Where's the Silver? Imaging Trace Silver Coverage on the Surface of Gold Nanorods

Stephen R. Jackson,[†] James R. McBride,[†] Sandra J. Rosenthal, and David W. Wright*

Department of Chemistry, Vanderbilt University, VU Station B 351822, Nashville, Tennessee 37235, United States

Ⓢ *Supporting Information*

ABSTRACT: The development of the seeded growth synthesis for gold nanorods provided the first simple, convenient wet chemistry route to these nanomaterials. Over the past decade, the original silver-assisted seeded growth procedure has been the subject of further modifications that have continuously expanded access to anisotropic gold nanoparticles; however, the role of silver in formation of gold nanorods remains poorly understood. We report the first experimental evidence on the position of silver present on gold nanorods using advanced energy dispersive X-ray spectroscopy. Our results indicate the deposition of silver ions on the surface shows no preference for a specific face or axis. Furthermore, we show that the "dog bone" structures developed from gold nanorod solutions show preferential deposition of silver atoms on the ends and in the crevices.

The development of seeded growth syntheses for gold nanorods (AuNRs) spurred a dramatic increase in interest in the optical properties and applications of these nanoparticles (AuNPs).[1] The original three-step seeded growth procedure using seed citrate-stabilized gold nanoparticles produced high aspect ratio AuNRs allowing researchers to clearly demonstrate their size and aspect ratio-dependent optical properties.[2,3] However, it was the evolution of the silver-assisted seeded growth approach, utilizing a silver nitrate salt, which provided access to AuNRs in much higher yield.[4–6] Shorter aspect ratios (AR) and single crystals are obtained compared to longer, penta-twinned AuNRs synthesized without silver(I) nitrate. Short AR rods present both transverse and longitudinal plasmon bands in the visible region of the spectrum, enabling a host of fascinating new AuNR-enabled sensing and imaging applications.[7]

Despite over a decade of research, many key features of AuNR growth mechanisms remain poorly understood.[8] Indeed, several synthesis components have been advanced as the driving force for anisotropy.[9] Research into the role of silver ions in the silver-assisted seeded growth synthesis has been a particularly challenging area of mechanistic investigation. The ability to control the aspect ratio of these single-crystalline AuNRs by varying the silver nitrate concentration used in the synthesis is well-established, but some disagreement exists as to the exact mechanism of its action.[10] Three primary mechanisms have been proposed to account for the aspect ratio control that silver provides: (a) the deposition of a submonolayer quantity of silver metal on the longitudinal faces of the AuNR (silver under-potential deposition, UPD);[11,12] (b) the action of a cetyltrimethylammonium-Br-Ag⁺ complex as a face-specific capping agent;[12,13] and (c) silver acting with bromide to alter the shape of cetyltrimethylammonium bromide (CTAB) micelles from spherical to cylindrical shapes (soft template).[14]

Part of the challenge in establishing the role of silver in this synthesis stems from the instrumental challenges in characterizing the speciation and location of silver at the AuNR surface. Here we report the first experimental evidence on the position of silver ions present on AuNRs using a Tecnai Osiris equipped with a Super-X EDS energy dispersive X-ray spectroscopy (EDS) system. High sensitivity and high spectral count rates are enabled by the simultaneous X-ray detection of four solid-state detectors in conjunction with a high brightness Schottky-type field emission gun, allowing for element-specific mapping at subnanometer resolution across the periodic table.[15] In particular, the system allowed for the spatial detection of trace amounts of silver without significantly damaging the AuNR.

The AuNRs in this study were synthesized using the popular seed-mediated, Ag-assisted growth procedure.[6] Briefly, a solution of Au seed particles was prepared by the rapid reduction of $HAuCl_4$ by $NaBH_4$ in the presence of CTAB. Growth solutions were then prepared by sequentially adding $HAuCl_4$, variable amounts of $AgNO_3$ (30–100 μM final concentration), and ascorbic acid to an aqueous solution of CTAB. The reactions were initiated by the addition of Au seed particles to the growth solutions, and then they were mixed gently and allowed to sit undisturbed overnight. The resulting nanorod solutions were dialyzed in deionized water for 3 days to remove unreacted reagents and excess surfactant.

