Nanoparticles

DOI: 10.1002/anie.200900545

Reconstruction of Silver Nanoplates by UV Irradiation: Tailored Optical Properties and Enhanced Stability**

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Colloidal noble-metal nanoparticles, especially of gold and silver, have proven to be good candidates for applications in catalysis,[1,2] surface-enhanced Raman scattering (SERS),[3,4] biosensors,[5] and plasmonics,[6] of which chemical and biological sensing are the most promising. Most of these attractive applications are based on the particles' surface plasmon resonance (SPR), which strongly depends on their specific composition, size, shape, local dielectric environment, and electromagnetic interactions with proximate particles.[7–10] Recently, it has been realized that particle shape plays an important role in determining the plasmon wavelength, therefore stimulating great interest in shape-controlled synthesis. For example, excellent work has been done to synthesize silver nanoparticles with shapes varying from spheres to cubes,[11,12] polyhedrons,[13] plates,[14–20] and wires,[21] which greatly broaden the range of the SPR wavelength.[22] In principle, the plasmon band of the nanoparticles can be systematically tuned by controlling their shape evolution during particle growth. In practice, however, it is usually difficult to quickly stop the reaction and harvest the growing particles at the desired stage. Moreover, these intermediate particles are not stable and they usually change shape during storage. As a result, in most cases, to obtain multiple samples with desired plasmon bands, the synthetic conditions, including the concentration of reagents and capping ligands, temperature, injection time and so forth, must be fine-tuned, which usually leads to low reproducibility and poor predictability because the nucleation and growth of the nanoparticles are very sensitive to small variations of synthetic conditions.

The synthesis of Ag nanoplates is no exception. Ag nanoplates have recently attracted much attention because their plasmon bands can be widely tuned by controlling the particle aspect ratio. Although it has been possible to obtain samples with plasmon bands within a considerable range by controlling the synthesis conditions, tailored synthesis of nanoplates with wider tuning of the plasmon band using a simple setup is still a great challenge. It is generally believed that the growth of nanoplates involves the gradual increase of aspect ratio. However, it is impractical to arrest the growth of nanoplates to achieve desired aspect ratio and plasmonic properties, because the reaction is usually so fast that the nanoparticles quickly evolve into plates with large aspect ratios. Furthermore, the as-synthesized products are generally unstable and will gradually convert to more stable forms along with a shift of the plasmon band. Achieving precise control of the synthesis, long-term stability, and wide plasmon tunability of the Ag nanoplates has been the subject of a number of recent studies.[23,24]

Herein, we describe an unconventional strategy which allows convenient and precisely controlled preparation of highly stable Ag nanoplates with broad tunability of their plasmonic properties. Unlike conventional methods that focus on controlling particle nucleation and growth, we start with fully grown Ag nanoplates and use UV irradiation to induce the reconstruction of these precursor particles. More specifically, upon exposure to UV light, triangular Ag nanoplates in aqueous solution undergo a gradual shape change, during which their sharp tips become rounded and their thickness increases (Figure 1 a). As a result, we can continuously tune the SPR wavelength backwards from approximately 870 to 450 nm and precisely harvest samples with desired optical properties by controlling the irradiation time. With protection from a poly(vinylpyrrolidone) (PVP) stabilizer, the Ag nanoplates can remain stable at room temperature for at least three months without notable changes in their optical properties. The described "backward tuning" strategy, in accord with prior demonstrations of nanocrystal reshaping,[24–27] represents a practical synthetic route to stable silver nanoplates that can have access to a wide range of plasmon wavelengths.

The photoinduced reconstruction process involves the conversion of the triangular nanoplates into round nanoplates under UV irradiation. Triangular Ag nanoplates were prepared through a modified thermal process developed by Mirkin and Métraux,[28] by reducing an aqueous solution of $AgNO_3$ with $NaBH_4$ in the presence of trisodium citrate (TSC), PVP, and H_2O_2. Upon stabilization of the solution color, the as-prepared Ag nanoplates are centrifuged and washed with deionized water. Irradiating the sample using UV light with a wavelength of 365 nm gradually blue shifts the plasmon band of the nanoplates, as evidenced by notable color changes of the solution from cyan to blue, purple, red,

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[**] Y.Y. thanks the University of California, Riverside for start-up funds and the Chinese–American Faculty Association of Southern California for the Robert T. Poe Faculty Development Grant. Acknowledgement is also made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We thank Dr. Bozhilov and Mr. McDaniel at the Central Facility for Advanced Microscopy and Microanalysis at UCR for assistance with TEM analysis.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200900545.

