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Correlating Second Harmonic Optical Responses of Single Ag Nanoparticles with Morphology

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The linear and nonlinear optical properties of nanoparticles are of significant importance for fundamental science and technological applications.^{1,2} The second harmonic (SH) response of nanoparticles is particularly interesting due to the potential dependence on particle shape and deviations from high symmetry (e.g., spherical). However, ensemble measurements³ (e.g. SH from colloidal solutions) obscure deeper insights due to the inevitable inhomogeneity of particle shape and size. Thus, measurements on a single-particle level are necessary to gain a more complete understanding of the optical properties of nanocrystal materials.⁴ Undertaking such measurements is, however, impeded by the lack of a methodology allowing precise correlation of optical measurements and high-resolution imaging of the particle morphology by transmission electron microscopy (TEM).

This communication reports the results of an approach that permits correlation of SH activity with nanoparticle morphology imaged by TEM, which achieves significantly higher resolution than atomic force microscopy and scanning electron microscopy. The essence of our approach is to create position markers on an optical and electron transparent substrate (Si_3N_4 thin film, ~ 100 nm in thickness) that allows both optical measurements and TEM imaging of the identical nanoparticles.⁵ The SH activities of single Ag nanoparticles (spheres versus rods) and cluster structures (e.g., dimers and trimers) are compared. The direct determination of the structure and the resultant structure–spectroscopic correlation allows gaining a new insight into the mechanism for the nonlinear (i.e., resonant second harmonic) response from each specific nanoparticle or cluster.

The position bar-markers were fabricated by electron-beam lithography on a specially designed Si_3N_4 window supported on a Si wafer. Briefly, the Si_3N_4 substrate was first coated with a thin layer (8 nm) of silicon monoxide via thermal evaporation. This changes the hydrophobic Si_3N_4 surface to hydrophilic, which provides better adhesion and distribution of aqueous Ag nanoparticles. The substrates were then spin-coated with electron resist, followed by electron-beam patterning. The patterned substrate was further deposited with a thin layer (20 nm) of chromium, which acts as the positional marker material, followed by liftoff of electron resist. The substrate with position markers was further coated with a positively charged polymer (polydimethyldidodecylammonia chloride, PDDA), which captures negatively charged Ag nanoparticles synthesized by citrate reduction of AgNO_3 . As shown in Scheme S1 (Supporting Information), SH maps were acquired with a home-built nonlinear optical microscopy system including a tunable Ti:sapphire femtosecond laser (Spectra Physics). The detection optics allowed detection of wavelengths from 400 to 500 nm, while the excitation was tunable from 800 to 1000 nm with ~ 100 -fs pulse (see Supporting Information).

We first investigated the SH activity of single Ag nanoparticles and clusters, including dimers and trimers that formed spontaneously

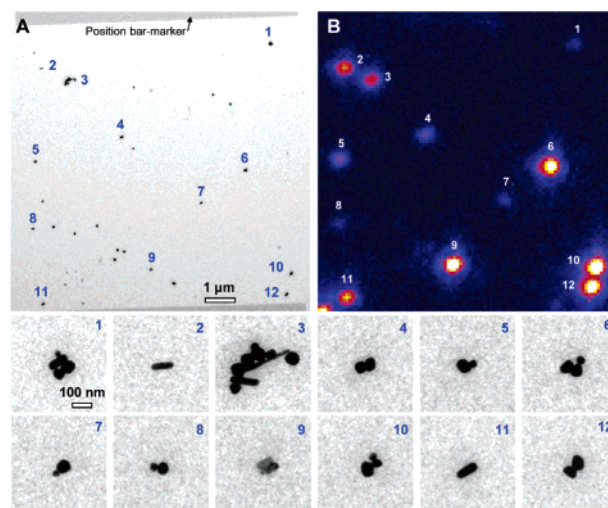


Figure 1. (A) TEM image of Ag nanoparticles. (B) SHG map (false color image, with white showing the most intense 415-nm signal) of the same area ($\lambda_{\text{ex}} = 830$ nm, 3 mW average power, 40 GW/cm² peak power). The bottom panel shows the zoomed-in images of the labeled particles.

when colloidal Ag nanoparticles were deposited onto the PDDA-coated $\text{SiO}/\text{Si}_3\text{N}_4$ windows (Figure 1). Ag nanoparticle clusters and nanorods yield a signal at the second harmonic (SH) wavelength (415 nm) when excited with femtosecond pulses (830 nm). The trimer structures (# 6 and 10) are most SH responsive (i.e. are observed at the least optical power), while dimers (# 4, 5, 7, and 8) are less. It was observed that if the shape of a particle within dimers deviates from spherical, then the dimers (e.g., # 9 and 12) may show activity comparable to that of trimers. Single spherical Ag particles (unlabeled in Figure 1A) do not yield detectable SH signals at this power but can be detected when using higher excitation power (> 400 GW/cm²). Interestingly, small aggregates (e.g., # 3) may not necessarily be more active than trimers (# 6 and 10), indicating that the SH signal is not simply proportional to the number of particles involved but that the local structure of interacting particles is critical. As compared with single spherical Ag particles, nanorods (# 2 and 11) show much greater SH activity.

