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1. Introduction

Plasmonic metal nanoparticles have been the subject of intensive research as a result of their unique optical properties. Light of the correct frequency can drive a collective oscillation of the conduction band electrons, a phenomenon known as localized surface plasmon resonance (LSPR).^{1,2} The LSPR gives rise to strongly amplified electric fields at the particle surface (near-field effects), in addition to resonant scattering and photothermal effects. These properties have led to the application of plasmonic nanoparticles in a wide variety of areas, including surface enhanced Raman scattering (SERS),^{3,4} metal enhanced fluorescence (MEF),^{5,6} sensing,^{7,8} biological imaging,^{9,10} theranostics,^{11,12} catalysis,^{13,14} and optoelectronics.^{15,16}

The plasmonic properties of these materials are highly dependent on the nanoparticle shape, size, composition, and dielectric environment.^{17–20} In particular, the near-field enhancements of anisotropic metal nanoparticles are often highly amplified by their sharp structural features. Synthetic routes to a wide diversity of anisotropic nanoparticle shapes (*e.g.*, cubes,²¹ triangular²² and hexagonal²³ nanoprisms, rods,²⁴ wires,²⁵ and polyhedra²⁶), are now well known for both silver and gold, and

Chemical stability and degradation mechanisms of triangular Ag, Ag@Au, and Au nanoprisms†

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Anisotropic metal nanoparticles have found use in a variety of plasmonic applications because of the large near-field enhancements associated with them; however, the very features that give rise to these enhancements (e.g., sharply curved edges and tips) often have high surface energies and are easily degraded. This paper describes the stability and degradation mechanisms of triangular silver, gold-coated silver, and gold nanoprisms upon exposure to a wide variety of adverse conditions, including halide ions, thiols, amines and elevated temperatures. The silver nanoprisms were immediately and irreversibly degraded under all of the conditions studied. In contrast, the core–shell Ag@Au nanoprisms were less susceptible to etching by chlorides and bromides, but were rapidly degraded by iodides, amines and thiols by a different degradation pathway. Only the pure gold nanoprisms were stable to all of the conditions tested. These results have important implications for the suitability of triangular nanoprisms in many applications; this is particularly true in biological or environmental fields, where the nanoparticles would inevitably be exposed to a wide variety of chemical stimuli.

these materials often outperform their isotropic, spherical analogues in applications such as SERS and MEF.

Triangular silver nanoprisms (AgNPrs) have attracted particular interest because of their highly tunable in-plane dipole LSPR band, which can be shifted throughout the visible region and well into the near-infrared.²⁷⁻²⁹ The sharp vertices of the triangular structure also lead to strong near-field enhancements via the lightning rod effect, making them ideal materials for plasmonic applications. Unfortunately, these same structural features are also highly unstable; recent work has demonstrated that the high surface energy vertices are readily degraded by halide ions,³⁰⁻³³ thiols,³⁴ UV radiation,³⁵ heat,^{36,37} and acid.³⁸ Chloride ions are one of the most ubiquitous etchants of the AgNPrs,³² and have been found to rapidly attack the side facets of the nanoprisms (bound by {110} planes), while leaving the more stable {111} faces relatively untouched. Owing to the Gibbs-Thomson effect, the sharp tips are even less stable than the nanoprism edges, and are therefore more rapidly degraded; the net result is a rounding of the nanoparticle structure, producing disk-like nanoparticles with dramatically blueshifted spectra. The dissociated silver is then either redeposited on the {111} basal planes, leading to an increase in the thickness of the nanoprism, or aggregates to form very small (<3 nm) nanoparticles in solution. Bromide and iodide were found to effect a similar shape transformation,³¹ although at a more rapid rate. Certain thiols also lead to a restructuring of the nanoprism surface.³⁴ Based on the analysis of X-ray absorption spectra at the Ag L3- and S K-edges, the etching process was determined to occur via the surface oxidation of the nanoprism

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to form the silver(I) thiolate complex; the thiolate is then in turn oxidized to the disulfide, leading to the redeposition of small metallic silver nanoparticles (similar to those observed after etching by chloride). Very similar restructuring processes have been shown to occur when the pH of the solution is lowered,³⁸ when the nanoprism solution is heated in the presence of ambient oxygen,³⁷ or when it is exposed to intense UV irradiation.³⁵ In all cases, the vertices of the triangular nanoprisms are etched away, leaving rounded nanoplates behind; this sensitivity to such a wide variety of stimuli limits their utility in many applications, especially those involving exposure to biological media or environmental contaminants.