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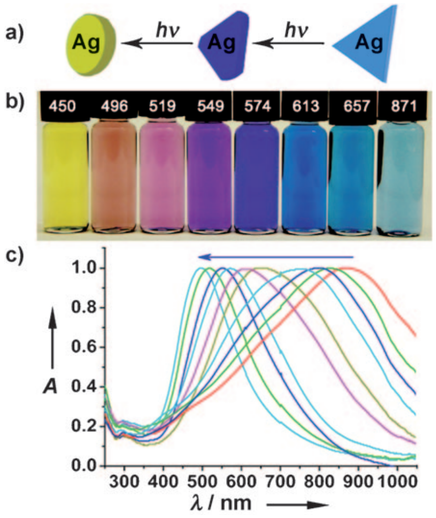

Figure 1. a) Schematic illustration of the evolution process of Ag nanoplates under UV irradiation: the sharp corners of triangular plates disappear, while the thickness of the nanoplates increases. b) Digital photographs and c) extinction spectra showing the backward tuning of the plasmon bands of the silver nanoplates by irradiation with UV light for different lengths of time. From right to left, the samples displayed in the photo were irradiated for 0, 60, 70, 80, 90, 100, 110, and 125 min. The numbers above the samples give the wavelength of plasmon resonance in nanometers. The spectra in (c) were taken after irradiating the nanoplate solutions for 0, 20, 40, 60, 70, 80, 90, 100, 110, and 125 min.

and finally yellow. Throughout the process, the solution remains transparent without any aggregation (Figure 1 b).

The irradiation process was also monitored by ultraviolet–visible–near-infrared (UV/Vis/NIR) spectroscopy (Figure 1 c). For the original cyan colloid solution, plate structure is the major morphology, as evidenced by the diagnostic plasmon bands at 305 nm, 470 nm, and 871 nm, assigned to the out-of-plane quadrupole, in-plane quadrupole, and in-plane dipole plasmon resonance of triangular nanoplates, respectively.[15] During UV irradiation, all three plasmon peaks experience a blue shift, with the in-plane dipole plasmon shifting fastest, from 871 to 450 nm. Such blue shift can be precisely tuned by controlling the irradiation time. At the same time, the out-of-plane quadrupole plasmon resonance changes only slightly, indicating the retention of plate structures.

It is generally accepted that the plasmon band position of Ag nanoplates is determined by their tip sharpness and aspect ratio (the ratio between the largest lateral dimension and thickness). Usually, sharp tips and high aspect ratio lead to a red-shifted resonance, while round tips and low aspect ratio exert the opposite influence.[10,29] As is evidenced by transmission electron microscopy (TEM; Figure 2), the blue shift of the major peak appears to result from the morphology change of the Ag nanoplates. Upon irradiation, as shown in Figure 2, the sharp tips of the Ag nanoplates with edge length of (48.52 ± 6.27) nm gradually evolves into truncated corners, eventually resulting in round nanoplates with the largest lateral dimension of (26.07 ± 5.87) nm. Although the morphology and size of such particles change distinctly, the particles still maintain their plate structure after irradiation. As shown in Figure 2 b, the representative selected area electron diffraction (SAED) pattern suggests that the original Ag nanoplate is a face-centered cubic (*fcc*) crystal. The six bright spots with six-fold symmetry can be indexed to the {220} reflections of the *fcc* crystal oriented in the [111] direction, indicating that the flat particle surface is parallel to the (111) plane. The forbidden 1/3{422} reflections are also observed in the ED pattern, which is consistent with reported results.[30] Comparing the ED patterns of nanoparticles before and after irradiation (Figure 2 b,f), we see that there is no major crystal structure change during the shape evolution.

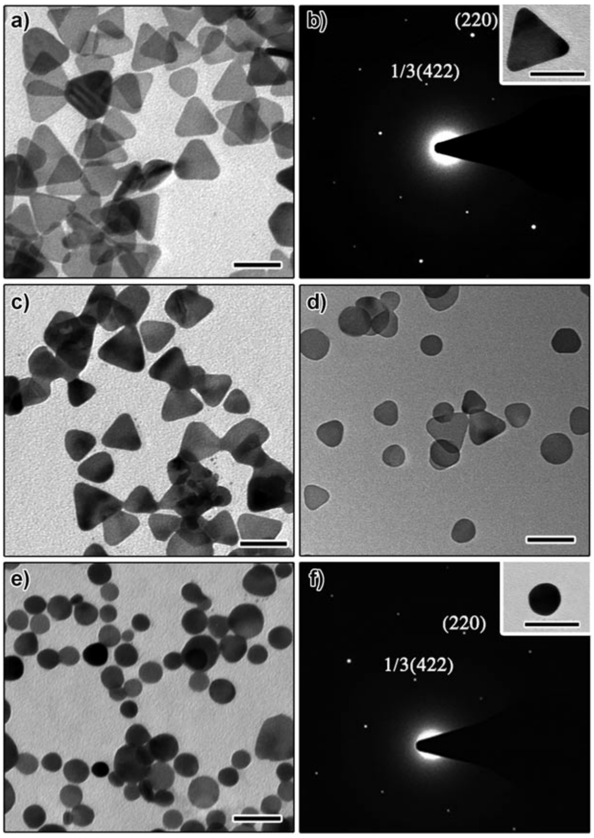

Figure 2. TEM images showing the shape evolution of Ag nanoplates upon UV irradiation for a) 0, c) 40, d) 80, and e) 125 min. b),f) Selected area electron diffraction patterns taken from a single particle (inset) from the samples in (a) and (e), respectively. Scale bars are 50 nm.

