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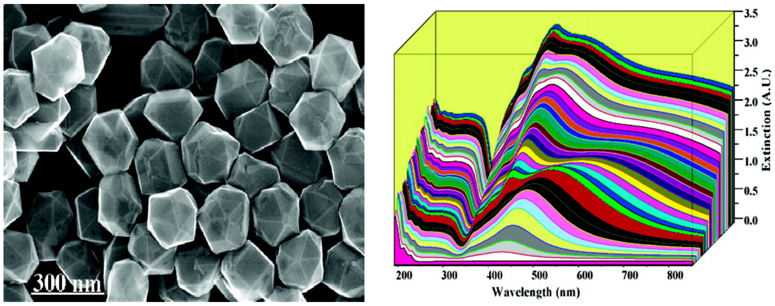

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Multipole Plasmon Resonances of Submicron Silver Particles

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Excitation of the collective oscillations of the electron density called plasmon resonance determines the optical properties of silver nanoparticles.[1] The frequency of the resonance can be tuned across the broad spectral range by selecting the particle size, shape, as well as the surrounding dielectric medium.[2,3] This tunability and the high efficiency for interaction with light make Ag nanoparticles promising in photonics,[4] sensor,[5] photocatalysis,[6] and enhanced spectroscopy[7] applications, and as such, their size-dependent optical properties become of fundamental importance.

For nearly spherical Ag nanoparticles in the size range from 10 to 50 nm, all electrons in the metal experience roughly the same phase of the incident electromagnetic field leading to the excitation of a dipole resonance. As the particle size increases, higher plasmon modes can be excited due to the phase retardation of the field inside the particle. In addition to the dipole resonance, a quadrupole mode was theoretically and experimentally observed for 50−150 nm spherical[1,8−10] and other shaped Ag particles.[11] Higher order multipole resonances have also been predicted[1,12] for even larger particles and reported for metallic nanoshells above 200 nm diameter.[13] The experimental observation of higher multipoles beyond the quadrupole for spherical Ag nanoparticles has been elusive conceivably due to lack of adequate synthetic methods capable of yielding large, single-crystal nanoparticles of narrow size and shape distribution. Relevant work published on this subject describes rather polycrystalline large Ag nanoparticles, and the corresponding plasmon resonance spectra appear featureless.[14]

We have recently introduced a new method for the controlled synthesis of single-crystal Ag nanoparticles in the size range of 10−140 nm[10] that are chemically clean without any other surface-associated chemical species except water and oxygen. In other commonly used synthetic procedures, the byproducts left after the chemical reduction of the metal or intentionally added capping molecules limit the growth of particles to large dimensions and affect their chemical and optical properties. Here, this method is extended to the synthesis of single-crystal Ag particles larger than 140 nm with the size polydispersity better than 5%, allowing the experimental observation of higher order multipole resonances, such as octupole and hexadecapole, for the first time. The synthetic procedure involves the reduction of aqueous saturated silver oxide solution by ultrapure hydrogen gas in a pressurized atmosphere at elevated temperature and is described in details elsewhere.[10] The generally understood mechanism is the catalytic reduction of silver oxide to small Ag "seeds" followed by their slow uniform growth along all crystallographic axes. The reaction can be conveniently terminated at any stage, resulting in the nanoparticles of a desired size. The growth of the particles was monitored by UV−visible extinction spectroscopy (Figure 1). At the initial stages of the reaction, the spectrum reveals the presence of a dipole plasmon resonance at 420 nm attributed to the formation of small Ag seeds. As the particle size increases, the dipole resonance progressively red shifts, rendering a green muddy color to the colloidal suspension due to strong resonance scattering of light. For ca. 90 nm Ag nanoparticles, the dipole resonance shows at 490 nm, and a new band corresponding to the quadrupole mode appears in the spectrum at 420 nm. As the size of the particles approaches 170 nm, the dipole and quadrupole resonances shift to 630 and 470 nm, respectively, and a new band corresponding to the octupole mode emerges in the spectrum at ca. 430 nm. This band gradually evolves into a distinct peak that also shifts to the red spectral range with the increase of the particle size. When the octupole peak moves to a position at 475 nm, a new shoulder corresponding to the hexadecapole mode of the plasmon resonance starts to appear at 430 nm. The particles continue to grow very slowly until they become so large that they fall off the suspension. The largest synthesized particles were 215 ± 10 nm and had the quadrupole, octupole, and hexadecapole modes of the plasmon resonance at 543, 483, and 432 nm, respectively, with the broad dipole peak moved into the near-IR spectral region. STEM images in Figure 2 show highly symmetric icosahedral particles with a small fraction of elongated rods also present in the suspension. The narrow size distribution supports the model in which the particles uniformly grow from the initially formed seeds without the formation of new