Owing to this chemical, thermal, and photochemical instability, substantial effort has gone into protecting the AgNPr surface, either through surface passivation with organic groups,^{30,33} or through the synthesis of core-shell AgNPrs.^{7,8,39-43} Both Lee et al.³⁰ and Jiang et al.³³ found that short chain alkanethiols could be used to arrest the etching normally observed in chloride solutions, and successfully used this approach to prepare silver nanoplates with highly tunable LSPR wavelengths. Metallic or metal oxide shells have also been employed to protect the underlying silver core from degradation. Silica-coated AgNPrs can be readily prepared via a Stöber process, and display improved chemical and thermal stability;³⁹ however, thick silica shells would also insulate the surrounding medium from the AgNPr near-field, limiting their utility in plasmonic applications. Core-shell Ag@Au nanoprisms (Ag@AuNPrs) offer an alternative method of improving nanoparticle stability.^{7,8,40-43} The more oxidatively-stable gold surface is less susceptible to etching than the underlying silver core, while remaining plasmonactive. Despite these advantages, due to the galvanic replacement reaction used in their preparation, it can be difficult to completely encase the AgNPr core without damage to the nanoparticle structure.40,42 While several studies have shown that Ag@AuNPrs are more stable to chloride than their pure silver analogues, comprehensive studies on their chemical stability are lacking, and their stability with respect to other key etchants (e.g., bromide, iodide, etc.) has not been investigated.

In all but the least demanding of applications, the stability of the metal nanoprism is a limiting factor. In biological imaging, label-free biosensing, or therapeutic applications, the high concentration of endogenous chloride ion rapidly degrades the nanoprism structure;¹⁰ similarly, in plasmon-enhanced dye sensitized solar cells, nanoparticle degradation by the iodide-containing electrolyte is a known issue.^{16,44} Thermal and photochemical degradation is also a concern in most optical and optoelectronic applications, especially at the high power densities associated with laser excitation sources; the AgNPrs are excellent photothermal converters,⁴⁵ while simultaneously being susceptible to thermal degradation.^{36,37} As such, there is a clear impetus to more fully and systematically understand the stability of these nanomaterials.

Here we report the chemical and thermal stability of silver, coreshell silver-gold, and gold nanoprisms (AuNPrs). As expected, the AgNPrs are immediately and irreversibly degraded by all halide ions, amines, thiols and elevated temperatures. The triangular nanoprisms undergo a shape transformation process, and are restructured into disk-like nanoplates, in agreement with previous work.^{31,32} Our results also show that while the Ag@AuNPrs are substantially more stable to chloride and bromide ions, the nanoprisms are still degraded by other etchants (*e.g.*, iodide, thiols, amines and heat). The AuNPrs were the only nanoparticles that were able to completely withstand all of the conditions tested, and our results therefore suggest that for applications involving chemical exposure, the AuNPrs are a much better choice than either their AgNPr or Ag@AuNPr analogues.

2. Experimental

2.1 Materials

AgNO₃ (99%) and NaBH₄ (98%) were purchased from EDC Chemicals. Polyvinylpyrrolidone (PVP, $M_w = 40$ kDa), trisodium citrate (TSC, 99%), NH₂OH·HCl (99%), NaOH (97%), aqueous dimethylamine (40 wt%), hydrogen tetrachloroaurate(III) hydrate and sodium thiosulfate were purchased from Sigma-Aldrich. Hydrogen peroxide (30 wt%), NaCl (99%), and NaI (99%) were purchased from Fisher Chemical. Thiol-terminated polyethylene glycol (PEG-SH, $M_w = 10$ kDa) was purchased from Laysan Bio. NaBr (99%) was purchased from Alfa Aesar. All solutions were prepared using Milli-Q water (18.2 M Ω cm).

