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Shape and size dependence of the surface plasmon resonance of gold nanoparticles studied by Photoacoustic technique

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Abstract. We report on the optical absorption properties of as prepared gold naoparticles of different shapes and sizes measured by photoacoustic (PA) method. The gold nanoparticles of two different shapes (dots, rods) have been prepared using the seed mediated growth method. The shape and the size of these different nanoparticles were determined by STM measurements. PA spectra show the splitting of the surface plasmon resonance (SPR) into two modes (transverse and longitudinal) in case of gold nanorods. The increase in the aspect ratio of the nanorods leads to clear redshifts of the longitudinal SPR. These shifts were used to determine the dielectric constant of the surrounding medium and its variation with the aspect ratios.

1 Introduction

The reduction of the size and dimensionality of metals results in drastic change in the electronic properties as the spatial length scale of the electronic motion is reduced with decreasing size. A transition from the bulk band structure to individual localized energy levels also occurs in nanometer size, and the quantum size effects with exciting new properties have led the search in metal nanoparticles [1,2]. Many new areas in the fields of optoelectronics, sensors, nanocatalysis, and nanomedicine make use of the exciting properties of gold nanoparticles. They absorb and scatter light orders of magnitudes stronger than other materials [3]. The enhanced scattering property has been used in imaging and allows for detecting single cancer cell once nanoparticles are conjugated to cancer cell antibodies [4]. The physical origin of the strong light absorption by noble metal nanoparticles is the coherent oscillation of the conduction band electrons (surface plasmon oscillation) induced by interaction with an electromagnetic field. Mie [5] first described theoretically the strong absorption band in the visible region by spherical gold nanoparticles by solving Maxwell's equations for a radiation field interacting with a spherical metal particle under the appropriate boundary conditions. The resonance frequencies as well as the width of the plasmon absorption band depend on the nanoparticles size and many theories have been developed to explain the observed experimental behavior [6]. Gans [7] extended Mie's theory to prolate and oblate spheroidal particles averaged over all orientations. In the case of gold nanorod the plasmon resonance splits into two modes: one longitudinal mode parallel to the long axis of the rod and a transverse mode perpendicular to the first. In this work we use photoacoustic (PA) technique to study the shape dependence of surface plasmon resonance of gold nanoparticles (dots and rods) in addition to their dependence on the aspect ratio in the

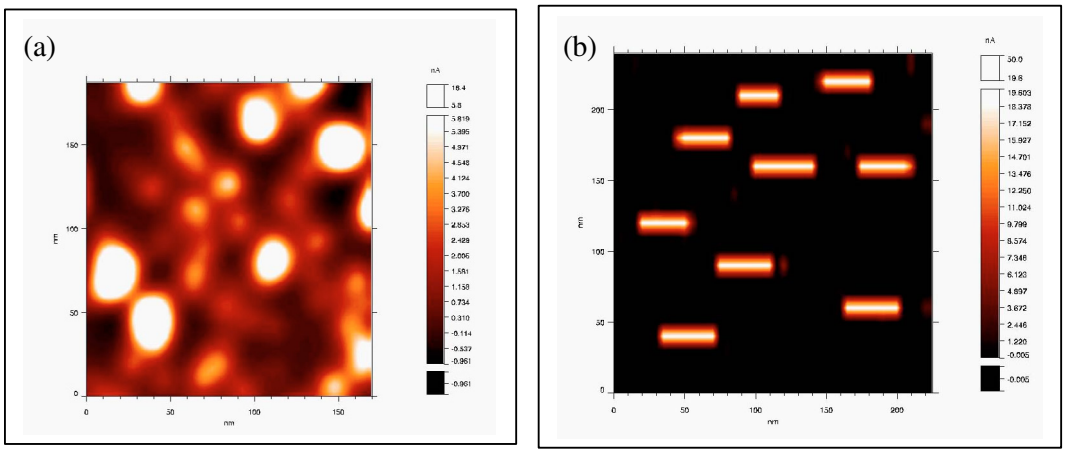

Fig. 1. STM pictures of Gold nanoparticles (a) nanospheres and (b) nanorods.

case of gold nanorods. The use of PA technique to measure the absorption of gold nanoparticles (as prepared) is quite advantageous to most other techniques.

