Nanoparticle Growth

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pH-Switchable Silver Nanoprism Growth Pathways**

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Over the past decade, major strides have been made in the development of methods for synthesizing and controlling the shapes of metallic nanocrystals. Such particles have been used in the development of many important applications in the fields of optics,[1] catalysis,[2] and biological diagnostics.[3] Nanocrystal size and shape are extremely important parameters because they substantially affect the physical and chemical properties of a particular composition. Indeed, a variety of new nonspherical nanostructures have been discovered, including rods,[4] boxes,[5] shells,[6] tetrahedra,[7] cubes,[8] and prisms.[9–11] Each of these structures exhibits unique plasmonic properties that depend upon their size and shape.

Our interest has been in the development of high-yielding photochemical and thermal methods for preparing triangular gold and silver nanoprisms.[9,10] The photoreaction used to generate silver nanoprisms allows one to synthesize these unusual prismatic nanocrystals by irradiating spherical nanoparticles at two wavelengths, one that suppresses prism fusion and one that facilitates slow growth of the prism until the prism no longer absorbs this wavelength of light.[9b] Indeed, if only a single wavelength is used under the conditions studied, these two processes generate a bimodal distribution of two different-sized prisms. The larger prisms have an edge length that is approximately twice the edge length of the small structures. While the prism fusion process is intriguing, it is synthetically limiting if one's goal is to prepare nanoprism samples of unimodal size.

Herein, we report a new method for the synthesis of silver nanoprisms through single-beam excitation by simply adjusting solution pH. We hypothesized that the nanoprism fusion process could be regulated by controlling interprism repulsion, which can be modulated by adjusting the solution pH and the overall surface charge on each particle. By controlling the pH, we can either suppress or promote the fusion process. Importantly, this observation can be used to substantially simplify the prism synthesis by eliminating the need for secondary irradiation (to suppress prism fusion), and it allows one to synthesize silver nanoprisms with relatively narrow plasmon bands that span the visible and NIR regions of the spectrum.

The colloidal silver spherical nanoparticle precursors were prepared according to a literature protocol[9b] (see the Experimental Section for details). The initial pH of the nanoparticle solution prior to irradiation was determined to be 9.5 with a benchtop pH meter. A typical photoreaction was carried out by irradiating the nanoparticle solution with 550-nm light using a 150-W halogen lamp as the light source and an optical bandpass filter centered at 550 ± 20 nm. As the silver nanoparticles were converted to nanoprisms, the characteristic plasmon band signature at 400 nm associated with the spherical particles exhibited a decrease in intensity with a concomitant growth of a new band at 616 nm (the dipole plasmon resonance for 60-nm edge-length prisms). Shortly thereafter, a new band associated with large prisms grew in at 1032 nm. These two bands grew in intensity as the band associated with the spherical particles decreased, a hallmark feature of bimodal growth (Figure 1 A).

Since the silver nanoprisms are protected by negatively charged ligands, such as citrate and bis(*p*-sulfonatophenyl)-phenylphosphine (BSPP), the repulsion between the nanoprisms in solution should be dependent on the net negative charge on the nanoprism surface. It has been reported that irradiation with visible light can induce optical attractive forces between metal nanoparticles.[12] Such optical forces are

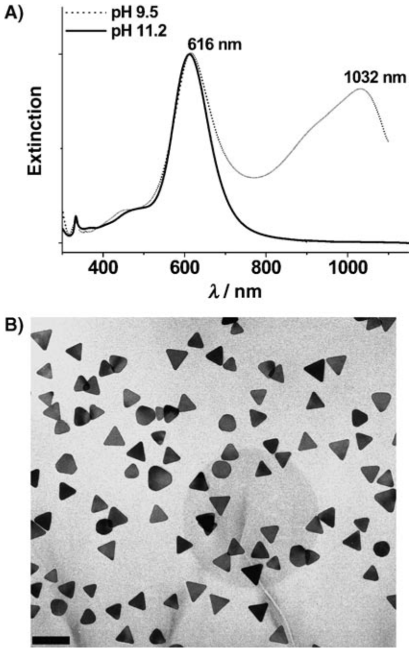

Figure 1. A) Extinction spectra of silver nanoprism solutions made at pH 9.5 and pH 11.2 by excitation at 550 ± 20 nm. B) TEM image of silver nanoprisms (average edge length of 60 ± 7 nm) synthesized by irradiation with $\lambda = 550 \pm 20$ nm light at pH 11.2. Scale bar: 100 nm.

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significantly enhanced at dipole plasmon resonance wavelengths. Thus we believe that based upon the work of the Schatz group[13] and our early experimental observations,[9b] when the nanoprisms are strongly excited by the incident light during the growth process, the tips and edges are polarized to the extent that they can overcome electrostatic repulsion and bring two or more nanoprisms together. This process facilitates prism fusion and stops when the prism no longer absorbs the excitation wavelength.