2.2 Characterization

UV/vis/NIR spectra were acquired on a Cary 6000i UV/vis/NIR spectrophotometer. For the kinetic experiments, spectra were acquired at 15 minute intervals. Transmission electron microscope (TEM) images were acquired on a Philips CM10 microscope operating at 100 kV. Dynamic light scattering (DLS) measurements were made using a Malvern Zetasizer NanoS.

2.3 AgNPr synthesis

Silver nanoprisms were prepared according to literature methods.⁴⁶ AgNO₃ (0.1 mL, 50 mM), PVP (2 mL, 17.6 mM), TSC (1 mL, 75 mM), and H₂O₂ (0.12 mL, 30 wt%) were combined in 48 mL of water and aqueous NaBH₄ (0.5 mL, 100 mM) was rapidly injected while the solution was stirred vigorously. After ~40 min the solution turned dark blue, indicating the formation of the AgNPrs. The as-prepared AgNPr solution was adjusted to an optical density of 1.0 and stored at 4 $^{\circ}$ C for up to one week.

2.4 Ag@AuNPr synthesis

The Ag@AuNPrs were prepared based on a modification of existing literature procedures.⁴³ The as-prepared AgNPr solution was adjusted to an optical density of 0.4 by diluting with water. HAuCl₄ and NH₂OH·HCl were simultaneously introduced into the AgNPr solution through two separate syringes on a mechanical syringe pump. Throughout the addition, the solution was immersed in an ice bath and stirred vigorously. In a first stage, HAuCl₄ (0.275 mM) and NH₂OH·HCl (3 mM) were added for 30 min at a rate of 1 mL h⁻¹. Next, basic NH₂OH·HCl (3 mM, prepared by adding 200 µL of 0.5 M NaOH to 6.0 mL of 3.0 mM NH₂OH·HCl) and HAuCl₄ (0.275 mM) were added at a rate of 1 mL h⁻¹ for 90 min. Finally, NH₂OH·HCl (3 mM) and HAuCl₄ (0.275 mM) were added at a rate of 2 mL h^{-1} for 7 min.

2.5 AuNPr synthesis

AuNPrs were prepared based on a slight modification of existing literature procedures.⁴⁷ Aqueous HAuCl₄ (20 mL, 2 mM) and Na₂S₂O₃ (24 mL, 0.5 mM) were combined, and after the solution turned brown (*ca.* 4 min), additional Na₂S₂O₃ (16 mL, 0.5 mM) was added at a rate of 1 mL min⁻¹. The solution was then centrifuged at 4000 r.p.m. (2218g) for 5 min and redispersed in either pure water or 1.5 mM TSC.

3. Results and discussion

3.1 Nanoparticle synthesis and characterization

Triangular AgNPrs were prepared by reducing an aqueous solution of AgNO₃ with NaBH₄ in the presence of trisodium citrate, PVP, and H₂O₂.⁴⁶ The absorption spectrum of the AgNPrs is shown in Fig. 1. The spectrum consists of three major bands (at 720, 465, and 328 nm), which are assigned to the in-plane dipole, in-plane quadrupole, and out-of-plane dipole LSPR modes, respectively.²⁰ TEM images of the AgNPrs (Fig. 2a) confirm their triangular structure, and show that the particles have an average edge length of 41 \pm 9 nm (Fig. S1, ESI^{\dagger}). Pure AuNPrs were also synthesized according to literature procedures, and have a qualitatively similar (although substantially red-shifted) absorption spectrum. The nanoprisms are again highly triangular in shape, with sharp vertices and a high aspect ratio (Fig. 2c). The AuNPrs are also larger than their AgNPr analogues, with an average edge length of 110 ± 30 nm (Fig. S1, ESI⁺). A small secondary population of spherical nanoparticles is also observed. Centrifugation and redispersion of the nanoprism solution could effect only a partial removal of the spherical nanoparticles; however, since the LSPR band of the AuNPrs is so far removed from that of the spherical nanoparticles (954 nm vs. 536 nm), their presence is not expected to interfere with the present study.



