Additions and Corrections

Plasmon Resonance Measurements of the Adsorption and Adsorption Kinetics of a Biopolymer onto Gold Nanocolloids

Dirk Eck, Christiane A. Helm,* Norman J. Wagner, and Abraham Vaynberg *Langmuir* **2001**, *17*, 957−960.

Equation 2 given in Eck et al.[1] is erroneous. Below are given the correct equations as well as some simulated extinction spectra.

The polarizability α of gold nanocolloids (radius R, number density N) with a shell characterized by a thickness d and a dielectric constant ε_s immersed in a medium with dielectric constant ε_m is given by[2,3]

$$\alpha = \varepsilon_0 \frac{(\varepsilon_s - \varepsilon_m)(\varepsilon + 2\varepsilon_s) + \left(\frac{R}{R+d}\right)^3 (\varepsilon - \varepsilon_s)(\varepsilon_m + 2\varepsilon_s)}{(\varepsilon_s + 2\varepsilon_m)(\varepsilon + 2\varepsilon_s) + 2\left(\frac{R}{R+d}\right)^3 (\varepsilon - \varepsilon_s)(2\varepsilon_s - 2\varepsilon_m)} \times \frac{4}{3}\pi(R+d)^3 \quad (1)$$

ε is the dielectric constant of gold, which is a complex number with a pronounced dependence on the wavelength.[4] Then, one obtains for the effective dielectric constant ε_{eff} of the core−shell system in the medium

$$\varepsilon_{eff} = \varepsilon_m \frac{1 + 2N\alpha/(3\varepsilon_0\varepsilon_m)}{1 - N\alpha/(3\varepsilon_0\varepsilon_m)} \quad (2)$$

The experimentally accessible variable is the extinction coefficient $\gamma = 4\pi\kappa/\lambda$, with κ as the imaginary part of ε_{eff}.[5]

To verify the equations, extinction spectra for gold core−shell particles ($R = 7.5$ nm) are calculated for two cases (Figure 1) describing the shell: constant dielectric constant ε_s with increasing thickness d and constant thickness d with increasing dielectric constant ε_s. In both cases, an increase in the maximum extinction as well as a shift of the maximum position to longer wavelengths is observed. Whereas in the former case both effects show saturation for $d \approx 15$ nm (Figure 2), limiting the sensitivity of the method to shells with 8 nm thickness, in the latter case both the peak maximum and red shift increase linearly with the dielectric constant, ε_{eff}, independent of d. If d approaches zero, then the equation is that of a naked colloid with radius R. However, if d exceeds 20 nm, then one obtains the spectrum of a naked colloid immersed in a medium with ε_s. Finally, we mention that with an increase in the nanoparticle radius a shell thickness exceeding 15 nm can be readily distinguished.

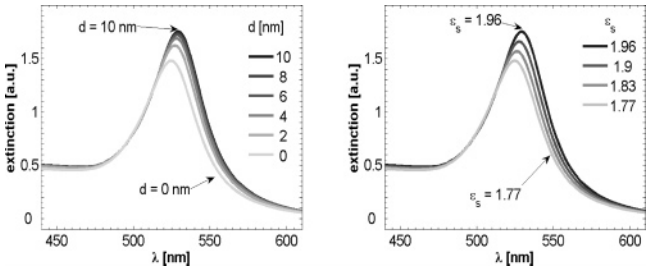

Figure 1. Simulated extinction spectra vs wavelength for gold nanoparticles (radius $R = 7.5$ nm) with adsorbed polymers in water. Two cases are shown: (left) varying thickness d with unchanging dielectric constant ($\varepsilon_s = 1.96$) and (right) constant thickness ($d =$ 10 nm) with varying dielectric constant ε_s (right). The simulation parameters are the radius of the nanoparticles, $R = 7.5$ nm; the dielectric constant of water, $\varepsilon_m = 1.77$; the number density $N = 5.66 \times 10^{19}$ m^{-3} = 56 μm^{-3} = 56 fL^{-1} (leading to a filling factor of 10^{-4}).

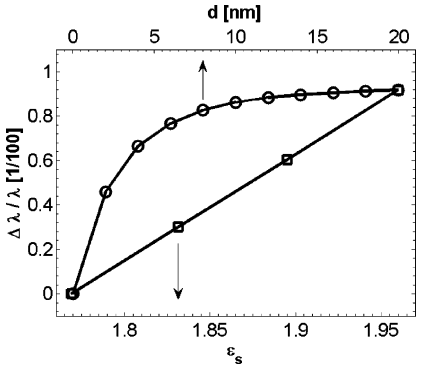

Figure 2. Maximum positions of the extinction spectra shown in Figure 1 as a function of shell thickness d. Open spheres indicate a fixed-shell dielectric constant of $\varepsilon_s = 1.96$ while the thickness is varied. Open squares symbolize constant thickness $d = 20$ nm and increasing dielectric constant ε_s.

Acknowledgment. We thank Junfeng Zhai (Chinese Academy of Sciences, Changchun) for bringing the problems in the paper to our attention. Financial support by SFB TR 24 is appreciated. We also thank Olaf Soltwedel for preparing the plots, and verified that the extinction in the limit of large and small shell thickness was sensible.

LA702200P

10.1021/la702200p
Published on Web 08/07/2007

(1) Eck, D.; Helm, C. A.; Vaynberg, K. A.; Wagner, N. J. *Langmuir* **2001**, *17*, 957−960.
(2) Kreibig, U.; Vollmer, M. *Optical Properties of Metal Clusters*; Springer-Verlag: Heidelberg, Germany, 1995.
(3) Guettler, A. *Ann. Phys.* **1952**, *11*, 5.
(4) *CRC Handbook of Chemistry and Physics*, 65th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1984−1985.
(5) Schmitt, J.; Mächtle, P.; Eck, D.; Möhwald, H.; Helm, C. A. *Langmuir* **1999**, *15*, 3256−3266.