

Synthesis and Characterization of Plasmonic Asymmetric Hybrid Nanoparticles

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AHNs were fabricated by vacuum evaporation of thin layers of SiO, LiF, Ti, Al, Cr, Ni, and Fe onto Ag nanoparticles immobilized on glass substrates modified with poly(4-vinylpyridine). After the deposition, the particles were stripped into solution and characterized by UV–vis spectroscopy as well as transmission and scanning electron microscopy. The presence of the caps shifted the plasmon resonance into the red spectral region according to the refractive index of the cap material. In the case of metals, specifically Fe, the cap damped the plasmon resonance, and to minimize this effect, a thin layer of SiO was deposited between the Ag core and Fe cap. A thin layer of SiO also was deposited on top of the Fe cap to protect the latter from oxidation in the aqueous environment. The Fe cap rendered magnetic properties to plasmonic AHNs.

Introduction

Asymmetric hybrid nanoparticles (AHNs) consist of a core with one or several caps of different materials deposited on its surface.^{1–10} Contrary to core–shell nanoparticles, the caps of AHNs cover only a part of the core surface, resulting in nanostructures that exhibit not only combined properties of both the core and caps but also have asymmetry of chemical and physical properties. The latter attribute renders AHNs capable of directional self-assembly leading to complex architectures not achievable with completely symmetric building blocks.

Physical vapor deposition⁹ provides a facile method for fabricating AHNs of various compositions by evaporating different materials on nanoparticles immobilized on solid substrates. Several groups have demonstrated this technique using glass or polystyrene beads as the solid support for asymmetric caps of gold,^{1–6} platinum, palladium,¹ nickel,³ Ag, Cu, Cr,² and Al.^{2,7} In these studies, glass or polymer beads were spin-coated onto substrates and physical vapor deposition was carried out to deposit the metal cap on the exposed side of the beads. The beads, however, served only as templates for the caps and were discarded or dissolved

after deposition. This approach was used to add anisotropic magnetic properties to fluorescent polymer beads, and the rotation of the beads was controlled by an external magnetic field.⁷ The deposited magnetic cap on the beads was thicker than the skin depth for light at both the excitation and emission wavelengths of the fluorescence therefore blocking any transmission of light through that side of the particles. As the magnetic field is modulated, all the beads rotate in unison and the fluorescence signal is only emitted in one direction at a time. This leads to a controllable “blinking” of the fluorescence signal increasing the S/N ratio of the measurements.

Other groups have developed synthetic methods for creating metal/ semiconductor asymmetric particles *in situ*, resulting in gold caps on CdSe nanocrystals.^{10,11} In this two-part synthesis, CdSe nanocrystals were formed via pyrolysis and then a gold cap was chemically deposited onto one or both ends of the nanocrystals. The authors proposed that the gold caps could be useful for integration into wiring and for self-assembly although no specific applications were provided.

Here, the fabrication of novel types of AHNs via thermal evaporation of different materials onto plasmonic Ag nanoparticles is described. We emphasize the extraordinary optical properties of these nanoparticles that result from the excitation of plasmon resonances as well as the ability to change these properties and to add new features by depositing, on their surface, caps of different materials. The silver core was not only used as a template supporting the caps but became an integral component of the asymmetric nanostructure. These particles are termed plasmonic AHNs. Combined physical, chemical, and optical properties of both the cap and the core materials results in nanoparticles for a variety of applications that are not accessible when unmodified, core/

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shell, or other previously described asymmetric nanoparticles are used. The main goal of the initial studies reported here is to demonstrate the feasibility for synthesizing plasmonic AHNs and to determine how different materials (both metals and nonmetals) affect their plasmon resonances. Using this approach, Ag plasmonic AHNs were synthesized with magnetic properties while simultaneously retaining strong plasmon resonances. Several layers of different materials were also applied to the same Ag NPs thereby producing multilayered plasmonic AHNs. Similarly to hemispherical “caps” deposited on silica spheres that were used to orient and reimmobilize nanoparticles onto substrates,³ plasmonic AHNs with magnetic caps were also vectorially oriented on substrates using a uniform magnetic field.