Figure 1 shows the HRTEM image of a AuNR paired with corresponding scanning transmission electron microscopy (STEM)-EDS map showing the gold signal (gray scale) and the silver signal (red to yellow intensity scale). The silver signal follows the surface of the AuNR, indicating that the detected silver is on the surface rather than doped into the particle. Levels of silver ranged from ~1 to 4 at. % relative to gold, consistent to values from published ICP[16] and scanning electron microscopy EDS[6] measurements. The results of mapping 38 individual AuNRs suggest that the location of silver atoms does not correspond with any one particular facet as previously suggested.[1,17,18] The analysis also indicates that the location of silver is found on all faces of the rod, sides, corners, and ends, seeming to give support to those growth
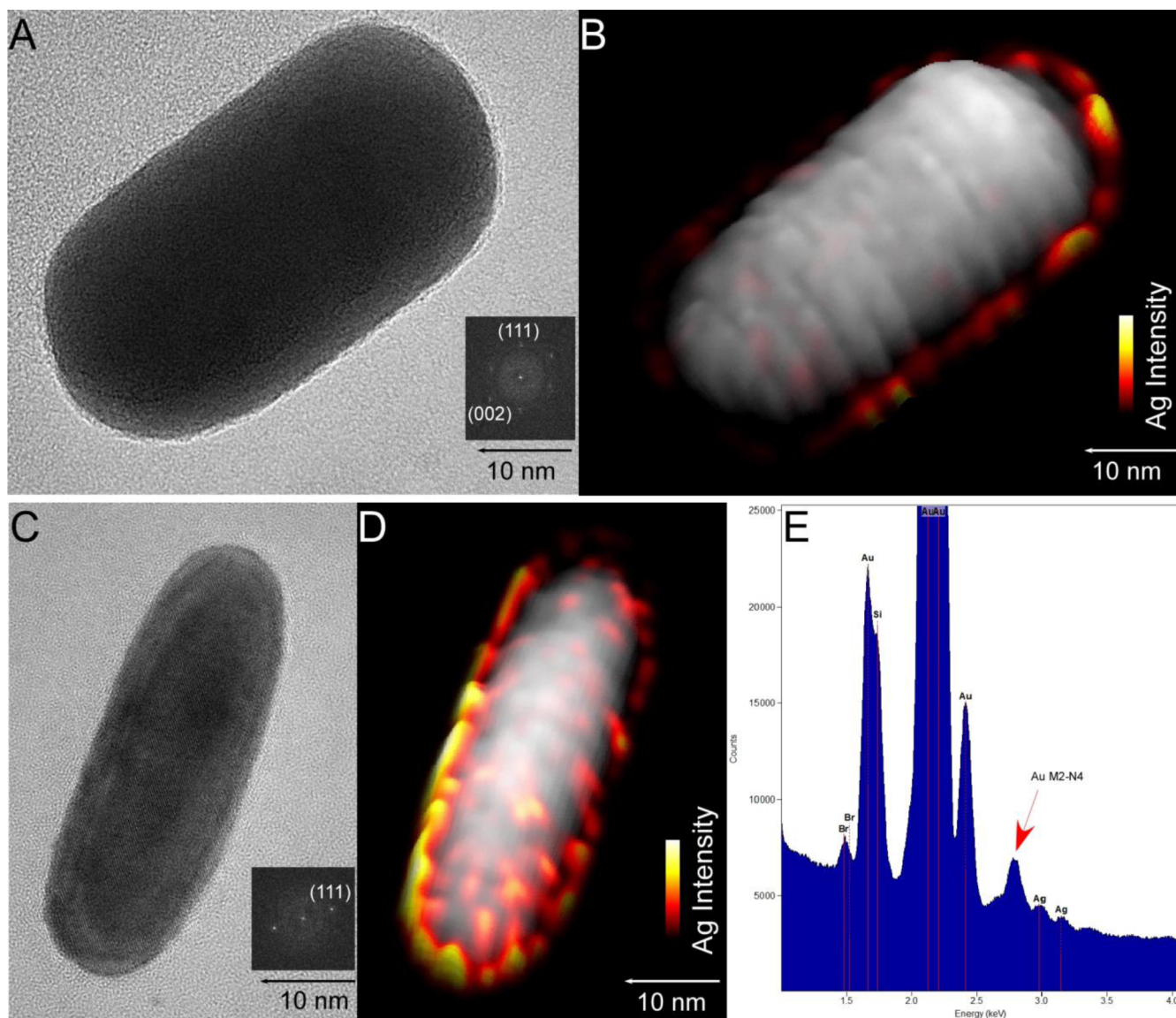
Figure 1. HRTEM images and correlated STEM-EDS maps of AuNRs (A and B, C and D). The EDS maps were generated by overlaying the background subtracted signals for gold and silver. The insets of A and C are fast Fourier transforms from the individual nanoparticles. (E) A typical EDS spectrum showing the presence of silver, gold, and bromine. The peak indicated with the red arrow is a gold M2-N4 transition typically too weak to detect.

mechanisms, like the proposed "soft template" mechanism, that do not rely on face-specific deposition of Ag species.