The measured emission spectra (Figure 2A) confirm the observed signal is SH, not two-photon fluorescence (spectrally broad).^{4c} The power dependence of the SH signal from dimers and nanorods was also measured (Figure 2B). The SH intensity of the various particles increases superlinearly with excitation intensity (I^n , $n = \{>1, 2\}$). The excitation spectrum (SH intensity vs excitation wavelength) of a dimer (dash line in Figure 2C, TEM image in Figure 2D) shows a peak at ~ 850 nm of the laser wavelength. Previous experiments on lithographically fabricated dimers exhibit significantly red-shifted spectra.^{4d} Simulations have shown that the coupling between two touching spherical Ag nanoparticles results in a new plasmon mode at ~ 820 nm.⁶ Therefore, the signals from the dimers are interpreted

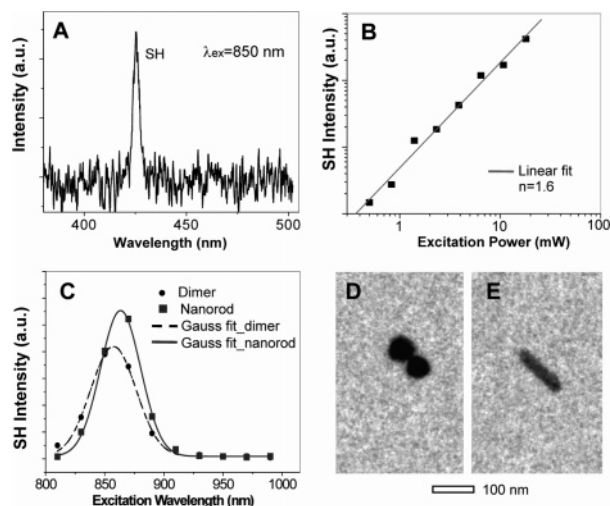


Figure 2. (A) SH emission spectrum; (B) the excitation power dependence and fit ($\lambda_{\text{ex}} = 830$ nm); (C) excitation spectra of a Ag dimer (TEM image: D) and a nanorod (TEM image: E). Note $3 \text{ mW} \Rightarrow 40 \text{ GW/cm}^2$.

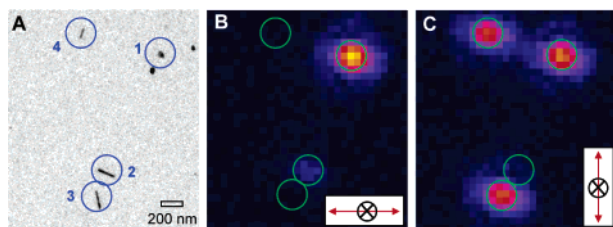


Figure 3. (A) TEM image of an area. (B) and (C) are SH maps (false color) for horizontal and vertical laser polarization ($\lambda_{\text{ex}} = 900$ nm).

as resulting from one-photon plasmon resonance enhancement. The Ag nanorods are known to exhibit two plasmon modes: a transverse mode (~ 400 nm) that oscillates along the radial direction and a longitudinal mode (that is red-shifted even into the near-IR) that oscillates along the long axis.¹ The SH excitation spectrum of a Ag nanorod (solid line in Figure 2C, TEM image in Figure 2E) shows a peak around 860 nm. Therefore, the SH response from the Ag nanorod is also interpreted as one-photon excitation of the longitudinal mode.

The polarization dependence of the SH response of Ag dimers and nanorods is studied by rotating the E-field direction of the excitation laser (Figure 3). Herein, Ag particles 1–4 are of particular interest. The laser polarization in Figure 3B is along the horizontal direction, which only results in weak excitation of the longitudinal plasmon mode of nanorod 2 and hence weak SH emission. For nanorods 3 and 4, their orientation is nearly perpendicular to the laser E-field. Thus, only the transverse plasmon mode (~ 400 nm) was two-photon-excited; no detectable SH emission is observed because the transverse plasmon mode is less SHG active. When the laser polarization is rotated by 90° (Figure 3C), i.e., vertical, nanorods 3 and 4 are parallel with the laser E-field and give intense SH emission, while nanorod 2 diminishes. Dimer structures show similar polarization effects (data not shown). All these results demonstrate that the longitudinal plasmon mode of the rods (or dimers) is excited and shows much higher SH activity than the transverse mode.

