ± 4 nm; (**b**) 57 ± 4 nm; (**c**) 82.5 ± 3.5 nm; and (**d**) 109.5 ± 3.0 nm. The scale bar is 100 nm for all images.

NPs, demonstrate precise size control by photochemical regrowth, and highlight the remarkable optical properties of these nanoparticles.

Experimental Section

Reagents. Silver nitrate (99%), sodium citrate tribasic dihydrate (Aldrich 99+%), polyvinylpyrrolidone (PVP, $M_w = 40K$), sodium borohydride (99%), L-arginine (TLC, 98%) were supplied by Aldrich and used as received. High-purity deionized water (>18.4 MΩcm) was produced using Millipore A10 Milli-Q.

Synthesis of Decahedra Silver Nanoparticles (AgNPs). First, a precursor solution of silver NPs was prepared. A mixture of 0.500 mL of 0.05 M sodium citrate, 0.015 mL of 0.05 M PVP, 0.050 mL of 0.005 M L-arginine, and 0.200 mL of 0.005 M $AgNO_3$ was added to 7.0 mL of deionized water in a 20-mL vial (VWR). Then silver was reduced by adding 0.080 mL of 0.10 M $NaBH_4$. The resulting pale yellow solution was stirred slowly magnetically until it became bright yellow after several minutes. The bright yellow solution was then immediately exposed to a 400-W metal halide lamp (Sunmaster). The intensity of the light was varied from ca. 0.1 to 0.5 mW/cm^2 by changing the distance from the lamp and focusing the light beam. To produce smaller decahedra of 35 to 45 nm in a diameter, the blue light was used (LS-500-R-HS07 Corion filter) with the exposure time varied from 2 to 15 h depending on intensity. The progress of reaction was monitored by UV−vis spectroscopy (see Figure 2).

Regrowth of Decahedra AgNPs. In a single regrowth step, 8.0 mL of the bright yellow silver NP precursor solution was added to 4.0 mL of the decahedral AgNP seed solution, prepared as described above, and exposed to white light of a metal halide lamp at ca. 0.1−0.2 mW/cm^2 for 20 h. By repeating these regrowth steps, while using the decahedra prepared in a previous step as a seed solution, it was possible to enlarge the decahedra size from ca. 40 nm to more than 120 nm.

Characterization. Electron microscopy (both TEM and SEM) was performed using Hitachi S-5200. Operating voltage was 30.0 kV. Hitachi HD-2000 was used for HR-TEM. Nanoparticle solutions were deposited on carbon-coated Formvar grid (EMS Corp.). The average size and standard deviation were determined from SEM and TEM images by averaging diameters of at least 100 particles. UV−vis spectra were acquired with either Ocean Optics QE65000 fiber-optic UV−vis spectrometer or Cary 50Bio UV−vis spectrophotometer. Raman spectra were recorded using R-3000QE fiber-optic Raman spectrometer equipped with 290 mW laser at 785 nm (RSI).

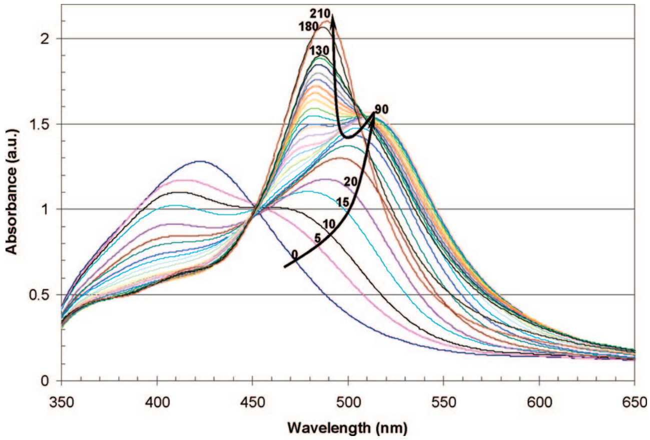

Figure 2. UV−Vis spectra illustrating kinetics of the formation of decahedral AgNPs. An initial yellow precursor solution converts first to larger platelets (fast, within 30−45 min) and then transforms more slowly to decahedra (several hours). The spectra were recorded every 5 min until 210 min. The arrows guide the progression of optical spectra. Selected spectra are also labeled with the time label (in min).