Experimental Section

Chemicals. Ag₂O (99.99%), Cr (99.99%), Ag (99.999%), and optical grade LiF (99.5%) were purchased from Alfa Aesar. Reagent alcohol (Ethyl alcohol) was purchased from Aaper Alcohol and Chemical Company. Fe pellets (99.95%), Ti pellets (99.995%), Ni pellets (99.995%), Al pellets (99.999%), and SiO (99.99%) were purchased from Kurt J. Lesker Company. HF (49%) and HNO₃ were purchased from Fischer Scientific. Poly(4-vinylpyridine) (PVP), 160 000 MW, was purchased from Aldrich. All chemicals were used as received. Ultrapure water with 18 MΩ·cm resistivity was obtained from a standard four-bowl Millipore Milli-Q water purification system.

Methods. Particles were prepared as described in ref 12, filtered four times, and used without centrifugation or concentration. Postmodification centrifugation was done using a Fisher Scientific Centrifuge Model 228. Extinction spectra were obtained using a Shimadzu UV-2501PC spectrometer. All spectra were processed and figures prepared using Spectra-Solve for Windows (LasTek Pty. Ltd.). Particle dimensions were measured and XPS spectra were acquired with a Hitachi HD-2000 STEM operating at 200 keV. Formvar-coated copper TEM grids with type B carbon were purchased from Ted Pella, Inc.

Results and Discussion

Single crystal, Ag NPs with a characteristic dimension of ca. 90 ± 5 nm were synthesized via the hydrogen reduction method.¹² The resultant bare particles did not have any extraneous chemicals adsorbed on their surface except silver oxide/hydroxide species that are not known to interfere with any surface chemistry. Contrary surface silver oxide and hydroxide stabilize the particles in aqueous suspensions by preventing their aggregation. The absence of extraneous species on the surface of these Ag NPs is an important feature that provides the flexibility for surface modification to tailor the adhesion properties of the core surface to the caps from a variety of different materials. The UV–vis extinction spectra of ca. 90 nm Ag NPs in water are characterized by the presence of an intense, broad band at 490 nm due to the dipolar component and a much weaker band at 418 nm that appears on the side of the broad band due to the quadrupolar component of the plasmon resonances.¹³

Silver NPs were self-assembled from aqueous suspensions on the surface of standard microscope slides modified with PVP. It was previously demonstrated that PVP is a universal surface modifier that can be used for the efficient immobilization of many different nanoparticles on various dielectric and metal substrates.¹⁴ The modified slides were exposed to a suspension of Ag NPs in deionized water at low ionic strength. Low ionic strength is required in order to maintain long-range electrostatic repulsion between particles and, consequently, for the formation of the assemblies in which particles do not touch each other and do not form 2D aggregates. By changing the exposure time, different density of particles on the slides can be obtained. Care also was exercised to minimize the aggregation of the particles, as the slides were dried before placing into a vacuum chamber. This surface aggregation was caused by the capillary forces that developed when solvent evaporated and further supported by the fact that the Ag NPs can freely move on the slide surface uniformly coated with PVP. Consequently, drying of the slides from solvents with smaller surface tension (e.g., alcohol) as well as blocking with metal ions the remaining pyridyl groups of PVP minimized the surface aggregation. After the self-assembly of Ag NPs, their surface can be additionally modified prior to the deposition of the caps. PVP and some other polymers were tested as the surface modifiers; however, there was no need to do any surface modification of the particles for the plasmonic AHNs reported here. It appeared that all caps adhered to the bare Ag surface sufficiently strong to withstand 15 min sonication in a standard ultrasonic bath. A mild, few-minute sonication step was used to strip off the plasmonic AHNs from the slides into water or any other suitable solvent that may contain additional molecules to stabilize the plasmonic AHNs or to further modify their surface. It also was concluded that the sonication does not destroy the PVP layer on the slides and the stripped plasmonic AHNs do not carry the PVP molecules on their exposed (not covered with the caps) surface. After the sonication, the slides retained their ability to adsorb Ag NPs when exposed to the particle suspension, and the stripped particles did not adhere to glass surfaces as one would expect if the AHNs carried a PVP moiety on their surface.

Several slides with Ag NPs were placed in the vacuum chamber for the deposition of different caps with one slide always being covered with a mask so that no caps were formed on the surface of Ag NPs on this slide. This slide was treated in the same way as the slides with caps, and the stripped particles from this slide were used as a reference in all measurements, including spectroscopic characterization.

