Published in final edited form as:

Nano Lett. 2009 August ; 9(8): 3038–3041. doi:10.1021/nl901513g.

Core–Shell Triangular Bifrustums

Hyojong Yoo, Jill E. Millstone, Shuzhou Li, Jae-Won Jang, Wei Wei, Jinsong Wu, George C. Schatz*, and Chad A. Mirkin*

Department of Chemistry and the International Institute for Nanotechnology, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208

Abstract

Au_{core}–Ag_{shell} triangular bifrustum nanocrystals were synthesized in aqueous solution using a seed-mediated approach. The formation of the Ag layer on the Au nanoprism seeds leads to structures with highly tunable dipole and quadrupole surface plasmon resonances. Discrete dipole approximation calculations show that it is the geometry of these novel structures rather than the addition of a new element that leads to the plasmon tunability. The structure and composition of these novel nanocrystals have been investigated by transmission electron microscopy, atomic force microscopy, X-ray photoelectron spectroscopy, and energy-dispersive spectrometry.

Nanomaterials composed of both gold and silver have complex optical features spanning the visible and near-infrared spectra, are generally considered to be low in toxicity, and exhibit facile surface functionalization chemistry.¹ These properties make them excellent testbeds for both fundamental studies and technological advances in fields ranging from nanobiodiagnostics² to catalysis.³ A composite nanomaterial containing these two elements is attractive, because it could provide significant plasmon tunability, hybrid chemical and surface modification properties, and insight into the growth of anisotropic nanostructures.^{4–6} Additionally, it is well known that multimetallic alloy and core–shell nanostructures exhibit unusual catalytic, electronic, and magnetic properties.⁷ However, while significant advances have been made in developing synthetic methods to prepare bimetallic pseudospherical particles^{4,7a} and anisotropic nanorods,⁵ only a few examples of crystalline triangular Au/Ag bimetallic nanostructures currently exist,⁶ in spite of the fact that these structures are ideal candidates for understanding both the evolution and consequences of nanoparticle anisotropy in core–shell systems. For example, our group has reported the photoinduced preparation of Au_{core}–Ag_{shell} nanoprisms, a study that has provided significant insight into the mechanism underlying the photochemical growth of Ag nanoprisms from spherical metal seeds.^{6a} In this paper, we describe the synthesis of a new class of two component triangular bifrustum nanocrystal,⁸ which consists of a triangular Au core with its broad {111} facets covered with a Ag layer of controllable thickness (Scheme 1). More importantly, we demonstrate plasmon tunability by controlling the amount of Ag deposited, the thickness of the bimetallic nanocrystal, and keeping the Ag and Au phases separated.

In a typical experiment, Au_{core}–Ag_{shell} triangular bifrustum nanocrystals were synthesized by reduction of Ag⁺ ions onto Au triangular nanoprism seeds (prepared according to literature procedures).⁹ The Au nanoprism solution was purified by centrifugation (3 min at 8000 rpm) and resuspended in a cationic surfactant solution (cetyltrimethylammonium

bromide, CTAB). The prism mixture was then grown by serial addition of L-ascorbic acid, Ag^+ ions (10 mM, AgNO_3 solution), and NaOH into the existing Au nanoprism solution (total volume of aqueous Au nanoprism solution before additions was 1.5 mL, where concentration of Au nanoprism seed solution was determined by optical density; 0.8 O.D. at 1230 nm, see Supporting Information).

Both transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) images of the $\text{Au}_{\text{core}}\text{-Ag}_{\text{shell}}$ nanocrystal structures obtained after addition of 10 μL of 10 mM AgNO_3 solution to the triangular Au seeds show the formation of the triangular bifrustum nanocrystals (Figure 1). The $\text{Au}_{\text{core}}\text{-Ag}_{\text{shell}}$ triangular bifrustum nanocrystals have an average edge length of 150 ± 20 nm (60 nanocrystals evaluated, Supporting Information Figure S1a). Individual particles exhibit a hexagonal electron diffraction pattern, indicating that the particle is a single crystal with broad faces consisting of $\{111\}$ lattice planes (Figure 1A inset). The diffraction pattern is indexed as the $[111]$ zone axis of a face-centered cubic structure. (The lattice parameters of Ag ($a = 0.4058$ nm) and Au ($a = 0.4079$ nm) are close, and therefore the diffraction spots are likely overlapped). The platelike triangular nanoprism seeds, as well as other platelike structures, share this common structural motif.^{10–13} Although the chemical identity of the Ag coating is not immediately apparent from the contrast in the image of the $\{111\}$ lattice planes, elemental analysis of these faces by X-ray energy dispersive spectroscopy (EDS) indicates the presence of both Ag and Au (Supporting Information Figure S2).