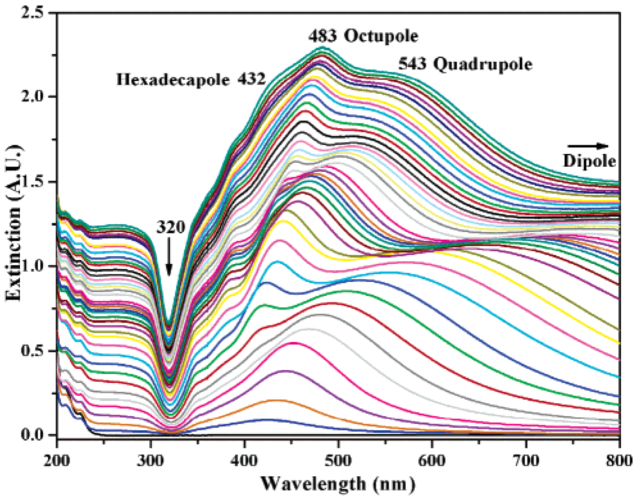

Figure 1. Extinction spectra of different sized Ag nanoparticles synthesized by hydrogen reduction method. The spectra correspond to different aliquots as is taken at 15 min intervals from the reactor. No additional normalization of the intensity was performed.

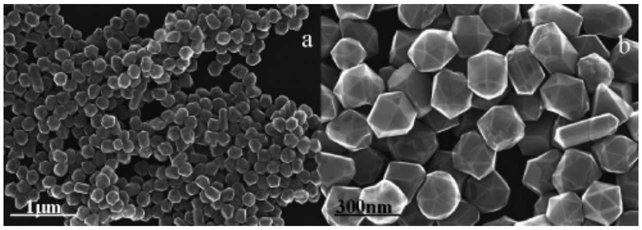

Figure 2. STEM images of silver particles prepared by hydrogen reduction of silver oxide solutions (a and b).

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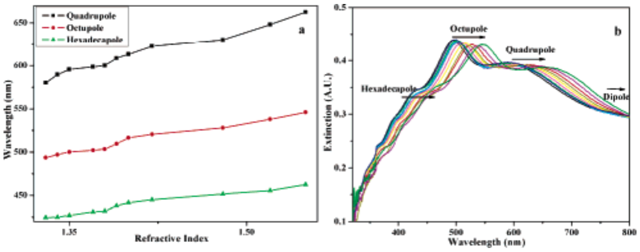

Figure 3. Effect of refractive index of the surrounding medium on the position of different plasmon modes of 215 ± 10 nm Ag particles (a and b).

seeds during the course of the reaction. As the particle grows, all plasmon modes red shift with the dipole mode shifting most rapidly followed by the quadrupole, octupole, and hexadecapole modes (Figure 1 in the Supporting Information).

Mie extinction calculations were performed using the code from ref 2 and the frequency-dependent dielectric function of silver metal from ref 15. The dielectric constant of surrounding medium was adjusted from that of pure water to account for local effects, specifically for adsorbed silver oxide species on the surface of the particles, and to better match the experimental and calculated values for the position of all modes. The results of calculations and their comparison with the experimental data are presented in Figure 2 of the Supporting Information showing the overall good agreement. The lack of complete overlap of the calculated and experimental spectra is rationalized as due to assumed spherical shape of the particles in the calculations rather than the real icosahedral structure. It is known that the sharp corners, such as those present in icosahedral structures, affect the spectra of plasmon modes.[16] Nevertheless, the calculated spectra reveal the presence of all plasmon modes as well as their red shift with increase of the particle size. Both the experimental and the calculated spectra show a minimum at ca. 320 nm due to the intraband transition in the metal[1] that damps the plasma oscillations in this spectral region.

The extinction spectra of 215 ± 10 nm Ag particles prepared by the hydrogen reduction method were measured as a function of the refractive index of the surrounding medium in order to determine how different plasmon modes are affected by the dielectric environment. It is well-known that the dipole plasmon resonance shifts to longer wavelengths with the increase of the medium dielectric function[1,3] due to the decrease of the restoring force on the electron oscillations. It was expected that the decrease of the restoring force caused by the increased medium refractive index will have a similar effect for the higher order multipoles because the effect should be independent of a specific "shape" which the electron oscillations adapt in the particles. Indeed, all modes red shift as expected, with the quadrupole mode exhibiting the largest shift for the same change of the refractive index followed by the octupole and hexadecapole modes (Figure 3). The measurements were performed on films prepared by adsorbing the Ag particles on poly(vinyl pyridine)-modified glass substrates[17] and immersing them into a water/ethanol/*m*-cresol mixture of various composition to tune the refractive index from 1.33 to 1.54. The films were used instead of the particle suspensions to avoid aggregation caused by changing of the solvent composition. The extinction spectra of the films closely resembled those of the particles in the suspension; the small differences can be accounted by the presence of the underlying glass substrate.