The generation of second-harmonic radiation from bulk Ag is symmetry-forbidden as Ag has a *fcc* crystal structure (inversion

symmetry). However, SH becomes allowed in Ag nanocrystals due to the surface contribution as well as plasmon resonance enhancement. For isolated Ag nanospheres, only two-photon excitation of the dipole plasmon mode near 400 nm can occur, which results in a small SH response. The same argument holds for the SH activity from two-photon excitation of the transverse mode of nanorods or dimers. Our results clearly show that the SH response from Ag nanorods and clusters (trimers and dimers) is greatly enhanced by one-photon excitation of the longitudinal plasmons. Thus, the mechanism for this SH response is a nonlinearity in the polarization created via the longitudinal plasmon excitation in the nanorods and dimers (and multiparticle collective plasmon modes in other clusters), see Scheme S2. The nonlinearity of the single-particle polarization would contain harmonics of the laser driving frequency (ω) and could, therefore, radiate at ω , 2ω , 3ω , etc. Furthermore, this nonlinearity would be enhanced from the large local field associated with the longitudinal plasmon excitation, which is larger than that from the transverse mode.⁶ An analogous nonlinearity has been observed in the ultrafast (pump–probe) scattering from single Au nanorods.⁷

The correlation of single-particle (or cluster) structure with the optical response is important for understanding the enhancement mechanism for SHG from metal nanoparticles. The present methodology for correlating optical measurements and TEM imaging is general and can easily be adapted for other single-particle studies, such as surface enhanced Raman scattering (SERS), which may unravel the fine structures of so-called “hot” nanoparticles that show enormous SERS enhancement.⁸

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Supporting Information Available: Experimental details and supporting schemes are included. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Kreibitz, U.; Vollmer, M. *Optical Properties of Metal Clusters*; Springer-Verlag: New York, 1995.
- (2) Shen, Y. R. *Principles of Nonlinear Optics*; Wiley: New Jersey, 1988.
- (3) (a) Novak, J. P.; Brousseau, L. C., III; Vance, F. W.; Johnson, R. C.; Lemon, B. I.; Hupp, J. T.; Feldheim, D. L. *J. Am. Chem. Soc.* **2000**, *122*, 12029. (b) Hao, E. C.; Schatz, G. C.; Johnson, R. C.; Hupp, J. T. *J. Chem. Phys.* **2002**, *117*, 5963. (c) Clark, H. A.; Campagnola, P. J.; Wuskell, J. P.; Lewis, A.; Loew, L. M. *J. Am. Chem. Soc.* **2000**, *122*, 10234. (d) Jean-Pierre, A.; Jerome, N.; Hubert, G.; Pierre-Francois, B. *J. Chem. Phys.* **2004**, *121*, 12577. (e) Antoine, R.; Brevet, P. F.; Girault, H. H.; Bethell, D.; Schiffrin, D. *J. Chem. Comm.* **1997**, 1901. (f) Sandrock, M. L.; Pibel, C. D.; Geiger, F. M.; Foss, C. A., Jr. *J. Phys. Chem. B* **1999**, *103*, 2668. (g) Jacobsohn, M.; Banin, U. *J. Phys. Chem. B* **2000**, *104*, 1.
- (4) (a) Liao, Y.-H.; Unterreiner, A. N.; Chang, Q.; Scherer, N. F. *J. Phys. Chem. B* **2001**, *105*, 2135. (b) Lippitz, M.; van Dijk, M. A.; Orrit, M. *Nano Lett.* **2005**, *5*, 799. (c) Mock, J. J.; Barbic, M.; Smith, D.; Schultz, D.; Schultz, S. *J. Chem. Phys.* **2002**, *116*, 6755. (d) Rechberger, W.; Hohenau, A.; Leitner, A.; Krenn, J. R.; Lamprecht, B.; Aussenegg, F. R. *Opt. Commun.* **2003**, *220*, 137. (e) Schuck, P. J.; Fromm, D. P.; Sundaramurthy, A.; Kino, G. S.; Moerner, W. E. *Phys. Rev. Lett.* **2005**, *94*, 017402.
- (5) Jin, R.; Jureller, J. E.; Scherer, N. F. Manuscript in preparation.
- (6) Jensen, T.; Kelly, L.; Lazarides, A.; Schatz, G. C. *J. Cluster Sci.* **1999**, *10*, 295.
- (7) Pelton, M.; Liu, M.; Park, S.; Scherer, N.; Guyot-Sionnest, P. *Phys. Rev. Lett.* Manuscript submitted.
- (8) Nie, S. M.; Emery, S. R. *Science* **1997**, *275*, 1102.

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