In most of the reported cases, the change of edge length and tip sharpness of silver nanoplates are said to be responsible for these spectrum shifts.[10,24] However, we can expect only a less than 60 nm shift in the plasmon band for particles with comparable tip morphologies and thicknesses, as opposed to the more than 400 nm shift observed in our experiments.[28] The large shift in the plasmon band, as suggested by Mirkin and Métraux, is induced by the increase in thickness of the plates, which can ultimately cause a sharp change in the aspect ratio. An interesting feature of Ag nanoplates is that they tend to stack upon each other face to face and stand vertically on their edges, making it convenient to measure the thickness. As shown in Figure 3, we have

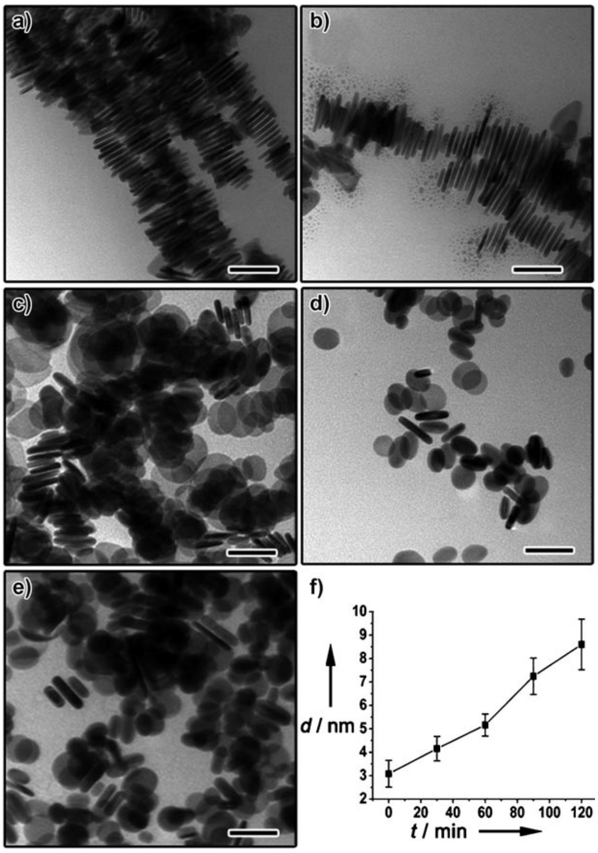

Figure 3. a)–e) TEM images showing the thickness evolution of Ag nanoplates upon UV irradiation for a) 0 min, thickness (3.08 ± 0.57) nm; b) 30 min, (4.15 ± 0.52) nm; c) 60 min, (5.16 ± 0.47) nm; d) 90 min, (7.24 ± 0.78) nm; e) 125 min, (8.6 ± 1.08) nm. Scale bars are 50 nm. f) Change of nanoplate thickness over irradiation time.

confirmed the gradual increase of the thickness of Ag nanoplates as the result of UV irradiation. As summarized in Figure 3 f, upon irradiation the plate thickness increases from the original (3.08 ± 0.57) nm ($\lambda_{abs} = 871$ nm) to a final (8.6 ± 1.08) nm ($\lambda_{abs} = 450$ nm). Accordingly, the estimated aspect ratio of the nanoplates changes from approximately 15.75 to 3.03.

According to the Gibbs–Thomson effect, the sharp corners are the most energetic areas in a triangular nanoplate.[31,32] Under irradiation with UV light, these less stable sharp corners gradually disappear.[33] Although the exact mechanism is still under investigation, we believe the shape transformation likely involves a migration process: under irradiation, the surface atoms in the highly energetic areas are forced to "migrate" to other places on the nanoplate to snip the sharp corners and form a more stable structure. They may be dissolved first (owing to high energy), and then reduced back to the two faces of the plates, thus increasing the thickness. This process is possible because the UV irradiation of water produces hydrated electrons that are highly reductive.[34] However, it is also possible that these atoms simply diffuse on the surface and form the final structure. The "migration" of Ag atoms from the corners to the surface is consistent with the fact that the original triangular nanoplates become rounded, with reduced size and increased thickness after UV irradiation.