Plasmonic AHNs were synthesized with silicon monoxide and lithium fluoride caps as examples of high and low refractive index materials, respectively (Figure 1a and Figure 1c). Some particles appear in TEM without the caps because they were adsorbed to the TEM grid in the cap-down orientation. The deposition was carried out in the direction normal to the slide surface; therefore, the caps covered approximately half of the Ag PN surface. It was expected

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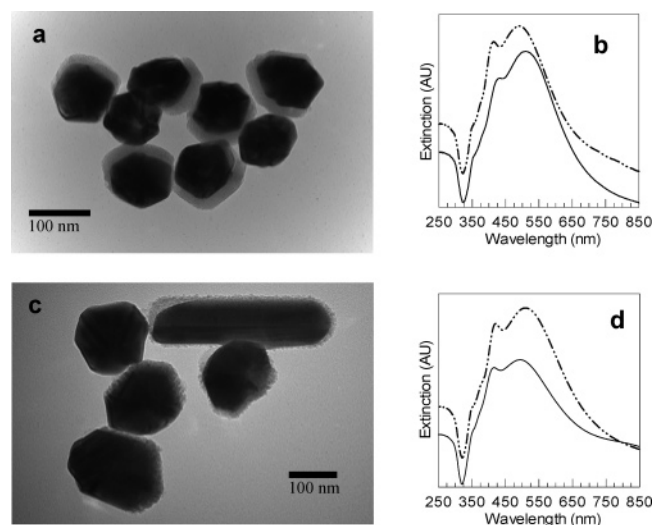


Figure 1. TEM (a,c) and UV-vis spectra (b, d) of plasmonic AHNs with 20 nm silica (a, b) and 10 nm LiF (c, d) caps. Solid curves correspond to plasmonic AHNs, and the dashed curves correspond to the same particles without the caps. UV-vis measurements were performed on stripped particles in water. The spectra in parts b and d are shifted vertically for clarity.

that the deposition of caps with the refractive index n larger than that of the surrounding medium (water, $n = 1.33$) will result in a red shift of the plasmon resonance compared to the same particles without the caps. The larger the refractive index, the larger, though different, the expected shift for both the dipolar and quadrupolar components of the resonance.¹⁵ The deposition of 20 nm thick SiO caps led to a 20 nm spectral shift of the dipole and a 17 nm shift of the quadrupole (Figure 1b). In previous studies, a 20 nm thick silica shell synthesized by the sol-gel chemical method around 80 nm Ag NPs produced a similar, 25 nm red shift.¹⁶ The refractive index of the bulk amorphous silica is 1.46, but the silica shell around Ag NPs had the effective refractive index smaller because the sol-gel layer was hydrated. From this point of view, the observed shift of the resonance in Ag AHNs appeared to be rather small for a typically high $n = 1.95$ of silicon monoxide films. Even if considering that the silicon monoxide caps cover only half of the NPs surface as compared to the entire surface covered by the silica shell in ref 16, the AHNs should experience a volume-weighted refractive index of ca. 1.6 that is still substantially larger than that of the hydrated silica shell, so that the observed red shift should be larger as well. On the basis of these numbers, it was concluded that the effective refractive index of the caps on the plasmonic AHNs was closer to that of amorphous silica than to dense silicon monoxide films, possibly due to the oxidation of SiO into SiO₂ in aqueous environment. Also, it is known that the refractive index of silicon monoxide strongly depends on the deposition conditions.¹⁷

Unexpectedly, LiF caps caused blue shifts for the dipole (16 nm) and quadrupole (4 nm) components of the plasmon resonance (Figure 1d) despite the fact that the refractive index