2 Experimental

Gold nanoparticles of different shapes have been prepared using the seed mediated growth method [8,9] to prepare metallic nanospheres and nanorods in aqueous solution. The shape and size distribution of the nanoparticles were determined by analysis of scanning tunnelling microscope (STM) images obtained by an OMICRON system operating in ultra-high-vacuum. During this operation the background pressure was maintained below 4×10^{-9} Torr. The Pt/Ir probe tips were prepared by electrochemical etching using a solution of $CaCl_2$ and an A.C voltage applied between the tip and the graphite electrode. The images of dried gold nanospheres and nanorods of average aspect ratio 3.31 are shown in Fig. 1 (a) and (b) respectively.

We synthesized and studied nanorods samples with aspect ratios of 2.75, 3.1 and 3.31 where most of them have comparable width of $\approx$ 10 nm. Measurements of the PA spectra were carried out at room temperature in the wavelength range 400–800 nm. The modulation frequency was 16 Hz using a mechanical chopper. The PA spectra were normalized (light intensity normalization) using carbon black. The data were averaged to improve the signal to noise ratio. The conditions for each of the PA measurements were kept the same in order to compare the PA signals directly.

3 Results and discussion

The optical absorption properties of gold nanoparticles in the visible range are very much dictated by the effect of the boundary conditions of the coherent electron oscillations and also due to the interband d ► sp electronic transitions. Figure 2 shows the PA spectra of the gold nanoparticles of different shapes (spheres and rods as indicated). The spectrum of gold nanospheres ($\sim$20 nm in diameter) shows the characteristic strong absorption band at $\approx$522 nm that is assigned to the dipole resonance of the gold nanospheres. Very small nanoparticles ($<$2 nm) as well as bulk gold do not show this absorption. On the other hand PA spectrum of gold nanorods is characterized by two bands, the short wavelength band is located at about 522 nm and is attributed to the transverse SPR. The short wavelength band may have some contribution from the spherical gold nanoparticles present with the nanorods as impurities. The longer wavelength band (698 nm) is attributed to the longitudinal SPR. Fig. 3 show that the PA spectra for gold nanorods of different aspect ratios as indicated. The transverse mode shifts

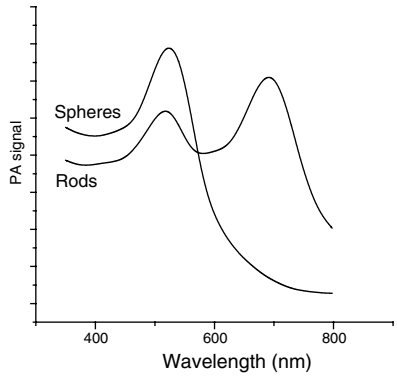

Fig. 2. PA spectra of gold nanoparticles of different shapes.

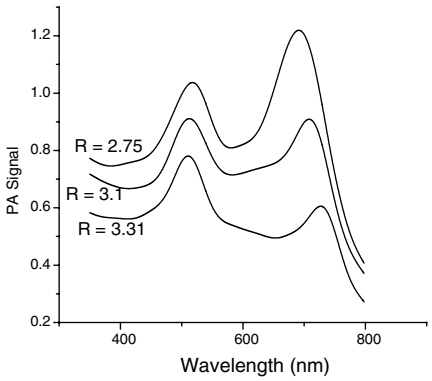

Fig. 3. PA spectra of gold nanorods of different sizes.