Fig. 1 Normalized UV-vis-NIR spectra of the AgNPrs (black line), Ag@AuNPrs (red line) and AuNPrs (blue line).



Fig. 2 TEM images of the (a) AgNPrs, (b) Ag@AuNPrs, and (c) AuNPrs

After preparing both pure silver and pure gold nanoprisms, core–shell Ag@AuNPrs were prepared following slight modifications to the procedures of Shahjamali *et al.*⁴³ The as-synthesized AgNPrs were coated with a thin layer of gold *via* a galvanic replacement reaction with HAuCl₄. In early stages of this reaction, gold deposits exclusively on the side {110} facets of the AgNPrs. This produces AgNPrs that have exposed silver {111} facets, and gold-protected {110} edges. The substantial red-shift of the in-plane dipole LSPR band in the UV-vis-NIR spectrum (Fig. 1) is consistent with this core–shell structure, and the layer of gold can be seen as a slight darkening and pitting of the nanoprism edges in the TEM image (Fig. 2b).

There was no evidence for the deposition of any gold on the basal planes of the nanoprisms; following the reaction by UV-vis-NIR spectroscopy showed only a continual red-shift in the LSPR bands, and not the blue-shift that would be expected upon Au deposition on the {111} basal planes³² (Fig. S2, ESI†). If additional HAuCl₄ was added to the sample, the galvanic replacement reaction led to complete dissolution of the nanoprism interior and the formation of hollow triangular structures (Fig. S3, ESI†); as such, the reaction was stopped after only the nanoprism edges were coated with gold.

3.2 Chemical stability of Ag nanoprisms

The as-synthesized AgNPrs were first evaluated for their stability with respect to a variety of conditions, such as halide ions, thiols, amines and elevated temperatures. The stability of the AgNPrs in aqueous solutions of 10 mM NaCl, NaBr and NaI was evaluated by monitoring the absorption spectra as a function of time (Fig. 3a-c). As expected, the in-plane dipole LSPR band at ca. 720 nm very rapidly blue-shifts upon exposure to the halide ion; after only 30 min a new band has appeared in the UV-vis-NIR spectrum at ca. 460 nm, and the color of the solution has changed from blue to yellow. These results are consistent with a rounding of the nanoprism vertices and the formation of disklike nanoplates;^{31,32} the reduced aspect ratio gives rise to the substantially blue-shifted absorption band. In the case of NaI, there is also a pronounced decrease in the intensity of the LSPR band; I⁻ is known to be a powerful etchant for Ag nanoparticles, and the decrease in LSPR intensity may be due to either oxidation of the underlying silver nanoparticle, or the formation of a thick AgI surface layer, which would be expected to damp the plasmon resonance.48 It can also be observed that the wavelength of the out-of-plane quadrupole mode red-shifts over the course of the reaction, from 328 nm to ca. 340 nm (Fig. S4, ESI[†]). The red-shift of the out-of-plane mode is indicative of a



Fig. 3 Time-dependent absorption spectra of AgNPrs in the presence of (a) 10 mM NaCl, (b) 10 mM NaBr, (c) 10 mM NaI, (d) 1 mM PEG-SH, and (e) 13 wt% dimethylamine, and (f) while heating at 95 °C. Line spectra are shown in Fig. S5 (ESI†).

thickening of the nanoplates over the course of the reaction,^{32,34} and would suggest that at least some of the silver being etched from the nanoprism tips is being redeposited onto the basal planes of the nanoplates.