To evaluate the use of pH to control the degree of electrostatic repulsion and the extent of prism fusion, we studied this process as a function of pH. When the photoreaction was carried out at an initial pH of 11.2 by exciting with 550-nm light, only the plasmon band associated with the 60-nm edge-length prisms was observed. The plasmon band of this size prism is red-shifted with respect to the excitation wavelength (Figure 1 A). Detailed studies of this process by UV/Vis spectroscopy (Figure 2) show that this procedure results in unimodal growth analogous to what has been observed with dual-beam excitation studies known to suppress prism fusion. Significantly, under these conditions one can simply change the excitation wavelength to control resulting prism size (edge length) and maintain unimodal growth. Indeed, we have studied the process over the 488- to 633-nm spectral window using bandpass filters (10–40 nm bandwidth). The resulting nanoprisms and the corresponding extinction spectra (Figure 3) show that the product is always a nanoprism colloid with a primary plasmon band red-shifted from the excitation wavelength.

At pH values above 12, the photoreaction does not proceed, and there is no evidence of prism formation. Since the K_{sp} value of AgOH is 2×10^{-8}, the high OH^- concentration results in the removal of the Ag^+ precursor from solution, which is necessary for prism growth. In addition, under highly basic conditions, a passivating layer of AgOH likely forms on the silver nanoparticle surface and inhibits the photoreaction. A similar phenomenon is observed by the introduction of 10 mM NaCl into the initial nanoparticle solution. At this concentration, AgCl forms and removes the Ag^+ precursor from the solution. Consistent with these observations and hypothesis, prism growth does take place in a solution of 10 mM $NaNO_3$. This rules out the notion that solution ionic strength is controlling the photoconversion reaction.

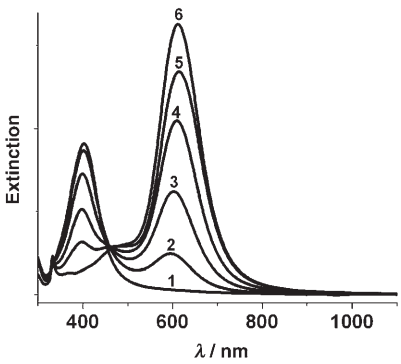

Figure 2. Time-resolved extinction spectra of the silver nanoparticle solution at pH 11.2 with 550 ± 20 nm light irradiation. Spectrum 1: initial solution; spectra 2–6: taken at 30-min intervals.

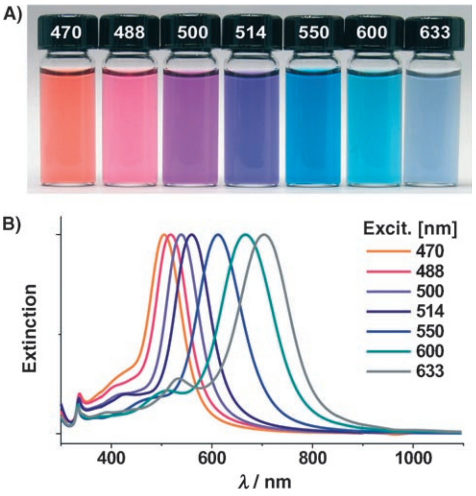

Figure 3. A) Photographs and B) corresponding extinction spectra of the silver nanoprism solution prepared at pH 11.2 with excitation at 470 ± 5 nm, 488 ± 5 nm, 500 ± 5 nm, 514 ± 5 nm, 550 ± 20 nm, 600 ± 20 nm, and 633 ± 20 nm, respectively.

If the solution pH is adjusted to about 7.4 with nitric acid, photoexcitation at 550 nm results in prism fusion and bimodal growth. These data are consistent with the conclusion that basic conditions result in more highly negative-charged prisms. This charge inhibits the prism fusion process. Indeed, zeta potential measurements of the prism colloid as a function of pH are also consistent with this conclusion (see Figure S1 in the Supporting Information).

The photoexcitation of the Ag spherical and prism precursors (note that the light absorbance of the Ag spheres is weak, but measurable) plays multiple roles in the growth process. First, it initiates the formation of the 60-nm edge-length prisms. Second, it excites the dipole plasmon band of these prisms and induces nanoprism fusion, potentially through optical attractive forces. Significantly, since the dipole plasmon band of the 130-nm prisms is red-shifted from the excitation wavelength, prism fusion to form even larger structures does not continue. However, the large prisms do absorb light through their quadrupole plasmon resonances and slow growth does continue.

