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## 2011 Summer Fellowship Committee



### The 2011 Edward G. Weston Summer Research Fellowship — Summary Report

# Design Rules for the Synthesis of Plasmonic Nanowires with Tailorable Surface Plasmon Resonances (SPRs)

*by Abrin L. Schmucker*

Advances in methodology for the synthesis of noble metal nanomaterials have led to the fabrication of increasingly sophisticated structures. When irradiated with light, coherent oscillations of the conduction electrons (surface plasmon resonances or SPRs) can be induced within these structures at specific frequencies.[1] These plasmonic nanorods are of particular interest because they can be easily synthesized using methods such as solution-phase synthesis[2] and template-based electrochemical deposition[3] and their SPRs can be tuned throughout the visible and near IR regions of the spectrum.[4] Despite advances in the synthesis and characterization of noble metal nanorods, a systematic study on how rod architecture (length, diameter, and aspect ratio) effects the locations of the SPR maxima of these materials has not been carried out. Such a study would allow for the optical properties of these structures to be programed to fulfill specific needs in a variety of applications, including sensing,[5] imaging,[6] and therapeutics.[6]

Herein, gold rods were synthesized using a template-based electrochemical approach (Fig. 1). In this technique, pore diameter and electric charge passed during synthesis controls the resulting nanorod diameter and length[7], respectively. Wires were produced with aspect ratios of approximately 8:1, 6:1, 4:1, 2:1, and 1:1 for rods with diameters of 100 nm, 80 nm, 55 nm, and 35 nm (characterized by scanning electron microscopy (SEM)). Collectively, the particles have an average length distribution of $\overline{x}$ = 14%. To correlate nanorod geometry with optical properties (i.e. SPR maxima), extinction measurements were carried out on the as-synthesized rods (Fig. 2, top). In addition, the discrete dipole approximation (DDA) was used to model the optical behavior of these structures (Fig. 2, bottom). After extensive analysis, it was discovered that the wavelength of the SPR maxima corresponding to the longitudinal dipole resonance increases linearly with increasing particle aspect ratio (AR = Length/Diameter) but is second order with respect to increasing nanorod diameter. This trend is attributed to the influence of radiative damping effects for particles much larger than the electrostatic limit.[8, 9]

Importantly, these experiments further our understanding of surface plasmon resonance in metal nanoparticles, which is critical for their application in the new technologies mentioned above. Further, investigating the SPRs of these wires with concomitant spectroscopic and theoretical discrete dipole approximation (DDA) calculations allows us to identify trends in SPR as a function of nanorod length, diameter and aspect ratio, and ultimately create a series of *a posteriori* design rules for synthesizing idealized structures. These rules would eliminate the need for lengthy characterization and optimization cycles for each unique application, and allow us to build upon previously reported results to develop a complete model that includes both radiative and non-radiative damping effects. These advances will ultimately lead to a more accurate predictive model for SPR maxima position.[10, 11]