The change in AgNPr morphology was confirmed by transmission electron microscopy (Fig. 4a–c). As can be seen from the TEM images, after exposure to Cl⁻, Br⁻ or I⁻, the AgNPrs adopt a disklike morphology and the original sharp vertices of the AgNPrs are no longer visible. A reduction in the overall particle size can



Fig. 4 TEM images of AgNPrs after exposure to (a) 10 mM NaCl, (b) 10 mM NaBr, (c) 10 mM NaI, (d) 1 mM PEG-SH, and (e) 13 wt% dimethylamine, and (f) after heating at 95 $^{\circ}$ C.

also be observed, further supporting the idea that the observed nanoplates are the product of nanoprism degradation. DLS measurements also support this conclusion, indicating a reduction in the hydrodynamic diameter from 30 nm in the AgNPrs, to 8, 5, and 10 nm after etching with Cl⁻, Br⁻, and I⁻, respectively (Fig. S6a, ESI†). The appearance of a bimodal size distribution also indicates the formation of larger particles in solution: these may be precipitates of silver halide, or aggregated nanoparticles caused by the increase in solution ionic strength.

In addition to halides, thiols and amines are both known etchants of the AgNPrs, as are elevated temperatures. The AgNPrs were therefore subjected to 1 mM thiol-terminated poly(ethylene glycol) and 13 wt% dimethylamine solutions, and the as-synthesized AgNPr solution was also heated to 95 °C; absorption spectra were again acquired as a function of time (Fig. 3d-f). In all three cases, the absorption band blueshifts, albeit more slowly and to a lesser extent ($\lambda_{LSPR} \sim 580$ nm), than in the case of the solutions exposed to halide ions ($\lambda_{LSPR} \sim$ 440 nm). The TEM images (Fig. 4d-f) again show rounded nanoplates as the product of the reaction. DLS measurements indicate that the products of the shape transformation process have only limited colloidal stability, and are prone to aggregation (Fig. S6a, ESI[†]); the amine-functionalized nanoparticles show a greater degree of aggregation than do the PEG-SH functionalized nanoparticles, consistent with their very short alkyl chains and limited degree of steric stabilization. In contrast to the halides, thiols and amines, which all led to the formation of relatively stable silver nanoplates, heating to 95 °C resulted in a continual degradation of the nanoprism solution, even after the rounding of the nanoprisms was complete. From Fig. 3f it can be seen that after 5-10 min, the usual shape transformation had occurred, and the solution was purple in color; however, the LSPR band then gradually bleached, such that after 3 h, the solution was nearly colorless. This suggests that at these temperatures, not only are the triangular nanoprisms degraded into rounded nanoplates, but that the nanoplates themselves can be further oxidized by ambient oxygen. Clearly, the AgNPrs are very unstable when exposed to halides, thiols, amines, and heat. As such, their plasmonic applications are inherently limited, and substantial care must be taken to protect the nanoprism surface in order to utilize them in e.g., biological imaging or plasmonenhanced solar cell applications.

3.3 Stability of core-shell Ag@Au nanoprisms

Owing to the instability of the AgNPrs, a number of research groups have investigated the synthesis of core–shell Ag@AuNPrs. Gold and silver both adopt a face-centered cubic crystal structure and have similar lattice constants; since gold also has a more positive standard reduction potential, it can be readily deposited on the silver nanoprism surface *via* a galvanic replacement reaction. Several reports have demonstrated that the increased oxidative stability of the gold can protect the underlying silver core from etching by chloride ion; however, very few of these reports investigate the stability of the Ag@AuNPrs to other etchants, and there have been no comprehensive studies regarding the stability of the Ag@AuNPrs. We therefore exposed



Fig. 5 Time-dependent absorption spectra of Ag@AuNPrs in the presence of (a) 10 mM NaCl, (b) 10 mM NaBr, (c) 10 mM NaI, (d) 1 mM PEG-SH, and (e) 13 wt% dimethylamine, and (f) while heating at 95 °C. Line spectra are shown in Fig. S7 (ESI†).

our Ag@AuNPrs to the same set of conditions as the AgNPrs, and the UV-vis-NIR spectra as a function of time are shown in Fig. 5.