Subsequent microscopy analysis of the edges of these particles shows that they are better described as core-shell rather than alloy structures. Figure 1B,C shows STEM edge-on images of $\text{Au}_{\text{core}}\text{-Ag}_{\text{shell}}$ triangular bifrustum nanocrystals (after adding 10 μL of 10 mM AgNO_3 solution). The STEM images show Z-contrast (the heavier the element, the brighter the contrast) and were collected using a high-angle annular dark field detector. Thus, in these images the core Au nanoprism is easily observed as a bright band, since the Au scatters electrons more effectively than Ag. An EDS line profile of the Ag and Au composition traversing the edge of an $\text{Au}_{\text{core}}\text{-Ag}_{\text{shell}}$ nanocrystal suggests that the Ag covers the entire surface of the Au nanoprism. On the edge, we can also observe Au with a clear interface between the Au and Ag regions.¹⁴ The average thickness of each nanocrystal, as determined by STEM at the center of the $\{111\}$ faces, is approximately 17 nm.

The thickness of the triangular bifrustum nanocrystals can be controlled by the amount of Ag deposited on the Au triangular seed (Supporting Information Figure S1b). For example, the average thickness of the triangular bifrustum nanocrystals changed from approximately 4 to 8 nm, respectively, depending upon whether the Au seeds were treated with 5 or 10 μL of 10 mM AgNO_3 solution. For any of these core-shell triangular bifrustum nanocrystals, as they are sputtered with Ar^+ ions, the ratio of Ag/Au decreases, which reinforces the conclusion that the Ag is in the outermost layer of the nanocrystal (Supporting Information Figure S3).

UV-vis-NIR spectroscopy allows one to easily follow the growth of the core-shell triangular bifrustum nanocrystals (Figure 2). Indeed, the dipole plasmon resonance is very sensitive to the amount of Ag deposited on the triangular Au seeds. Note that in the spectrum of the triangular Au seeds, the bands at 1230 and 790 nm are assigned to the dipole and quadrupole surface plasmon resonances (SPRs), respectively (Figure 2 and Supporting Information Figure S4, spectrum a).^{9a} Significantly, a gradual blue shift and strong enhancement in the both of these resonances is observed as a function of Ag deposition and increased triangular bifrustum nanocrystal thickness (Figure 2 and Supporting Information Figure S4, spectra b–g).

It is important to note that with monometallic triangular nanoprism systems, plasmon tunability is possible via size control, by either changing nanoprism thickness or edge length;^{10,11a} however, this new class of nanocrystal exhibits a much greater range of plasmon tunability. In addition, one can realize structures with SPRs as low as 800 nm, which have not been observed with well-formed Au triangular nanoprisms.^{9,11}

We previously showed that the reduction of Au ions on seed Au nanoprisms predominately occurs on the Au{112} facet and leads to Au nanoprisms with larger edge lengths.^{11a} In the current study, Ag⁺ ion is reduced and deposited on both the Au{111} and Au{112} facets and forms Ag shells with notable changes in nanocrystal thickness and geometry. We believe that the interaction of Ag⁺ and Br⁻ ion (from CTAB) on the metallic surface may affect the crystal growth process. Groups have studied the mechanism of Ag nanoplate formation by varying the concentration of components including CTAB and demonstrated a key interaction between a CTAB molecular layer adsorbed on the metallic surface and Ag⁺ ions.¹² Interestingly, the Ag shells created here show truncation on the edges (Figure 1), which leads to the observed triangular bipyramid structure. While mixed samples of monometallic Ag triangular bipyramids have been prepared using a different approach,^{12a} the Au/Ag bimetallic triangular bipyramid structure has not been synthesized. The truncation is retained after subsequent additions of growth solutions to give bimetallic nanocrystals that can be described as thicker triangular bipyramids or complete bipyramidal structures. Control over morphology of bimetallic nanocrystals can be affected by changing the amount of Ag⁺ added (Supporting Information Figure S5).