Results and Discussions

Silver decahedra NPs, shown in Figure 1, were prepared by photochemical transformation of a precursor solution of silver NPs. The precursor solution was produced by reduction of aqueous silver nitrate with sodium borohydride in the presence of polyvinylpyrrolidone (PVP) and citrate as stabilizers and arginine as a photochemical promoter. Upon reduction, a yellow solution with a single broad plasmon peak centered around 420 nm (Figure 2) was formed. This solution consisted of small AgNPs (5 to 15 nm in diameter), most of which were platelet-like and some with PT defects (Figure 3). Upon exposure to intense visible light from a metal halide lamp, the precursor solution became initially transparent red or purple. At this stage, it was comprised of larger platelets and a noticeable but still minor fraction of small decahedra (Figure 3). Upon further exposure, the plasmon peak started to shift toward blue (Figure 2) and the solution displayed noticeable scattering, which indicated the presence of larger 3-D NPs. These large NPs were decahedra produced with >99% shape yield (Figures 1 and 6) and narrow size distribution (3% to 8%). Due to strong scattering, the appearance of the solutions of larger decahedra AgNPs is markedly different in reflection and transmission (Figure 4). In the case of narrow absorption peaks at 510−530 nm (see Figure 5), it imparts startling bicolored green and red hues to solutions, similar to those of the famous Lycurgus cup.

The decahedra size could be varied to some extent (from 35 to 60 nm in their largest dimension across the pentagonal rim) by changing the intensity and spectral properties of the irradiating light in a single-stage exposure. Higher intensity and shorter wavelength, such as blue light, gave rise to smaller decahedra. At the same time, we found that the best

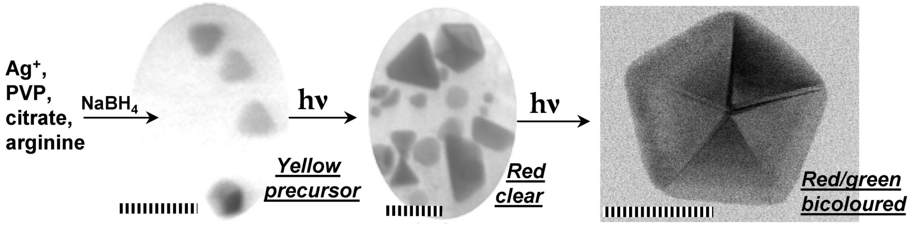

Figure 3. Pathway of photochemical formation of the precursor solution into decahedral AgNPs monitored by TEM. The scale bar is 25 nm for all images.

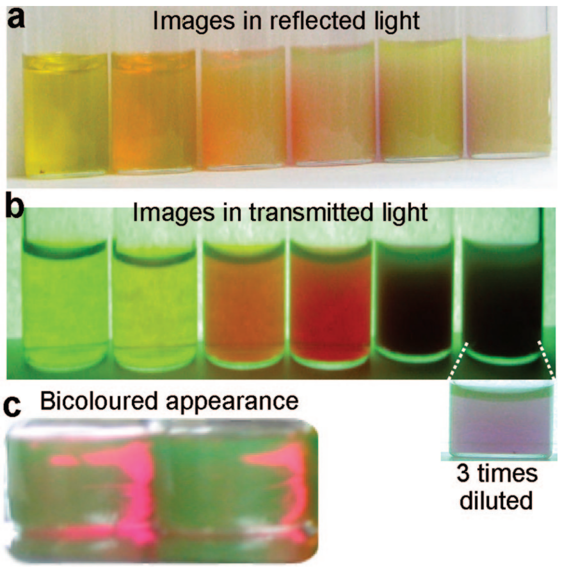

Figure 4. Optical images of aqueous dispersions of decahedral AgNPs of different size: ca. 35, 46, 57, 69, 88, and 123 nm left to right, silver concentration is 1.4 × 10^{-4} M for all samples. Samples were imaged (**a**) in reflected light; (**b**) in transmitted light with 3× diluted solution of 123-nm decahedra provided for color comparison below; (**c**) bicolored appearance of ca. 69 nm decahedral AgNP solution in larger vials.