Our results indicate that a thin layer of gold on the nanoprism edges is entirely sufficient to prevent etching of the nanoprism by either chloride or bromide ions. In both cases, there is very little change in either the intensity or peak position of the LSPR band upon exposure to 10 mM solutions of NaCl and NaBr over the course of 20 h. The dramatic improvement in nanoprism stability is in agreement with the previous report of Aherne *et al.*,⁴⁰ who showed that the Ag@AuNPrs did not degrade in the presence of Cl⁻; clearly this stability also extends to the bromide ion as well. TEM (Fig. 6) and DLS (Fig. S6b, ESI†) measurements confirm this improved stability, and show no change in either particle shape or size upon exposure to NaCl and NaBr.

In contrast, the LSPR band dramatically red-shifts ($\lambda_{\text{LSPR}} \sim 1200 \text{ nm}$) upon exposure of the nanoprisms to 10 mM solutions of NaI, with a concomitant reduction in the peak intensity to almost zero. Clearly, the Ag@AuNPrs are not stable to the iodide ion, but neither are they degrading in the same fashion as the parent AgNPrs; if the nanoprism edges were being etched by iodide, the LSPR band would be expected to blue-shift, and instead the opposite behavior is observed. Similar, although less pronounced, red-shifts ($\lambda_{\text{LSPR}} \sim 950 \text{ nm}$) are also observed upon exposure of the Ag@AuNPrs to 1 mM solutions of PEG-SH. TEM images of both samples were acquired after 20 h, and indicate the formation of hollow (and often broken or incomplete) triangular



Fig. 6 TEM images of Ag@AuNPrs after exposure to (a) 10 mM NaCl, (b) 10 mM NaBr, (c) 10 mM NaI, (d) 1 mM PEG-SH, and (e) 13 wt% dimethylamine, and (f) after heating at 95 $^{\circ}$ C.

rings (Fig. 6c and d). These unique nanostructures are consistent with the original size and shape of the Ag@AuNPrs, and most likely result from the complete dissolution of the silver core from the Ag@AuNPrs, leaving the gold shell behind. Taken together, these results suggest that the iodide and PEG-SH solutions do not attack the nanoprism edges, which are adequately passivated by gold; instead, both compounds have strong enough affinities for the silver surface that they attack the silver {111} faces, effectively etching the Ag@AuNPr from the inside out. This mechanism explains the observed red-shift in the absorption spectrum, since hollow nanostructures are known to have red-shifted LSPR bands as compared with their solid counterparts.⁴¹ These results clearly indicate that while the silver {111} faces are relatively stable to chloride and bromide, they are readily degraded by etchants with a stronger affinity for the silver surface, such as NaI and PEG-SH.

The Ag@AuNPr solutions are also unstable when exposed to dimethylamine. The degradation mechanism appears to be similar to what is observed in the pure AgNPrs, namely a rounding of the nanoprism vertices which leads to the production of nanoplates. The blue-shift observed in the UV-vis-NIR spectra (Fig. 5e) and the rounded particles observed in the TEM (Fig. 6e) are both consistent with this mechanism. As was also observed in the case of the AgNPrs, the dimethylamine has a very detrimental effect on the colloidal stability of the resultant nanoparticles; aggregates of up to 1000 nm are observed by dynamic light scattering (Fig. S6b, ESI⁺).

Finally, the thermal stability of the Ag@AuNPrs was evaluated by heating the solution to 95 °C. After heating for 3 h, the LSPR band of the Ag@AuNPrs was relatively unchanged in shape; however, it had decreased in intensity to less than half of its original value. This suggests a very different degradation mechanism to those observed previously (Fig. 7). Instead of the ensemble of particles being slowly and homogenously degraded into either rounded or hollowed structures (which would lead to either blue-shifts or red-shifts in the LSPR band, respectively), individual nanoprisms are rapidly degraded into colorless (*i.e.*, plasmon-inactive) byproducts. This can be understood based on the relative stability of the degraded products. In the case of the etching of the AgNPrs by halides, the resulting



