Cavity resonators of metal-coated dielectric nanorods

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Metallic nanoparticles bridge the length scale between atoms and crystals, exhibiting mesoscopic properties unique to their size. Thus, they have generated much interest for their potential applications as chemical or biological sensors and particularly as waveguides for light in nanoscale structures. [Y. W. C. Cao, R. C. Jin, and C. A. Mirkin, Science **297**, 1536 (2002); H. J. Lezec *et al.*, Science **297**, 820 (2002); S. A. Maier, P. G. Kik, and H. A. Atwater, Appl. Phys. Lett. **81**, 1714 (2002); J. M. Oliva and S. K. Gray, Chem. Phys. Lett. **379**, 325 (2003)]. One important direction of research into the properties of individual metal nanoparticles involves the controlled variation of their geometry, which can yield new and tunable optical properties that simple spherical configurations do not possess. [T. S. Ahmadi, Z. L. Wang, T. C. Green, A. Henglein, and M. A. Ei-Sayed, Science **272**, 1924 (1996)]. A prime example of this is the core-shell nanostructure that has a central material surrounded by differing cladding layer. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1869393]

In this paper, we will discuss our theoretical investigation of cylindrical nanostructures that have been demonstrated to have unique, tunable optical properties.[1–8] Much work, to date, has emphasized the role of the surface plasmon resonance of spherical metal-coated nanoshells based on Mie's scattering theory.[9–12] Thus, our work stands in contrast by focussing on the bulk resonance arising from a metallic shell surrounding a dielectric nanorod. Our results show that in addition to a plasmon resonance, a cavity-type resonance contributes to the electromagnetic response of nanoparticles, and both can be tuned to give a desired electromagnetic response. These effects have been observed in the optical response of gold-coated TiO_2 and SiO_2 nanorods.[7]

The model geometry of the metal-coated nanorod is shown in Fig. 1, i.e., a miniature classical cylindrical resonator. We find the dominant cutoff mode (the lowest frequency mode) by solving wave equations for the electric and magnetic fields. In a cylindrical, as opposed to a coaxial resonator, no TEM wave is found; and only TE and TM modes are predicted. For a classical cylindrical waveguide cavity, the resonant frequency of the TE_{nml} mode is given by

$$f_{nml} = \frac{c}{2\pi\sqrt{\mu_1\epsilon_1}}\sqrt{\left(\frac{p'_{nm}}{r_1}\right)^2 + \left(\frac{l\pi}{L}\right)^2}. \tag{1}$$

The resonant frequency of the TM_{nml} mode is given by

$$f'_{nml} = \frac{c}{2\pi\sqrt{\mu_1\epsilon_1}}\sqrt{\left(\frac{p_{nm}}{r_1}\right)^2 + \left(\frac{l\pi}{L}\right)^2}, \tag{2}$$

where c is the speed of light in vacuum, r_1 is the radius, and L is the length of the cavity, μ_1 is the relative permeability, and ϵ_1 is the relative permittivity of the dielectric nanorods. P_{nm} and P'_{nm} are the mth root of the nth Bessel's function and its derivative.[13] By checking values of P_{nm} and P'_{nm}, we find the dominant TE mode is TE_{111} with $P'_{11}=1.841$, while the dominant TM mode is the TM_{010} with $P_{01}=2.405$. Under the condition of $2r_1<L$, the cutoff mode is TE_{111}.[13] Thus, for a cylindrical cavity resonator, the frequency of the main, TE_{111}, mode is obtained

$$f_{111} = \frac{c}{2\pi\sqrt{\mu_1\epsilon_1}}\sqrt{\left(\frac{1.841}{r_1}\right)^2 + \left(\frac{\pi}{L}\right)^2}. \tag{3}$$

Equation (3) shows that the cavity's resonance can be controlled by adjusting the radius and the length of the nanorod's dielectric core. Of particular interest are gold-coated nanorods, which are actually wirelike structures, 100–200 nm in diameter and ~10 μm in length. For nanowires with $L \gg r_1$, the resonant frequency can be written compactly as

$$f_{111} \approx \frac{1.841c}{2\pi r_1\sqrt{\mu_1\epsilon_1}}. \tag{4}$$

Thus, a nanowire's resonant frequency depends only on the radius of its dielectric core.

The optical properties of gold-coated TiO_2 and SiO_2 nanorods have been measured by Cao's group.[7] Some of the spectra exhibit two peaks, consistent with a surface plasmon resonance and with a bulk, geometric resonance. For ex-

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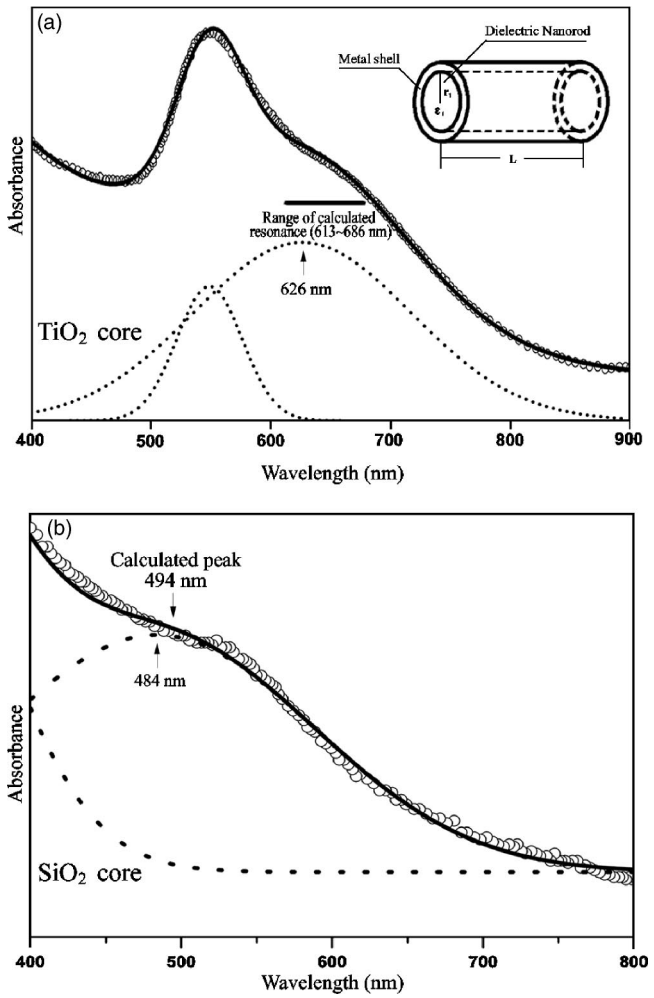