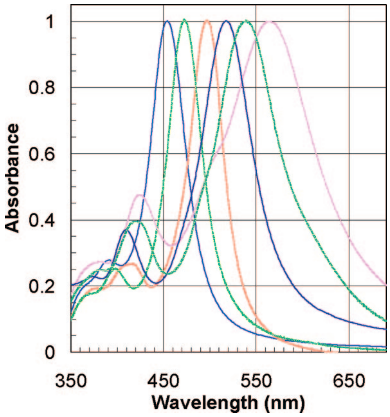

Figure 5. Normalized UV–vis spectra of aqueous dispersions of decahedral AgNPs of different size: ca. 35, 46, 57, 69, 88, and 123 nm left to right.

strategy to control the decahedral size was to produce smaller decahedra using intense blue light (380 to 510 nm spectral range and intensity of ca. 0.5 mW/cm^2) and then to regrow these decahedra photochemically to larger sizes while preserving their shape and monodispersity. The regrowth was accomplished by adding yellow AgNP precursor solution to decahedra seeds under white light exposure. Using this approach, decahedra as large as 120 nm were synthesized successfully without reaching any practical limitation for further enlargement.

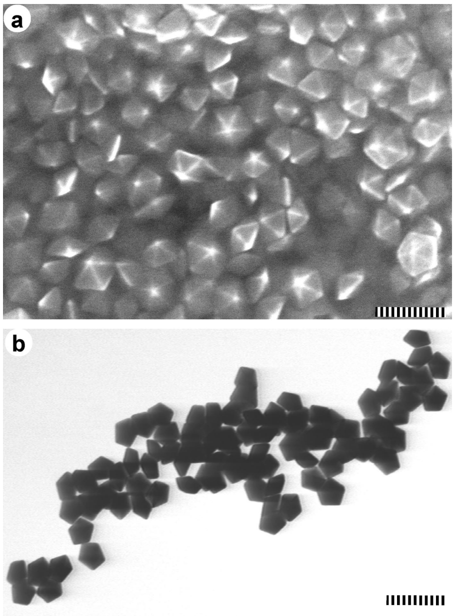

Figure 6. SEM and TEM images illustrating stability of silver decahedral NPs (and also shape yield): (a) 53.5 ± 4.3 nm decahedra; (b) 109.5 ± 3.0 nm decahedra. The scale bar is 100 and 250 nm, respectively, for (a) and (b).

The UV–vis spectra of decahedra AgNPs (Figure 5) feature two resolvable peaks which correspond to transverse and longitudinal plasmon modes.[16,18] Peak maxima of the dominant longitudinal mode varied from 455 to 570 nm for decahedra ranging in size from 35 to 120 nm. These peaks are remarkably narrow: fwhm is as low as 37 nm for 55–60 nm decahedra owing to a symmetric NP shape, highly degenerate longitudinal plasmon mode[16] and good size monodispersity.

Light exposure is essential for the decahedra formation, the precursor solution does not develop into decahedra upon thermal treatment. The role of light is to promote transformation of the yellow precursor solution. The intense irradiation and constant plasmonic excitation play a role analogous to oxidative etching of silver nanoshapes in a polyol process[10] and use of peroxide in thermal preparation of silver prisms.[23] Precursor AgNPs with the absorption peak around 420 nm are unstable under continuous excitation. Upon light exposure, two processes take place simultaneously: growth of platelets and decahedra. The platelets are less stable relative to the decahedra, so upon further irradiation, the platelets dissolve and the released silver incorporates into the growing decahedra seeds. During the exposure to light, the AgNP

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solution is in a state of dynamic equilibrium: the final NP size depends on irradiation wavelength and intensity (as it was demonstrated with silver prisms[24,25]), while the final shape is determined by morphologies of the seed precursor NPs[3] and their relative stability. On the basis of our evidence, decahedra are the exclusive final product as the only shape in the precursor AgNP solution[11] that remains stable under intense irradiation. The only minor byproduct shapes observed were tetrahedra, which were mostly truncated,[26] as the natural product of prism enlargement (Figure S1a) and decahedra with distorted or merged facets (Figure S1b, see Supporting Information).

Citrate and PVP are essential for preparation of the decahedra precursor solution, since they allow formation of stable AgNPs, for which decahedra dominate other PT shapes.[20] At the same time, concentrations of these reagents do not have a strong effect during the light exposure. The concentrations reported in the Experimental Section were found to be optimal for the shape yield and monodispersity. The role of arginine is to accelerate the photochemical transformation largely by limiting the size of the transient platelets. In the absence of arginine, decahedra formation takes place to some extent, but larger platelets described elsewhere[24,25] become a dominant product.