The stability of nanostructures is critical to many practical applications. For example, plasmon-enhanced spectroscopy requires stable and well-defined resonances. When nonlinear optical enhancements are involved, the signal intensities can be reduced by orders of magnitude, even if a shift of only a few nanometers occurs.[35] Ag nanoplates prepared by direct synthesis often suffer from a gradual blue shift of the spectrum during storage.[18,23,36] The as-prepared precursor nanoplates in our case are not yet stable, because they all contain relatively sharp corners. Four samples with different plasmon bands were taken as examples and stored at room temperature for seven days. As Figure 4 a shows, all of these colloids experienced a blue shift of approximately 100 nm. Moreover, the extinction spectra broadened during the aging process (see the Supporting Information), implying the non-uniform transformation of the Ag nanoplates, which is not ideal for applications.

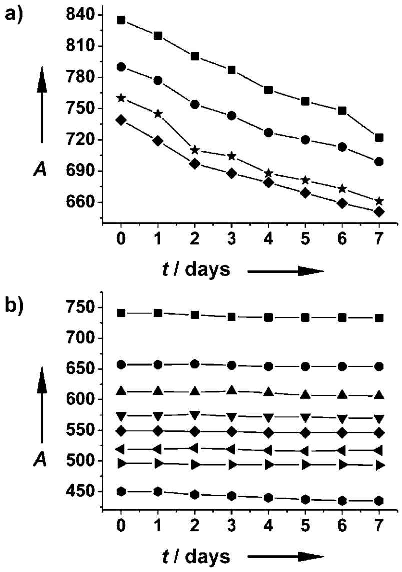

Figure 4. Comparison of the stability of optical properties for nanoplates with and without UV irradiation: a) The plasmon bands of Ag nanoplates without UV treatment blue shift over time. The synthetic conditions were altered to obtain samples with four different plasmon bands. b) The plasmon bands of the UV-irradiated Ag nanoplates remain stable over time. The samples with different plasmon bands were produced by irradiating the same original plate solution for different lengths of time.

The plates show significantly improved stability after UV irradiation. Figure 4 b shows the evolution of the optical properties of seven irradiated samples after storage at room temperature for seven days, after which only a marginal change (several nanometers) can be detected for these samples. More importantly, no broadening of the absorption spectra is observed, implying that the thickness and shape of the Ag nanoplates remained the same during storage. We attribute the significantly enhanced stability of the irradiated samples to the pre-removal of highly energetic corners by UV treatment and the surface protection provided by PVP. The

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UV-treated samples can be stored at room temperature for at least three months without notable change in either color or extinction spectrum. Yu and co-workers reported previously that shape evolution can also be prevented by modifying the particle surface with alkane thiols.[23] The use of PVP as the capping ligand, however, has the advantages of retaining the high water dispersity of the particles and avoiding the significant peak broadening associated with oxidation of the Ag surface by thiols.

In summary, we have demonstrated that the optical properties of Ag nanoplates can be precisely tuned in a wide range through a UV-light-induced reconstruction process, in which the morphology of the nanoparticles is changed from thin triangular plates to thick round plates. Stabilized with PVP, the as-obtained Ag nanoplates remain stable for a long time without any noticeable changes in their optical properties. This unconventional "backward tuning" strategy provides a convenient method for preparing Ag nanoplates with broad tunability of their plasmon resonance while avoiding the poor reproducibility and stability associated with conventional direct synthesis approaches. We believe that the convenient access to Ag nanoplates with tailored optical properties and superior stability will greatly promote their practical applications in areas such as biological and chemical sensing, Raman signal enhancement, and photothermal therapy.

Experimental Section

Triangular Ag nanoplates were prepared by a modified version of a process developed by Mirkin and Métraux.[28] Typically, an aqueous solution of $AgNO_3$ (0.1 mM, 25 mL), TSC (30 mM, 0.3 mL), PVP (Mw $\approx$29000 g mol^{-1}, 3.5 mM, 1.5 mL), and aqueous H_2O_2 (30 wt%, 60 μL) were mixed and vigorously stirred at room temperature in air. $NaBH_4$ (100 mM, 250 μL) was then rapidly injected into this mixture. Ag nanoplates were obtained after approximately 30 min as the solution color turned to cyan. After washing with deionized water, the sample was irradiated with UV light ($\lambda = 365$ nm, 120 V, 1.05 amp), which gradually induced a blue shift of the plasmon band. To stabilize the as-prepared sample, aqueous PVP (1 mL, 3.5 mM) was injected into the system. Ageing of the samples was carried out under daylight illumination.

Received: January 29, 2009
Revised: February 23, 2009
Published online: April 3, 2009

Keywords: irradiation · nanoparticles · optical properties · silver · surface plasmon resonance

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