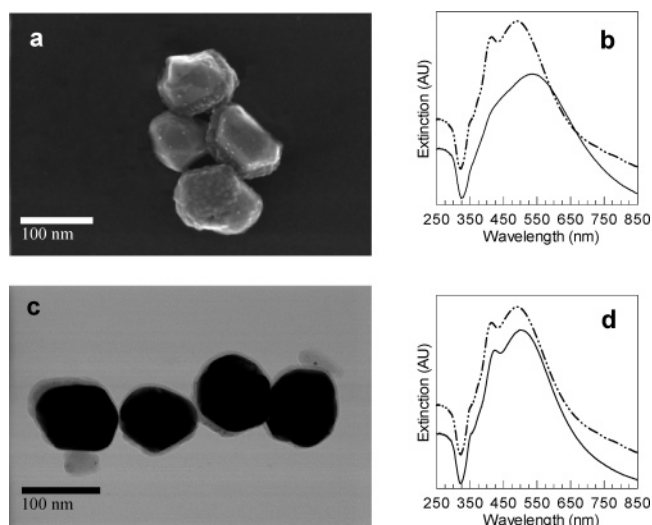


Figure 2. TEM and SEM (a, c) and UV-vis spectra (b, d) of plasmonic AHNs with 10 nm titanium (a, b) and 10 nm aluminum (c, d) caps. Solid curves correspond to plasmonic AHNs, and the dashed curves correspond to the same particles without the caps. UV-vis measurements were performed on stripped particles in water. The spectra in parts b and d are shifted vertically for clarity.

of this material (1.4) is also higher than that of water. This behavior can be explained by the large difference in the electric dipole moments of the two materials. Whereas the dipole moment of silica is zero, the dipole moment of lithium fluoride is large, 6.33 Debye.¹⁸ Conceivably, the vectorially oriented lithium fluoride molecules produce at the surface of Ag NPs a static electric field that interacts with the electron density by 'pushing' the electrons from the surface layer more into the interior of the particles or by 'pulling' the electrons more into the surface layer depending on the orientation of the molecules. Both effects alter the effective electron density that participates in the plasmon oscillation thereby causing red or blue spectral shift of the plasmon resonance. A similar interpretation was suggested to explain the observed red/blue shift of the plasmon resonance in Ag NPs coated with electron-withdrawing/-donating chemical species.¹⁹

Titanium and aluminum were deposited onto Ag NPs to exemplify the caps with high refractive index materials (Figure 2a and Figure 2c). Because the direct thermal evaporation of the oxides is difficult, the pure metals were evaporated first and then oxidized upon exposure to the ambient atmosphere and aqueous environment to form titanium dioxide and aluminum oxide caps. The refractive index of both materials strongly depends on the deposition conditions and is assumed to be around 2 for titania and 1.7 for alumina. A 10 nm cap of titania caused a large, 43 nm red shift of the dipole component of the plasmon resonance (Figure 2b) which is commensurate with its high n , whereas the same thickness alumina cap shifted the resonance by only 10 nm. Aluminum is known to form porous oxide layers upon oxidation, and the observed small shift was most likely due to this porous hydrated cap.

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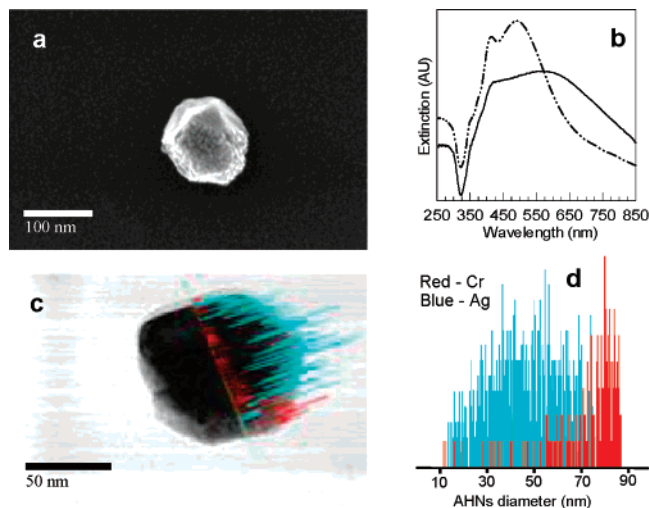


Figure 3. SEM (a) and TEM (c), UV-vis spectra (b), and EDX linescan of plasmonic AHNs with 10 nm chromium caps. The solid line in part b corresponds to plasmonic AHNs, and the dashed line corresponds to the same particles without caps. UV-vis measurements were performed on stripped particles in water. The spectra in part b are shifted vertically for clarity.