The silver decahedra are remarkably stable provided they are kept in their native solution containing citrate and PVP. Both their morphology and optical properties remain unchanged for at least several months. For instance, TEM images of decahedra shown in Figure 6 were produced several weeks after decahedra synthesis. In the presence of PVP, decahedra can be completely redispersed immediately after drying. The decahedra remain unaffected by ambient daylight and fluorescent light. At the same time, decahedra overexposed to the intense light used in their original preparation (>10 h past the optimal exposure time) become partially truncated (rounded) at the vertices of the pentagonal rim (Figure S2, see Supporting Information).

Due to ease of preparation, excellent shape and size control, and remarkable stability, the reported decahedra should be suitable for a variety of practical applications of metal NPs, e.g., in plasmonics,[7] sensing,[9] and medical treatment.[8] For instance, using Xia's approach to metallic cages,[27] gold pentagonal shells with two plasmon absorption modes tuneable across visible and NIR spectra can be created. Silver NPs can also serve as an effective substrate for surface-enhanced Raman scattering (SERS). In this respect, SERS efficiency of decahedra was compared with the SERS efficiency of other common AgNPs using dry submonolayer films on glass with ca. 10% average surface coverage. At such low amounts, common quasi-spherical AgNPs (typical yellow solutions) did not exhibit appreciable enhancement, while silver prisms with the main plasmonic absorption peak at 650 nm showed some enhancement accompanied by high background distortion due to scattering (Figure 7a). Decahedra featured the greatest enhancement (2.5× better than that of the prisms) as well as a flat undistorted background. In a separate experiment, thicker decahedra films (ca. 1.5 monolayers) enabled the detection of as little as 50 femtomoles of thiosalicylic acid in nonoptimized trials (Figure 7b). Such detection levels make decahedra AgNPs a highly promising SERS substrate. Supported by the fact of minimal SERS enhancement in solution, it suggests that interparticle cavities play a dominant role in this system. The extensive interstices are expected for decahedral films due to intrinsic incompatibility of 5-fold symmetry and close packing (Figure 1c and 6). Consequently, decahedra may provide an opportunity to systematically explore packing of uniform nanoscale objects with 5-fold symmetry. Future research directions also include decahedra transformation into pentagonal rods, since silver decahedra were postulated to be a key intermediate in formation of silver rods and wires.[10,22]

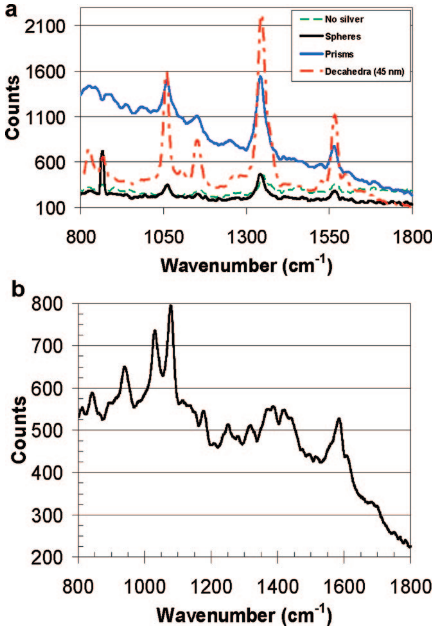

Figure 7. (a) Comparison of surface enhanced Raman scattering (SERS) efficiency for different silver NPs (with the same silver concentration and surface coverage of ca. 10% of a monolayer) using 5,5′-dithiobis(2-nitrobenzoic acid) as a probing molecule. Note that there is a barely noticeable enhancement by quasi-spherical AgNPs. (b) SERS spectrum illustrating detection of 50 fmol (2 μL droplet, 2.5×10^{-8} M) of thiosalicylic acid using 88-nm silver decahedra NPs as a substrate (ca. 1.5 monolayer thickness). The integration time was 5 s; the laser power was ca. 250 mW at 785 nm.

In conclusion, novel shape-selective photochemical synthesis of monodisperse size-controlled silver decahedra NPs is reported and the pathway of the NP morphology development is elucidated. High symmetry and low size variation of the synthesized silver decahedra result in narrow plasmon peaks tuneable over a 100-nm range. Finally, films of decahedra exhibited remarkable enhancement of Raman signal due to favorable interparticle spacing. In light of these outstanding optical properties and the reliable synthetic

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approach, the reported silver NPs should be promising for various optical applications, e.g., plasmonics and photonic sensing.

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Supporting Information Available: TEM images of byproduct shapes in decahedral AgNP synthesis and decahedral AgNPs partially etched due to prolonged exposure to intense light (PDF). This information is available free of charge via the Internet at http://pubs.acs.org.

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