*(continued on next page)*

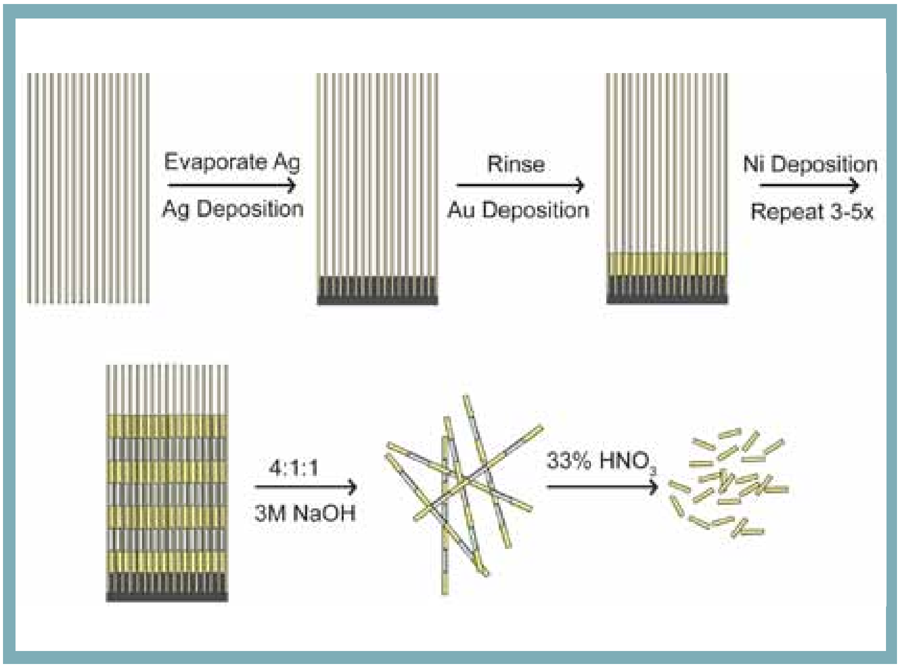


**Fig. 1:** *The template-directed electrochemical growth of metal nanorods.*

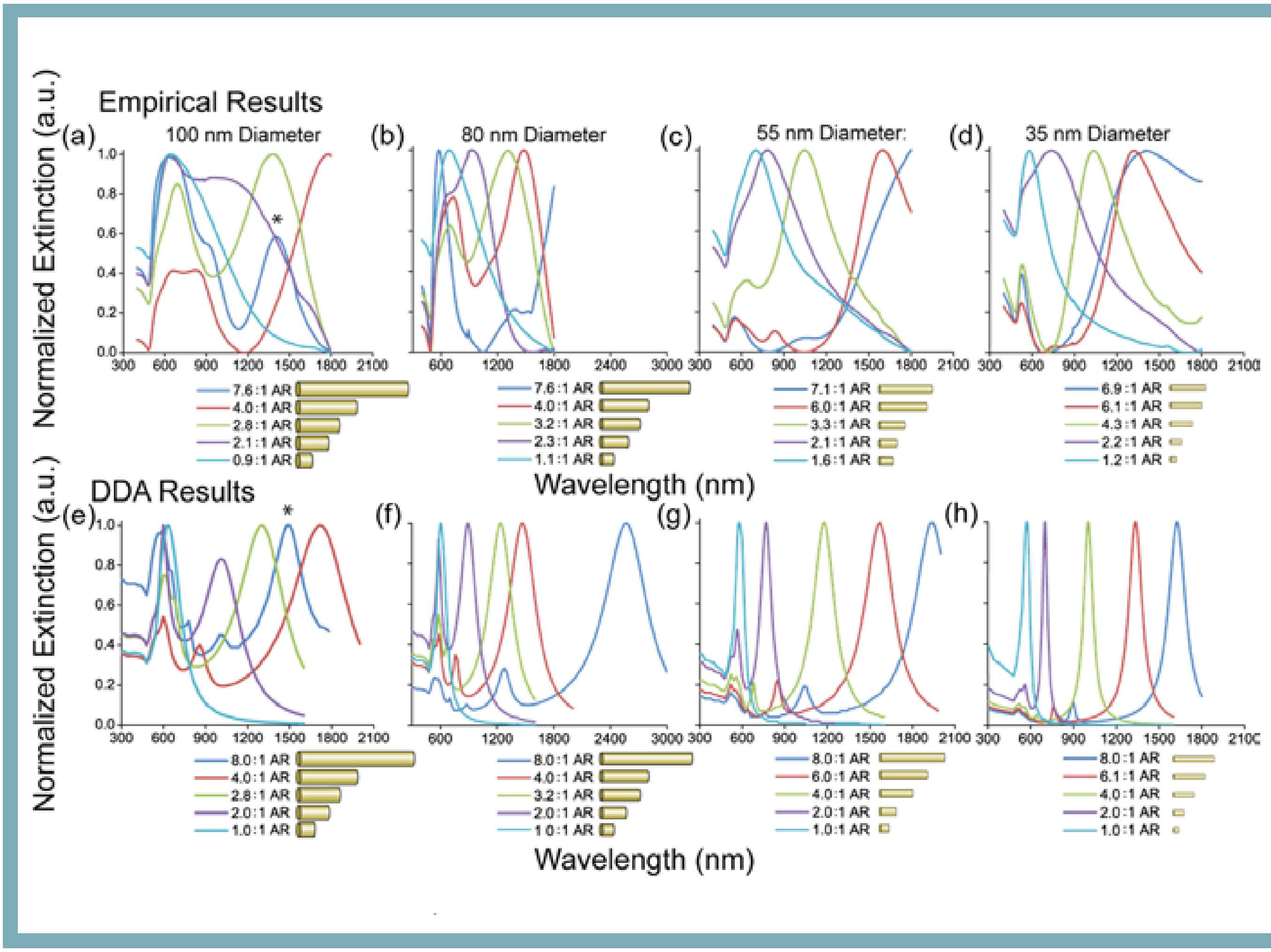


Fig. 2. *Normalized extinction spectra for electrochemically synthesized Au nanorods having (a) 100 nm, (b) 80 nm, (c) 55 nm, (d) 35 nm diameters in $D_2O$. Normalized extinction spectra for orientation-averaged Au nanorods of (e) 100 nm (f) 80 nm (g) 55 nm, and (h) 35 nm diameters as modeled by the discrete dipole approximation (DDA). Different traces indicate rods of varying aspect ratio (AR=Length/Diameter), as specified by the individual legends. Asterisks in the 100 nm diameter panels denote the prominent quadrupole resonance mode of these structures. These data were collected in collaboration with Nadine Harris of the Schatz group.*

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## References

1. K. L. Kelly, E. Coronado, L. L. Zhao, and G. C. Schatz, *J. Phys. Chem. B*, **107**, 668 (2003).
2. S. Link, M. B. Mohamed, and M. A. El-Sayed, *J. Phys. Chem. B*, **103**, 3073 (1999).
3. G. E. Possin, *Rev. Sci. Instrum.*, **41**, 772 (1970).
4. B. Nikoobakht and M. A. El-Sayed, *Chem. Mater.*, **15**, 1957 (2003).
5. C. Sonnichsen and A. P. Alivisatos, *Nano Lett.*, **5**, 301 (2005).
6. X. Huang, I. H. El-Sayed, W. Qian, and M. A. El-Sayed, *J. Am. Chem. Soc.*, **128**, 2115 (2006).
7. C. R. Martin, *Science*, **266**, 1961 (1994).
8. S. W. Prescott and P. Mulvaney, *J. Appl. Phys.*, **99**, 123504 (2006).
9. G. W. Bryant, F. J. G. De Abajo, and J. Aizpurua, *Nano Lett.*, **8**, 631 (2008).
10. A. L. Schmucker, N. Harris, M. J. Banholzer, M. G. Blaber, K. D. Osberg, G. C. Schatz, and C. A. Mirkin, *ACS Nano*, **4**, 5453 (2010).
11. A. L. Schmucker, N. Harris, M. J. Banholzer, M. G. Blaber, K. D. Osberg, G. C. Schatz, and C. A. Mirkin, *ACS Nano*, **5**, 7685 (2011).