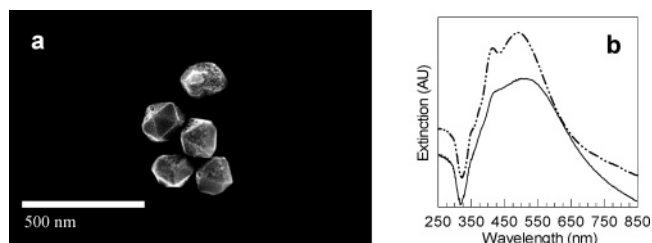


Figure 4. SEM (a) and UV-vis spectra (b) of plasmonic AHNs with 10 nm nickel caps. The solid curve in part b corresponds to plasmonic AHNs, and the dashed curve corresponds to the same particles without caps. UV-vis measurements were performed on stripped particles in water. The spectra in part b are shifted vertically for clarity.

The AHN technology provides an opportunity for adding magnetic properties to different nanoparticles. For this purpose plasmonic AHNs were synthesized with caps of chromium, nickel, and iron. A 10 nm Cr cap on Ag NPs, however, did not produce noticeable magnetic properties as concluded from no response of the AHN suspension to the magnetic field from a permanent magnet. SEM and TEM revealed a cap on the Ag NPs (Figures 3a and 3c), and the EDX scan confirmed the presence of chromium species on their surface (Figure 3d). The lack of magnetic properties indicates that the chromium metal was oxidized upon exposure to ambient atmosphere and aqueous environment into oxides, most likely Cr(II) and Cr(III) and not into Cr(IV) that is known to be strongly magnetic. As can be seen from the SEM image (Figure 3a), the cap consisted of small oxide particles. The EDX scan also indicates that the chromium metal did not alloy with Ag NPs during the synthesis and remained on the surface (Figure 3c and Figure 3d). The red shift of the plasmon in Figure 3b is due to the larger refractive index of chromium oxide species relative to that of water.

The deposition of Ni caps (Figure 4) rendered magnetic properties to plasmonic AHNs as was evident from the reversible coagulation of the particles when their aqueous suspension was subjected to a magnetic field gradient. SEM

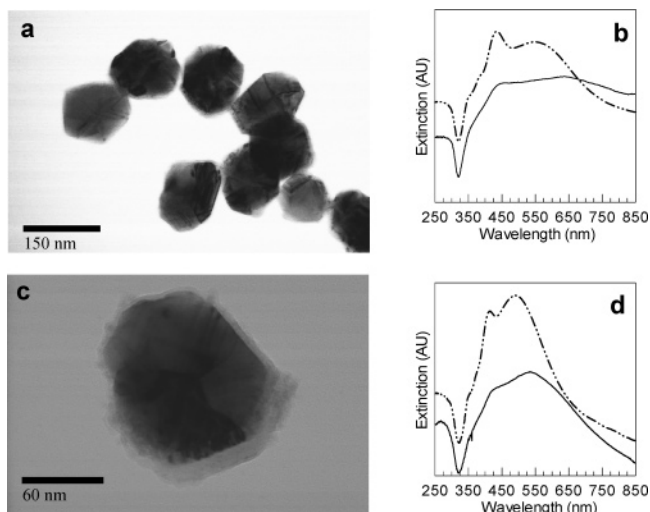


Figure 5. TEM (a,c) and UV-vis spectra (b,d) of plasmonic AHNs with 8.3 nm iron (a,b) and 10 nm iron capped with 10 nm silica (c,d) caps. Solid curves in parts b and d correspond to plasmonic AHNs, and the dashed curves correspond to the same particles without the caps. UV-vis measurements were performed on stripped particles in water. The spectra in parts b and d are shifted vertically for clarity.

indicated that the cap consisted of small, sub-10 nm particles, most likely of NiO which is known to superparamagnetic.^{20,21} Nickel hydroxide could also exhibit magnetic properties, but is very slightly soluble in water, and it is believed that it will dissolve upon transferring the plasmonic AHNs into an aqueous environment. It can be noted that the deposition of the Ni caps shifted the dipole component of the plasmon resonance by ca. 20 nm (Figure 4b) while the chromium caps shifted it by 65 nm. In addition, the plasmon resonance of AHNs with Cr caps is somewhat damped and broadened as compared to Ag NPs without caps (Figure 3b). The observed differences between Cr and Ni caps can be explained in terms of the different complex refractive index of the two oxides, specifically their imaginary part (extinction coefficient k). Whereas NiO is a transparent oxide with a low k , chromium oxides are often used as green pigments, implying a bigger k in the visible spectral range. This is only a qualitative argument because it is difficult to speculate on the actual values of n and k of the caps. The refractive index of oxide films is different from that of the bulk materials and strongly depends on the structure of the films and on the deposition conditions used to fabricate the films.