Fig. 7 Schematic of possible nanoprism etching processes. (a) Rounding of the nanoprism tips leads to more stable products; the nanoprism solution etches as an ensemble, leading to a blue-shift in the LSPR wavelength. (b) Hollowing of the silver core leads to empty gold shells with red-shifted LSPR wavelengths. (c) Fragmentation produces less stable products that rapidly degrade further, leading to a decrease in LSPR intensity (but no shift in the LSPR wavelength).

rounded structures have lower surface energies than the AgNPrs, and are therefore etched more slowly than the parent nanoprism; as such, the entire nanoprism ensemble is degraded together at the same rate. In contrast, if the nanoprisms were to degrade via a sudden fragmentation process, rather than a gradual rounding, the exposed surfaces and/or defect sites would be less stable than the original structure; in this case, the already-fragmented nanoprism would very rapidly degrade further, eventually producing a mixture of both colorless byproducts and intact nanoprisms. The TEM image of the Ag@AuNPrs after heating for 3 h shows a mixture of both triangular Ag@AuNPrs and very small, round nanoparticles (presumably the byproduct of nanoprism degradation); this bimodal distribution of particles is more consistent with the degradation pathway proposed in Fig. 7c, and is further supported by DLS measurements (Fig. S6b, ESI[†]). While this mechanism would explain the decrease in the intensity of the LSPR band in the absence of a shift in the LSPR wavelength, other plausible mechanisms (e.g., precipitation or coalescence of the nanoprisms) are also possible and cannot be completely ruled out.

3.4 Chemical stability of Au nanoprisms

The preceding results clearly demonstrate that chemical compatibility of the core-shell Ag@AuNPrs is much more limited in scope than previously thought, and that the nanoprisms exhibit multiple different degradation pathways depending on the chemical species involved. Therefore, pure AuNPrs were also prepared in an attempt to determine what influence the unprotected Ag{111} faces had over the nanoprism degradation mechanisms, and whether a plasmon-active nanoprism could be prepared with a much wider range of chemical compatibility.

The AuNPrs were obtained by the reduction of chloroauric acid (HAuCl₄) with sodium thiosulfate $(Na_2S_2O_3)$,⁴⁷ and were purified by centrifugation and redispersion prior to use. They were then tested for their stability with respect to the same conditions employed previously, and the UV-vis-NIR spectra are shown in Fig. 8. The corresponding TEM images are shown in Fig. 9. As can be seen from the data, there is very little change in the absorption spectra under any of the conditions studied. The spectra of the AuNPrs before and after exposure to chloride and bromide are essentially superimposable, as might be expected based on the lack of degradation observed in the Ag@AuNPr samples. In the case of iodide, there is a very slight decrease in the peak intensity, but no corresponding shift in the LSPR frequency. As with the case of the heated Ag@AuNPr solution, this may indicate either the rapid degradation of a small population of defect-rich nanoprisms, or, the slow precipitation of the AuNPrs. The TEM image of the AuNPr sample exposed to 10 mM NaI shows no change in particle morphology, consistent with the UV-vis-NIR findings. These results further support the conclusion that the Ag@AuNPr degradation that is observed upon exposure to iodide is most likely coming from iodidemediated etching of the exposed Ag{111} faces, rather than through any degradation of the gold shell.

In the case of the PEG-SH, dimethylamine, or heated solutions, the AuNPrs again displayed a very high level of stability. No change



Fig. 8 Time-dependent absorption spectra of AuNPrs in the presence of (a) 10 mM NaCl, (b) 10 mM NaBr, (c) 10 mM NaI, (d) 1 mM PEG-SH, and (e) 13 wt% dimethylamine, and (f) while heating at 95 °C. Line spectra are shown in Fig. S8 (ESI \dagger).