Discrete dipole approximation (DDA) calculations based on the AFM and STEM experiments were carried out to simulate the optical features of the Au_{core}-Ag_{shell} nanocrystals (Figure 3).¹⁵ For the simulations, an average of the layered structure with truncations was used. Since the Ag layer on the Au{112} facet is not clear from the TEM images (Figure 1), the average edge length of Au seed nanoprisms (144 nm) has been used without modification.^{9a} The locations of the calculated dipole and quadrupole plasmon peaks do not exactly match the experimentally measured spectrum; however, the resonance wavelengths are extremely sensitive to fine details of the structures (particularly to the degree of rounding of the tips and thickness of the Ag and Au layers) so small deviations are expected. The experimental spectrum also shows broader SPR peaks than those in the DDA calculation due to polydispersity of bimetallic nanocrystals in solution. In addition to the model in Figure 3, the alloy and single component models (pure Au or pure Ag) as well as other hypothetical models have been simulated for comparison purposes (Supporting Information Figure S6, S7), and there is related work in ref 11c. Significantly, the results show that the component change (i.e., Ag versus Au) is not crucial to obtain the observed blue shifts in SPRs, since the wavelengths of maximum extinction in each model are very close to each other (Supporting Information Figure S6). Therefore, it is the geometry of the structure, which is tuned by the amount of Ag added and the corresponding increase in thickness, that leads to high SPR tunability in this class of nanocrystal structures.

This work is significant for the following reasons. First, the growth of Ag on the Au nanoprism surfaces displays a unique growth pattern, resulting in the first example of Au_{core}-Ag_{shell} triangular bipyramids. Second, the dipole and quadrupole SPRs in these structures are highly tunable based upon the thickness of the outer Ag shell. Third, the theoretical calculations suggest that it is the geometry and not the second chemical component that is primarily responsible for the large observed shifts. Next, many of these plasmon wavelengths are not accessible with pure Au triangular nanoprisms. Finally, the Au_{core}-Ag_{shell} bipyramid nanocrystals show stronger surface plasmon resonances (higher extinction) than pure Au nanoprisms, therefore we believe that this material will be useful for surface enhanced Raman scattering.¹⁶ Taken together, the results suggest that the use of

Ag to modulate the geometry of Au seeds is a facile way to potentially extend the utility of these structures in many areas where plasmonic wavelengths are important, including diagnostic labels,² energy harvesting,¹⁷ optical transport,¹⁸ and therapeutics.¹⁹

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This work was supported by the ONR and AFOSR. C.A.M. is also grateful for an NIH Director's Pioneer Award and a NSSEF Fellowship. G.C.S. and S.L. were supported by AFOSR/DARPA Project BAA07-61 (FA9550-08-1-0221). J.E.M. is grateful to Northwestern University for a Presidential Fellowship.