To improve magnetic response of plasmonic AHNs, particles with iron caps were synthesized (Figure 5). Direct deposition of 8.3 nm thick Fe caps onto 90 nm Ag NPs made the magnetically induced coagulation of the particles three to four times more efficient than in the case of Ni caps as was determined by the time required for the same volume and the same concentration of plasmonic AHNs to precipitate on the walls of the vessel. However, the particles, while being in a noncoagulated state, displayed significant changes in the plasmon, specifically a large red shift and flattening of the dipole component of the resonance as compared to the

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particles without the caps (Figure 5b). Such optical changes could be either due to the partial aggregation of the particles in the suspension or due to the direct effect of the Fe caps on the plasmon resonance of individual particles. Because the magnetically induced particle coagulation was completely reversible resulting in the same spectrum every time (Figure 5b, solid line), it was concluded that the observed plasmon changes were caused by the caps. A mixture of superparamagnetic iron oxide species was likely formed after the plasmonic AHNs with Fe caps were dispersed into water. Among different possible oxides, Fe_2O_3 is a semiconductor with the band gap (2.2 eV) in the visible spectral range.²² This band gap introduced additional k to the complex refractive index of the plasmonic AHNs thereby damping the resonance as manifested by a typical spectral behavior seen in Figure 5b. In addition to the complex refractive index of the cap, the plasmon resonance is also affected by the direct electronic coupling between conduction electrons in the silver core and the cap. Such coupling is also known to cause red shifts and damping of the plasmon resonance.

To protect iron from oxidation, AHNs were synthesized with Fe caps overcoated with a 10 nm layer of SiO (Figure 5c). Even though this approach can potentially render ferromagnetic properties to plasmonic particles, no permanent magnetization was observed in our experiments with a magnet: the magnetically induced coagulation was completely reversible without any additional particle aggregation. Additional aggregation was expected if the residual magnetization in the ferromagnetic caps remained after the removal of the external magnetic field. However, the results of this simple experiment cannot be used to completely eliminate the possibility of ferromagnetic properties in these particles. The presence of the 10 nm SiO layer on top of the Fe caps could separate particles sufficiently to prevent their aggregation caused by residual magnetization of the ferromagnetic caps. It was also noted that overcoating the Fe caps with a protective SiO layer reduced the damping of the plasmon resonance (Figure 5d) most likely because of the differences in the complex refractive index of Fe metal and its oxides.

The observed plasmon damping by the Fe caps prompted the synthesis of plasmonic AHNs with Fe caps separated from the metal surface by a thin SiO layer (Figure 6). As expected, placing a spacing SiO layer between the Fe cap and Ag NP surface preserved the resonance in plasmonic AHNs (Figure 6b). The effect of the thickness of the spacing layer on the plasmon resonance in AHNs with the Fe cap is shown in Figure 7a. The optical measurements were performed on the triple-cap AHNs consisting of a SiO spacer layer of various thicknesses and 10 nm thick Fe cap overcoated with 12 nm thick SiO layer to prevent iron oxidation. The addition of increasingly thicker spacing layers progressively reduced the damping of the resonance, as can be seen from the recovery of the plasmon resonance intensity (Figure 7a). At the same time, the resonance continued to shift further into the red spectral range. The largest effects occurred between 0 and 2.5 nm thick spacing layers that was attributed to the elimination of the direct electronic coupling