Other detected elements include nitrogen, bromine, and trace amounts of iodine. Nitrogen and bromine atoms are found in CTAB, and iodine is known to be a common impurity in commercially available CTAB.[19] No clear correlation with the AuNR structure was observed for any of these elements. The halide signals were of particular interest, since a number of reports have been recently published regarding the specific use of halides to direct the formation of certain nanocrystal shapes;[20,21] however, the signals were difficult to resolve, as signal would often be generated from excess surfactant that deposited on the support film, even after extensive purification of the AuNR solutions.

To confirm that the ubiquitous presence of Ag atoms seen on AuNRs is not simply due to poor elemental spatial resolution, we show that distinct regions of trace Ag content are discernible on a similar nanostructure. This was accomplished

by imaging gold nano 'dog bones'. Nanoscale gold 'dog bone'-like structures have been formed by preferentially depositing more Au metal at the ends of AuNRs prepared by a seed-mediated approach.[22,23] Fully formed AuNRs act as the seed particle, and additional Au atoms in solution are reduced by ascorbic acid. The Au atoms accumulate at the ends of the rod, inflating the corners of the particle, giving rise to the 'dog bone' morphology.

Au nano 'dog bones' were synthesized for this study by modification of a previously published procedure.[23] Briefly, an aqueous solution of $HAuCl_4$ and ascorbic acid was added to a sample of purified AuNRs at room temperature. The sample was left undisturbed for 24 h before being purified by dialysis for three days. Figure 2 shows HRTEM images and STEM-EDS maps of two AuNR 'dog bones' produced from a sample of seed-mediated synthesized AuNR. In each case, the silver intensity is shown to be greater in the indentations on the ends than in the inflated lobes. Since the only metal atoms being
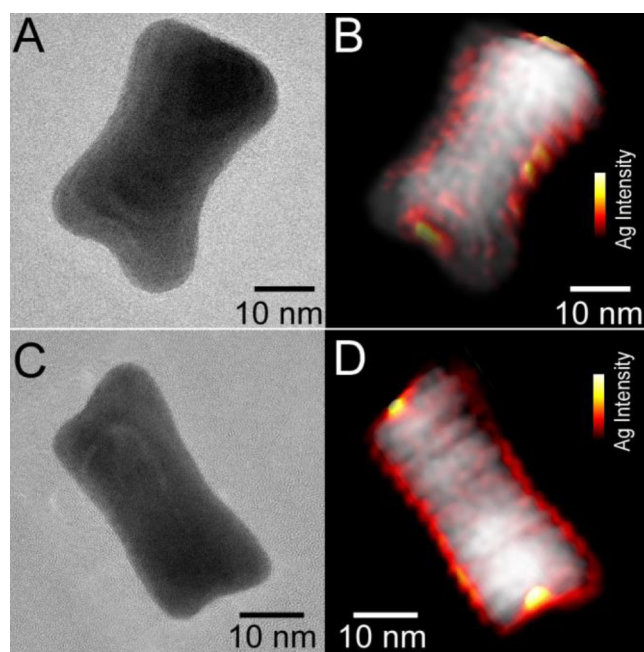
Figure 2. HRTEM images (A and C) and correlated STEM-EDS maps (B and D) of gold nano 'dog bones'. The silver EDS intensity is, in general, greater in the regions that are not formed as a result of excess Au atom deposition.

reduced at this time were Au, the deposition in these specific areas creates relatively Ag-rich and Ag-poor regions on the same nanostructure. It is also important to note that this was achieved without adding to the trace amounts of silver used to synthesize the original AuNR, confirming that the unbiased localization of silver seen on AuNRs in this study is neither a result of poor spatial resolution nor an undetectable amount of Ag atoms present.

The analysis described here presents another step toward the full structural and elemental characterization of AuNRs. Such information will provide needed insight into the mechanisms by which AuNRs grow, ultimately allowing for the improvement of the performance of AuNR syntheses. Further, STEM-EDS mapping will have a notable impact in the field by allowing for the characterization of modified AuNRs by evaluating efficiencies of surface modification and ligand exchange protocols. It is our hope that insights into the composition of nanomaterials like these will ultimately allow for improved seeded growth reactions, manipulating anisotropic AuNP shapes in more exquisite detail, and reduce our reliance on large amounts of cytotoxic surfactants to achieve shape control. Beyond AuNPs, trace metals play important roles in many types of nanomaterials syntheses.[24−26] The ability to visualize and understand the role of these trace elements on nanostructures will enhance capabilities to achieve new complex architectures and more efficient syntheses for existing systems.