References

- (a) Jain PK, Huang X, El-Sayed IH, El-Sayed MA. *Acc Chem Res.* 2008; 41:1578–1586. [PubMed: 18447366] (b) El-Sayed MA. *Acc Chem Res.* 2001; 34:257–264. [PubMed: 11308299] (c) Hu M, Chen J, Li Z-Y, Au L, Hartland GV, Li X, Marquez M, Xia Y. *Chem Soc Rev.* 2006; 35:1084–1094. [PubMed: 17057837]
- (a) Nam J-M, Thaxton CS, Mirkin CA. *Science.* 2003; 301:1884–1886. [PubMed: 14512622] (b) Park SY, Lytton-Jean AKR, Lee B, Weigand S, Schatz GC, Mirkin CA. *Nature.* 2008; 451:553–556. [PubMed: 18235497] (c) Rosi NL, Mirkin CA. *Chem Rev.* 2005; 105:1547–1562. [PubMed: 15826019] (d) Alivisatos AP, Johnsson KP, Peng X, Wilson TE, Loweth CJ, Bruchez MP Jr, Schultz PG. *Nature.* 1996; 382:609–611. [PubMed: 8757130] (e) Haes AJ, Van Duyne RP. *J Am Chem Soc.* 2002; 124:10596–10604. [PubMed: 12197762]
- (a) Jana NR, Sau TK, Pal T. *J Phys Chem B.* 1999; 103:115–121. (b) Liu J-H, Wang A-Q, Chi Y-S, Lin H-P, Mou C-Y. *J Phys Chem B.* 2005; 109:40–43. [PubMed: 16850981]
- (a) Shibata T, Bunker BA, Zhang Z, Meisel D, Vardeman CF II, Gezelter JD. *J Am Chem Soc.* 2002; 124:11989–11996. [PubMed: 12358545] (b) Hostetler MJ, Zhong C-J, Yen BKH, Anderegge J, Gross SM, Evans ND, Porter M, Murray RW. *J Am Chem Soc.* 1998; 120:9396–9397. (c) Liz-Marzán LM. *Langmuir.* 2006; 22:32–41. [PubMed: 16378396] (d) Cao YW, Jin R, Mirkin CA. *J Am Chem Soc.* 2001; 123:7961–7962. [PubMed: 11493092]
- (a) Ah CS, Hong SD, Jang D-J. *J Phys Chem B.* 2001; 105:7871–7873. (b) Song JH, Kim F, Kim D, Yang P. *Chem-Eur J.* 2005; 11:910–916. [PubMed: 15593133] (c) Liu M, Guyot-Sionnest P. *J Phys Chem B.* 2004; 108:5882–5888. (d) Huang C-C, Yang Z, Chang HT. *Langmuir.* 2004; 20:6089–6092. [PubMed: 15248687] (e) Xiang Y, Wu X, Liu D, Li Z, Chu W, Feng L, Zhang K, Zhou W, Xie S. *Langmuir.* 2008; 24:3465–3470. [PubMed: 18294010]
- (a) Xue C, Millstone JE, Li S, Mirkin CA. *Angew Chem.* 2007; 119:8588–8591. (b) Xue C, Millstone JE, Li S, Mirkin CA. *Angew Chem, Int Ed Eng.* 2007; 46:8436–8439. (c) Tsuji M, Miyamae N, Lim S, Kimura K, Zhang X, Hikino S, Nishio M. *Cryst Growth Des.* 2006; 6:1801–1807. (c) Sanedrin RG, Georganopoulou DG, Park S, Mirkin CA. *Adv Mater.* 2005; 17:1027–1031.
- (a) Ferrando R, Jellinek J, Johnston RL. *Chem Rev.* 2008; 108:845–910. [PubMed: 18335972] (b) Cozzoli PD, Pellegrino T, Manna L. *Chem Soc Rev.* 2006; 35:1195–1208. [PubMed: 17057845] (c) Caruso F. *Adv Mater.* 2001; 13:11–22. (d) Aiken JD III, Finke RG. *J Mol Catal A: Chem.* 1999; 145:1–44. (e) Mizukoshi Y, Fujimoto T, Nagata Y, Oshima R, Maeda Y. *J Phys Chem B.* 2000; 104:6028–6032.
- Harris, JW.; Stocker, H. *Handbook of Mathematics and Computational Science.* Springer-Verlag; New York: 1998. p. 99
- (a) Millstone JE, Park S, Shuford KL, Qin L, Schatz GC, Mirkin CA. *J Am Chem Soc.* 2005; 127:5312–5313. [PubMed: 15826156] (b) Millstone JE, Wei W, Jones MR, Yoo H, Mirkin CA. *Nano Lett.* 2008; 8:2526–2529. [PubMed: 18642955]
- (a) Jin R, Cao YW, Mirkin CA, Kelly KL, Schatz GC, Zheng JG. *Science.* 2001; 294:1901–1903. [PubMed: 11729310] (b) Jin R, Cao YC, Hao E, Métraux GS, Schatz GC, Mirkin CA. *Nature.* 2003; 425:487–490. [PubMed: 14523440]