Fig. 9 TEM images of AuNPrs after exposure to (a) 10 mM NaCl, (b) 10 mM NaBr, (c) 10 mM NaI, (d) 1 mM PEG-SH, and (e) 13 wt% dimethylamine, and (f) after heating at 95 $^{\circ}$ C.

in either the UV-vis-NIR spectra (Fig. 8d-f) or the particle morphology was observed (Fig. 9d-f). The only major difference observed in these samples was a change in the degree of colloidal stability (Fig. S6c, ESI⁺). The hydrodynamic diameter of the as-synthesized AuNPrs was measured to be 60 nm by dynamic light scattering, and is relatively unchanged on exposure to 10 mM NaCl, NaBr, and NaI; in contrast, upon PEGylation by PEG-SH, a bimodal particle size distribution is observed, which consists of both relatively unaggregated particles with a diameter of 80 nm, as well as much larger (\sim 700 nm) aggregates. In the case of the dimethylamine solution, the hydrodynamic diameter of the AuNPrs was measured to be ~ 100 nm; the increased size again suggests some aggregation of the AuNPrs. These results are consistent with both the Ag and Ag@AuNPr samples, which also show pronounced aggregation after functionalization with either PEG-SH or dimethylamine.

Since both the Ag and Ag@AuNPrs were synthesized in solutions containing sodium citrate, whereas the AuNPrs were not, the stability of the AuNPrs was reevaluated in 1.5 mM citrate solution. This was done in order to confirm that the enhanced stability of the AuNPrs is due to the underlying gold core, as opposed to any change in surface chemistry. Citrate is known to stabilize the AgNPrs through a preferential binding to the {111} facets,²⁵ and this may affect either the etching rate or degradation mechanism. The absorption spectra as a function of time for the AuNPrs dispersed in citrate are shown in Fig. S9 (ESI[†]). The citrate clearly has a negative impact on the stability of the AuNPrs. The slow AuNPr etching observed in the case of the 10 mM NaI solution appears to be accelerated in the presence of citrate. Additionally, both the dimethylamine-functionalized and heated AuNPr solutions display an even more rapid decrease in the intensity of the LSPR band. While the plasmon band does appear to narrow, there is no accompanying red- or blue-shift, again suggesting that either the nanoprisms become less stable after the etching process begins, or that they are precipitating from solution. While we do not have a definitive explanation for this behavior, it may be that the citrate displaces existing surface groups from the surface of the AuNPrs, resulting in

poorer surface coverage, and a greater propensity for precipitation. Given the large size of these nanoprisms (Fig. S1, ESI[†]), even a modest reduction in colloidal stability may be sufficient to induce precipitation. While the weakly basic nature of the citrate anion may also contribute to the faster degradation rates, given the stability of the AuNPrs to concentrated dimethylamine solutions (Fig. 8e), this is considered less likely.

4. Conclusions

We have carried out a thorough and comprehensive investigation of the stability of triangular metal nanoprisms under a variety of conditions relevant to their eventual use in plasmonic applications (e.g., halide ions, thiols, amines, and elevated temperatures). The AgNPrs were unstable to each of the conditions tested, and displayed a distinctive rounding of the nanoprism tips that was accompanied by a blue-shift in the in-plane dipole LSPR mode. Importantly, the Ag@AuNPrs, while more stable to chloride and bromide ion, still revealed an important vulnerability of the Ag{111} facets to etching by iodide and PEG-SH, leading to the formation of hollow triangular structures. Since these Ag@Au core-shell structures have been proposed as more stable alternatives to pure silver nanoparticles, it is crucial to better understand their range of chemical compatibilities. As an example, these nanoprisms would be unsuitable for applications in plasmon-enhanced dye-sensitized solar cells, where the iodide-based redox mediator would rapidly degrade the underlying nanoprism morphology. In contrast to the two other types of nanoprisms studied in this work, the AuNPrs were exceptionally robust, and were insensitive to each of the conditions tested. Our results suggest that the AuNPrs (or, presumably, Ag@AuNPrs featuring a much more complete gold shell) are the best choice for plasmonic applications involving all but the most benign environmental conditions.

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