ASSOCIATED CONTENT

Ⓢ Supporting Information

STEM-EDS conditions, raw STEM-EDS maps, and an example raw EDS spectrum. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
david.wright@vanderbilt.edu

Author Contributions
†These authors contributed equally.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

REFERENCES

(1) Murphy, C. J.; Sau, T. K.; Gole, A. M.; Orendorff, C. J.; Gao, J.; Gou, L.; Hunyadi, S. E.; Li, T. *J Phys Chem B* **2005**, *109*, 13857.

(2) Jana, N. R.; Gearheart, L.; Murphy, C. J. *J. Phys. Chem. B* **2001**, *105*, 4065.

(3) Jana, N. R.; Gearheart, L.; Murphy, C. J. *Adv. Mater.* **2001**, *13*, 1389.

(4) Nikoobakht, B.; El-Sayed, M. A. *Chem. Mater.* **2003**, *15*, 1957.

(5) Sau, T. K.; Murphy, C. J. *J. Am. Chem. Soc.* **2004**, *126*, 8648.

(6) Sau, T. K.; Murphy, C. J. *Langmuir* **2004**, *20*, 6414.

(7) Stone, J.; Jackson, S.; Wright, D. *Wiley Interdiscip. Rev.: Nanomed. Nanobiotechnol.* **2011**, *3*, 100.

(8) Lohse, S. E.; Murphy, C. J. *Chem. Mater.* **2013**, *25*, 1250.

(9) Vigderman, L.; Khanal, B. P.; Zubarev, E. R. *Adv. Mater.* **2012**, *24*, 4811.

(10) Murphy, C. J.; Thompson, L. B.; Chernak, D. J.; Yang, J. A.; Sivapalan, S. T.; Boulos, S. P.; Huang, J. Y.; Alkilany, A. M.; Sisco, P. N. *Curr. Opin. Colloid Interface Sci.* **2011**, *16*, 128.

(11) Grzelczak, M.; Perez-Juste, J.; Mulvaney, P.; Liz-Marzan, L. M. *Chem. So.c Rev.* **2008**, *37*, 1783.

(12) Jain, P. K.; Huang, X.; El-Sayed, I. H.; El-Sayed, M. A. *Acc. Chem. Res.* **2008**, *41*, 1578.

(13) Niidome, Y.; Nakamura, Y.; Honda, K.; Akiyama, Y.; Nishioka, K.; Kawasaki, H.; Nakashima, N. *Chem. Commun. (Cambridge, U.K.)* **2009**, 1754.

(14) Jana, N. R. *Small* **2005**, *1*, 875.

(15) Schlossmacher, P.; Klenov, D. O.; Freitag, B.; von Harrach, H. S. *Microscopy Today* **2010**, *18*, 14.

(16) Orendorff, C. J.; Murphy, C. J. *J. Phys. Chem. B* **2006**, *110*, 3990.

(17) Nikoobakht, B.; El-Sayed, M. A. *Langmuir* **2001**, *17*, 6368.

(18) Leontidis, E.; Kleitou, K.; Kyprianidou-Leodidou, T.; Bekiari, V.; Lianos, P. *Langmuir* **2002**, *18*, 3659.

(19) Smith, D. K.; Miller, N. R.; Korgel, B. A. *Langmuir* **2009**, *25*, 9518.

(20) Lohse, S. E.; Burrows, N. D.; Scarabelli, L.; Liz-Marzán, L. M.; Murphy, C. J. *Chem. Mater.* **2014**, *26*, 34.

(21) Langille, M. R.; Personick, M. L.; Zhang, J.; Mirkin, C. A. *J. Am. Chem. Soc.* **2012**, *134*, 14542.

(22) Xu, X. D.; Cortie, M. B. *Adv. Funct. Mater.* **2006**, *16*, 2170.

(23) Gou, L. F.; Murphy, C. J. *Chem. Mater.* **2005**, *17*, 3668.

(24) Chu, Y. T.; Chanda, K.; Lin, P. H.; Huang, M. H. *Langmuir* **2012**, *28*, 11258.

(25) Chen, Y. H.; Hung, H. H.; Huang, M. H. *J. Am. Chem. Soc.* **2009**, *131*, 9114.

(26) Li, L.; Hu, F.; Xu, D.; Shen, S.; Wang, Q. *Chem. Commun. (Cambridge, U.K.)* **2012**, *48*, 4728.