11. (a) Millstone JE, Métraux GS, Mirkin CA. *Adv Funct Mater.* 2006; 16:1209–1214. (b) Millstone JE, Georganopoulou DG, Xu X, Wei W, Li S, Mirkin CA. *Small.* 2008; 4:2176–2180. [PubMed: 19016498] (c) Shuford KL, Ratner MA, Schatz GC. *J Chem Phys.* 2005; 123:114713/1–114713/9. [PubMed: 16392589]
12. (a) Chen S, Carroll DL. *Nano Lett.* 2002; 2:1003–1007. (b) Zhou Y, Wang CY, Zhu YR, Chen ZY. *Chem Mater.* 1999; 11:2310–2312. (c) Bradley JS, Tesche B, Busser W, Maase M, Reetz MT. *J Am Chem Soc.* 2000; 122:4631–4636. (d) Curtis AC, Duff DG, Edwards PP, Jefferson DA, Johnson BFG, Kirkland AI, Wallace AS. *Angew Chem.* 1988; 100:1588–1590. (e) Curtis AC, Duff DG, Edwards PP, Jefferson DA, Johnson BFG, Kirkland AI, Kirkland AI. *Angew Chem, Int Ed Engl.* 1988; 27:1530–1533.
13. Chen S, Carroll DL. *J Phys Chem B.* 2004; 108:5500–5506.
14. Williams, DB.; Carter, CB. *Transmission Electron Microscopy IV: Spectrometry.* Springer; New York: 1996. Chapter 36
15. (a) Kelly KL, Coronado E, Zhao LL, Schatz GC. *J Phys Chem B.* 2003; 107:668–677. (b) Goodman JJ, Draine BT, Flatau PJ. *Opt Lett.* 1991; 16:1198–1200. [PubMed: 19776919]
16. Nie S, Emory SR. *Science.* 1997; 275:1102–1106. [PubMed: 9027306]
17. Kamat PV. *J Phys Chem C.* 2007; 111:2834–2860.
18. (a) Ghosh SK, Pal T. *Chem Rev.* 2007; 107:4797–4862. [PubMed: 17999554] (b) Krenn JR, Dereux A, Weeber JC, Bourillot E, Lacroute Y, Goudonnet JP, Schider G, Gotschy W, Leitner A, Aussenegg FR, Girard C. *Phys Rev Lett.* 1999; 82:2590–2593.
19. (a) Huang X, El-Sayed IH, Qian W, El-Sayed MA. *J Am Chem Soc.* 2006; 128:2115–2120. [PubMed: 16464114] (b) Hirsch LR, Stafford RJ, Bankson JA, Sershen SR, Rivera B, Price RE, Hazle JD, Halas NJ, West JL. *Proc Natl Acad Sci USA.* 2003; 100:13549–13554. [PubMed: 14597719]

Figure 1.

(A) TEM image of $\text{Au}_{\text{core}}\text{-Ag}_{\text{shell}}$ triangular bifrustum nanocrystals ($10\ \mu\text{L}$ of $10\ \text{mM}$ AgNO_3 solution) Inset: Electron diffraction pattern of the top of a nanocrystal; (B,C) STEM images of the nanocrystals. The bright bands in the center of each nanocrystal indicate the core Au nanoprism; (D) EDS line profile showing Au and Ag content along the nanocrystal edge. Arrows indicate truncation of Ag shell at the edges.

Figure 2. Normalized UV-vis-NIR spectra of $\text{Au}_{\text{core}}\text{-Ag}_{\text{shell}}$ triangular bipyramid nanocrystal colloids after adding (a) 0, (b) 1, (c) 2, (d) 3, (e) 5, (f) 8, and (g) 10 μL of 10 mM AgNO_3 solution, 50 μL of 100 mM L-ascorbic acid, and 75 μL of 100 mM NaOH.

Figure 3. Experimental (dotted line) and theoretical (DDA calculation, solid line) extinction spectra of $\text{Au}_{\text{core}}\text{-Ag}_{\text{shell}}$ nanocrystals. Inset: structural model of $\text{Au}_{\text{core}}\text{-Ag}_{\text{shell}}$ nanocrystal for the DDA calculation.

Scheme 1.

Formation of $\text{Au}_{\text{core}}\text{-Ag}_{\text{shell}}$ Triangular Bifrustum Nanocrystals