In conclusion, the hydrogen reduction method allows the synthesis of submicron Ag particles that exhibit unique optical properties, specifically the ability to optically excite high order modes of the plasmon resonance. The observation of these modes not only is of fundamental importance for understanding optical properties of plasmonic structures but also renders the potential for new practical applications. The latter stems from the properties of various plasmon modes to produce local fields with different energy distribution around the particles[18] as well as to selectively absorb and scatter light in specific regions of the visible spectrum.[19] These properties are unique for large plasmonic particles and cannot be found in molecular and semiconductor chromophores or small plasmonic particles.

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Supporting Information Available: Details of characterization and calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Kreibig, U.; Vollmer, M. *Optical Properties of Metal Clusters*; Springer Series in Materials Science, Vol. 25; Springer-Verlag: New York, 1995.
(2) Bohren, C. F.; Huffman, D. R. *Absorption and Scattering of Light by Small Particles*; John Wiley & Sons: New York, 1998.
(3) Mulvaney, P. *Langmuir* **1996**, *12*, 788−800.
(4) Wang, W.; Asher, S. A. *J. Am. Chem. Soc.* **2001**, *123*, 12528−12535.
(5) (a) Haes, A. J.; Hall, W. P.; Chang, L.; Klein, W. L.; Van Duyne, R. P. *Nano. Lett.* **2004**, *4*, 1029−1034. (b) McFarland, A. D.; Van Duyne, R. P. *Nano Lett.* **2003**, *3*, 1057−1062.
(6) Kumbhar, A.; Chumanov, G. *J. NanoSci. Nanotech*. **2004**, *4*, 299−303.
(7) (a) Zhang, X.; Young, M. A.; Lyandres, O.; Van Duyne, R. P. *J. Am. Chem. Soc.* **2005**, *127*, 4484−4489. (b) Cao, Y. C.; Jin, R. C.; Mirkin, C. A. *Science* **2002**, *297*, 1536−1540. (c) Nie, S.; Emery, S. R. *Science* **1997**, *275*, 1102.
(8) (a) Kelly, K. L.; Coronado, E.; Zhao, L.; Schatz, G. *J. Phys. Chem. B* **2003**, *107*, 668−677. (b) Haynes, C. L.; Van Duyne, R. P. *J. Phys. Chem. B* **2003**, *107*, 7426−7433.
(9) Sosa, I. O.; Noguez, C.; Barrera, R. G. *J. Phys. Chem. B* **2003**, *107*, 6269−6275.
(10) Evanoff, D. D., Jr.; Chumanov, G. *J. Phys. Chem. B* **2004**, *108*, 13948−13956.
(11) (a) Jin, R. C.; Cao, Y. C.; Hao, E. C.; Me'traux, G. S.; Schatz, G. C.; Mirkin, C. A. *Nature* **2003**, *425*, 487−490. (b) Jin, R. C.; Cao, Y. C.; Mirkin, C. A.; Kelly, K. L.; Schatz, G. C.; Zheng, J. G. *Science* **2001**, *294*, 1901−1903. (c) Chen, S.; Carroll, D. L. *J. Phys. Chem. B* **2004**, *108*, 5500−5506. (d) Sun, Y.; Xia, Y. *Adv. Mater.* **2003**, *15*, 695−699.
(12) (a) Jensen, T.; Kelly, L.; Lazarides, A.; Schatz, G. *J. Cluster Sci*. **1999**, *10*, 295−317. (b) Noguez, C.; Sosa, I. O.; Barrera, R. G. *Mater. Res. Soc. Symp. Proc*. **2002**, W9.24.1−W9.24.6.
(13) Oldenburg, S. J.; Jackson, J. B.; Westcott, S. L.; Halas, N. *J. Appl. Phys. Lett*. **1999**, *75*, 2897−2899.
(14) (a)Velikov, K. P.; Zegers, G. E.; Van Blaaderen, A. *Langmuir* **2003**, *19*, 1384−1389. (b) Yamamoto, N.; Araya, K.; Garcia de Abajo, F. *J. Phys. Rev. B* **2001**, *64*, 205419/1−205419/9.
(15) Lynch, D. W.; Hunter, W. R. In *Handbook of Optical Constants of Solids*; Palik, E. D., Ed.; Academic Press: New York, 1985.
(16) Haes, A. J.; Zou, S.; Schatz, G. C.; Van Duyne, R. P. *J. Phys. Chem. B* **2004**, *108*, 109−116.
(17) Malynych, S.; Luzinov, I.; Chumanov, G. *J. Phys. Chem. B* **2002**, *106*, 1280−1285.
(18) Hao, E.; Schatz, G. C. *J. Chem. Phys*. **2004**, *120*, 357−366.
(19) Evanoff, D. D., Jr.; Chumanov, G. *J. Phys. Chem. B* **2004**, *108*, 13957−13962.

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