In the case of bimodal growth at pH 7.4, at the end of the photoreaction, most 60-nm edge-length nanoprisms have been converted to the 130-nm nanoprisms, and the residual smaller nanoprisms can be separated by centrifugation. A representative TEM image (Figure 4 A) shows that the average edge length of the final nanoprisms after filtration is 130 ± 18 nm. Other excitation wavelengths, (for example, 500 nm and 600 nm) also were utilized to synthesize large nanoprisms by a similar strategy. The extinction spectra of the solution of large nanoprisms after filtration by centrifugation indicate that the in-plane quadrupole plasmon band of the resulting large nanoprisms is red-shifted with respect to the excitation wavelength (Figure 4 B).

It should be noted that at lower pH values (<7), although the interprism repulsion will be further reduced, the probabilities of face-to-face and other random fusion processes increase. These processes generate large anisotropic nano-

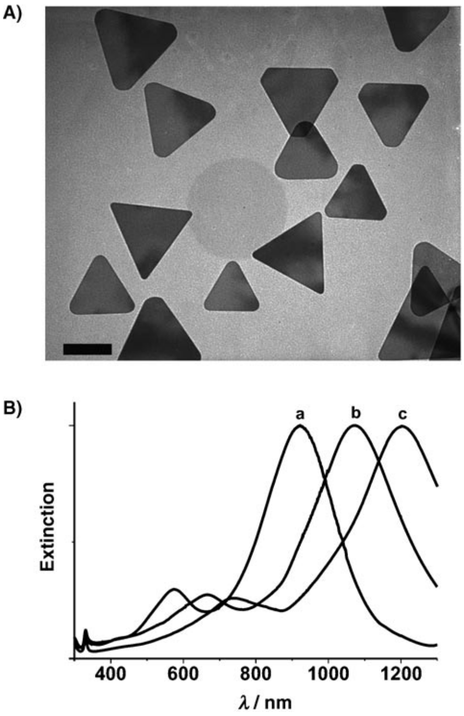

Figure 4. A) TEM image of the filtered silver nanoprisms prepared at pH 7.4 by 550 ± 20 nm light excitation. Scale bar: 100 nm. B) Extinction spectra of the silver nanoprism solution prepared at pH 7.4 through the excitation at 500 ± 5 nm (a), 550 ± 20 nm (b), and 600 ± 20 nm (c), respectively.

particles with irregular shapes, which exhibit quite different and uncontrollable optical properties and can not be separated from the large nanoprisms.

In conclusion, we have demonstrated a straightforward new route for controlling the bimodal growth of silver nanoprisms by simply adjusting solution pH, thus allowing one to synthesize nanoprisms with uniform and tailorable plasmon bands that span the visible and NIR range. This work also provides significant insight into the role of surface charge in the photoinduced growth of silver nanoprisms and begins to explain the unusual and subtle interplay between photoexcitation and pH in controlling the pathway for nanoprism formation.

Experimental Section

Synthesis of silver nanoparticles: Nanopure water (95 mL), $AgNO_3$ (0.5 mL, 20 mM), and sodium citrate (1 mL, 30 mM) were mixed in a 250-mL three-neck flask. The flask was immersed in an ice bath, and the solution was bubbled with N_2 in the dark with vigorous stirring for about 20 minutes. Aqueous $NaBH_4$ (1 mL, 50 mM, freshly prepared with ice-cold Nanopure water prior to injection) was rapidly injected into the solution. Over the next 15 min, five drops of $NaBH_4$ solution were added every two minutes into the solution. Then BSPP solution (1 mL, 5 mM) and $NaBH_4$ solution (1 mL) were added dropwise to the solution. The resulting Ag colloid was gently stirred for 5 h in an ice bath and allowed to age overnight at about 4 °C in the dark. The size of prepared silver nanoparticles was characterized as 4.2 ± 0.9 nm by TEM.

Photoinduced silver nanoprism growth: In a typical experiment, an aged solution (20 mL) of silver nanoparticles, at a pH of 9.5, was irradiated with a 150-W halogen lamp coupled with an optical bandpass filter (550 ± 20 nm).

To achieve photocontrolled unimodal growth, aqueous NaOH (0.1 mL, 0.2 M) was introduced dropwise into a solution (20 mL) of silver nanoparticles while shaking. A variety of optical bandpass filters with center wavelength at 470 ± 5 nm, 488 ± 5 nm, 500 ± 5 nm, 514 ± 5 nm, 550 ± 20 nm, 600 ± 20 nm, and 633 ± 20 nm, respectively, were used and coupled with a 150-W halogen lamp for the irradiation of the pH-adjusted solution.

For the large nanoprism synthesis under neutral conditions, the initial nanoparticle solution (20 mL) was adjusted to pH 7.4 by adding nitric acid (0.1 mL, 0.2 M) dropwise while shaking. Then the solution was irradiated by light with center wavelengths at 500 ± 5 nm, 550 ± 20 nm, and 600 ± 20 nm, respectively.

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