FIG. 1. Experimental absorbance data (open circles) and multipeak fit (solid line) for Au-coated TiO_2 and SiO_2 nanorods (Ref. 7). The dotted lines represent the deconstruction of the multipeak fit. (a) Results for 180 nm TiO_2 nanorods coated with 4 nm thick Au and (b) for 200 nm SiO_2 nanorods coated with 6 nm of gold. The inset shows the idealized geometry upon which our calculation is based: r_1 is the core radius and L is the length of the nanorod.

ample, Fig. 1(a) depicts the absorbtion spectrum of 180 nm TiO_2 nanorods coated with 4 nm Au. We fit the apparent peak and broad shoulder to two peaks: one at 549 ± 1 nm and the other at 626 ± 3 nm. The bulk resonance is predicted by Eq. (4) to lie between 613 and 686 nm with the range bracketed by the uncertainty in the dielectric constant of the porous nanostructure of TiO_2, $4 < \epsilon_1 < 5$.[14,15] The shorter wavelength peak, at 549 ± 1 nm, is attributed to Mie scattering by surface plasmon as described in the original experimental paper, Ref. 7.

The same effect is shown in Fig. 1(b) for 200 nm SiO_2 nanorods coated with 6 nm of Au. The spectrum shows two peaks, one at 484 nm and one clearly below 400 nm (fitted with a centroid of 300 ± 112 nm). The peak at 484 ± 13 nm is very close to our prediction for the bulk cavity resonance, and the 300 nm peak is likely due to Mie scattering. In a macroscopic system, the thickness of the metal shell would exceed the electromagnetic skin depth. However, for nanoshells, the metallic shell is much thinner, a few nanometers. Thus, the incident electromagnetic wave can penetrate into the cavity, but only for cases in which the metallic coating is less than the electromagnetic skin depth, ~ 10 nm for gold. This fact is consistent with Cao's experiments, in which only one Mie scattering peak is observed for gold shells thicker than 10 nm.[7] The fact that the peak is broad is likely due to the nonuniform radii of the nanorods (giving a statistical spread in frequencies)[7] but also attributable to energy lost by radiating through ultrathin or incomplete shells.[6]

Thus, in this paper, we present a study of mini cylindrical resonators, formed by dielectric nanorods coated by thin metallic shells. These core-shell structures act as cylindrical electromagnetic cavities, whose resonance displays tunability controlled by their geometry. Our theoretical results describe previously unexplained peaks in the electromagnetic spectrum of gold-coated TiO_2 and SiO_2 nanorods.

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[1] Y. W. C. Cao, R. C. Jin, and C. A. Mirkin, Science **297**, 1536 (2002).
[2] H. J. Lezec, A. Degiron, E. Devaux, R. A. Linke, L. Martin-Moreno, F. J. Garcia-Vidal, and T. W. Ebbesen, Science **297**, 820 (2002).
[3] S. A. Maier, P. G. Kik, and H. A. Atwater, Appl. Phys. Lett. **81**, 1714 (2002).
[4] J. M. Oliva and S. K. Gray, Chem. Phys. Lett. **379**, 325 (2003).
[5] T. S. Ahmadi, Z. L. Wang, T. C. Green, A. Henglein, and M. A. Ei-Sayed, Science **272**, 1924 (1996).
[6] S. J. Oldenburg, R. D. Averitt, S. L. Westcott, and N. J. Halas, Chem. Phys. Lett. **288**, 243 (1998).
[7] S. J. Limmer, T. P. Chou, and G. Cao, J. Phys. Chem. B **107**, 13313 (2003).
[8] J. J. Diao and G. D. Chen, J. Phys. D **34**, L79 (2001).
[9] S. J. Oldenburg, G. D. Hale, J. B. Jackson, and N. J. Halas, Appl. Phys. Lett. **75**, 1063 (1999).
[10] R. D. Averitt, S. L. Westcott, and N. J. Halas, J. Opt. Soc. Am. B **16**, 1824 (1999).
[11] C. Radloff and N. J. Halas, Nano Lett. **4**, 1323 (2004).
[12] E. Hao, S. Li, R. C. Bailey, S. Zou, G. C. Schatz, and J. T. Hupp, J. Phys. Chem. B **108**, 1224 (2004).
[13] P. M. Pozar, *Microwave Engineering*, 2nd ed. (Wiley, New York, 1998).
[14] D. Mardare and P. Hones, Mater. Sci. Eng., B **B68**, 42 (1999).
[15] D.-J. Won, C.-H. Wang, H.-K. Jang, and D.-J. Choi, Appl. Phys. A: Mater. Sci. Process. **A73**, 595 (2001).