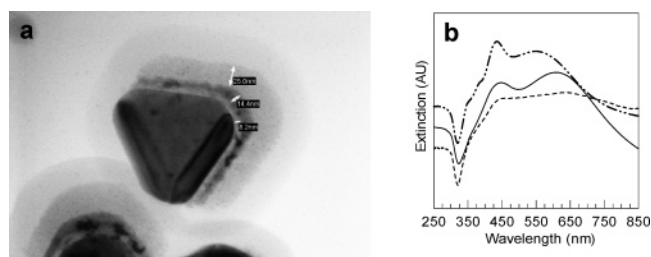


Figure 6. TEM (a) and UV-vis (b) spectra of plasmonic AHNs with 8.2 nm silica caps directly between Ag NPs and a 14.4 nm iron cap which is overcoated with a 25.0 nm silica cap to prevent oxidation. In part b, the solid curve corresponds to plasmonic AHNs and the dashed curve corresponds to the same particles without caps. UV-vis measurements were performed on stripped particles in water. The spectra in part b are shifted vertically for clarity. A charging halo is also visible around the particles (a).

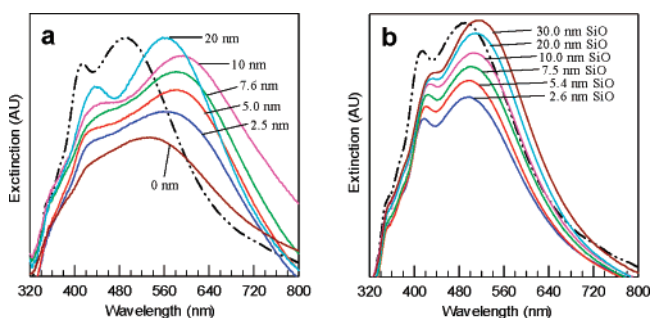


Figure 7. UV-vis spectral series (a, b) of plasmonic AHNs with 10 nm silica caps on top of 10 nm iron caps, and an intermediate layer of silica between the Ag NPs and the iron layer of varying thickness (a) as indicated in each spectra. The same colloid was modified with varying thicknesses of silica caps (b) as indicated for each spectra. The solid curves correspond to plasmonic AHNs, and the dashed curve corresponds to the same particles without caps. Measurements were performed on stripped particles in water.

between the Fe metal and the Ag core when the 2.5 nm layer was introduced. The increasing red shift was due to the increasing effective refractive index of the combined of Fe cap and the SiO spacing. However, the rate of this red shift decreased with the increasing thickness of the spacing layer because of the diminishing contribution of the Fe cap to the effective refractive index. At some thickness between 10 and 20 nm, the plasmon started to shift back because the effect of the Fe cap on the plasmon resonance of the silver core was greatly diminished, and the remaining red shift of the AHNs as compared to plasmon resonance position of Ag NPs in water (Figure 7a, dashed curve) was caused solely by the thick SiO spacing layer. Note that with the 20 nm spacing layer, the plasmon resonance completely recovered from the damping caused by the Fe cap, and the resultant plasmonic AHNs maintained their strong magnetic properties. The effect of the SiO spacing layer on the resonance of the plasmonic AHNs without the Fe cap is shown in Figure 7b for reference.

Finally, plasmonic magnetic AHNs were vectorially oriented on a substrate using a uniform magnetic field. In this experiment, a glass substrate modified with PVP was placed in the container with the suspension of plasmonic AHNs with Fe caps and the container was further placed into the region of the uniform magnetic field of a permanent magnet. After several hours of self-assembly, the substrate was removed and imaged with SEM, revealing that the AHNs were vectorially oriented on the substrate. Peculiarly, the vast

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majority of the particles appeared in the cap-down orientation despite the fact that cap-down and cap-up are two equivalent orientations. A possible explanation could be based on slightly different affinities of the Ag core and SiO cap for the PVP-modified surface.

Conclusion

It was demonstrated that the AHNs technology enables manipulation of resonance properties of plasmonic nanoparticles. At the same time, new properties can be added as was exemplified by the deposition of the magnetic caps onto the surface of Ag NPs. By placing a dielectric spacer layer between the magnetic cap and the surface of the plasmonic

particle, the damping of the plasmon resonance by the magnetic material can be avoided. This represents a general strategy for minimizing the interference of the caps with plasmon resonances of the core. Future work related to magnetic plasmonic AHNs will include SQUID and XPS measurements among others for characterizing magnetic properties and the oxidation state of the metals on the surface of the Ag NPs.

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