only slightly to shorter wavelength with increasing the aspect ratio of the nanorods whereas the longitudinal mode red shifts with increasing the aspect ratio. Our PA measurements are in agreement with the optical absorption measurements obtained for gold nanorods [10]. While the PA intensity of the transverse mode is nearly the same, the intensity of the longitudinal mode decreases with increasing the aspect ratio, this can be understood as follows. It is known that the longitudinal mode is more effective in amplifying the fluorescence in gold nanoparticles compared to the SPR of spheres because the longitudinal mode is less damped [11]. The PA signal is produced mainly by the nonradiative decay of the absorbed energy, hence the reduction of this nonradiative decay part as a complementary to the increase in the radiative decay (fluorescence) leads to a reduction in the PA signal. S. Link et al. [12] derived an interesting equation

$$\Lambda_{\max} = (33.34R - 46.31)\varepsilon_{\mathrm{m}} + 472.31 \tag{1}$$

correlating wavelength maximum ($\lambda_{\max}$) of the longitudinal mode to both the average aspect ratio (R) and the dielectric constant of the surrounding medium ε_{m}. This relation was derived considering that the real part of the gold dielectric function is decreasing nearly linearly with the wavelength of the light in the range between 500 and 800 nm and also that $\lambda_{\max}$ varies linearly with R.

They found that to fit the experimental results to eq. (1), ε_{m} should be size dependent and increasing in a nonlinear fashion with decreasing the aspect ratio of the nanorods. Using eq. (1) we can calculate ε_{m} in terms of $\lambda_{\max}$ and R that are obtained from the PA spectra and STM measurements respectively. The calculated values of ε_{m} are 4.97, 4.25 and 3.99 for surrounding media of the nanorods of aspect ratios 2.75, 3.1 and 3.31 respectively. These values are reasonable when compared to other organic chemicals with structures similar to surfactants used in this study [13]. A dependence of the medium dielectric constant on the nanorod aspect ratio means that the structure of the surrounding micelle is different for different nanorods sizes. This may be due to the change in the organization of the molecules at the gold surface with changing the rods length. These PA results are in complete agreement with results obtained by other more conventional optical absorption methods [12].

4 Conclusion

PA measurements of the gold nanoparticles show a single peak for the absorption in the case of nanospheres and a splitting of the absorption bands into transverse and longitudinal in the case of nanorods. The longitudinal mode red shifts with the increase in aspect ratio. The position of peaks in the absorption gives dimensionalities of the nanoparticles that are in agreement with direct measurements of STM.

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References

1. A.P. Alivisatos, J. Phys. Chem. **100**, 13226 (1996)
2. G. Schmid, LF. Chi, Annu. Adv. Mater. **10**, 515 (1998)
3. I. El-Sayed, H. Xiaohua, M.A. El-Sayed, Nano Lett. **4**, 829 (2005)
4. I. El-Sayed, H. Xiaohua, M.A. El-Sayed, Cancer Lett. (online) **239**, 129 (2006)
5. S. Link, M.A. El-Sayed, J. Phys. Chem. B **103**, 8410 (1999)
6. U. Kreibig, M. Volmer, A. Hilger, *Optical Properties of Metal Clusters* (Springer, Berlin, 1995)
7. R. Gans, Ann. Physik **47**, 270 (1915)
8. N.R. Jana, L. Gearheart, C.J. Murphy, J. Phys. Chem. B **13**, 1389 (2001)
9. B. Nikoobakht, M.A. El-Sayed, Chem. Mater. **15**, 1957 (2003)
10. S. Link, M.A. El-Sayed, Annu. Rev. Phys. Chem. **54**, 33 (2003)
11. V. Volkov, Chem. Phys. Lett. **317**, 517 (2000)
12. L. Stephan, M.B. Mohamed, M.A. El-Sayed, J. Phys. Chem. B **103**, 3073 (1999)
13. D.R. Lide, *Handbook of Chemistry and Physics*, 75^{th} edn. (CRC Press, Boca Raton, 1994)