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Spectrally-Resolved Atomic-Scale Length Variations of Gold Nanorods

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Surface plasmons, or coupled oscillations of electronic charge and electromagnetic field,[1] localized on nanoparticles of gold or other noble metals, are widely exploited in nanotechnology and nanoscale photonics,[2,3] scanning microscopy,[4] nonlinear spectroscopy,[5,6] and optical sensing.[7−11] These applications often require arrays of nanoparticles whose shape, size, and orientation is as identical as possible. The sensitivity of plasmon resonances to variations in the nanoparticles' size and shape[12] generally presents a challenging task to nanofabrication, since the particles must be defined with subnanometric accuracy. On the other hand, this sensitivity can be exploited as a tool for distance monitoring between the nanoparticles.[13,14] Here we demonstrate that rod-shaped nanoparticles, fabricated with high resolution, can serve as ultrasensitive optical rulers providing subnanometric resolution. Using electron-beam lithography and lift-off techniques we have fabricated structures comprising hundreds of gold nanorods, whose high statistical uniformity allows the optical detection of size variations on a subnanometer scale; an increase in their length by the thickness of a few gold atomic layers leads to a detectable spectral red-shift of their plasmonic scattering band at the wavelength of 1.5 μm. This result opens ways for quantitative length measurements on an atomic scale in ambient environment using optical techniques.

Patterns of gold nanorods were defined on cover glass substrates by electron-beam lithography (EBL). The designed patterns have a rectangular footprint with dimensions $(x = 120) \times (y = 360 + \Delta y)$ nm^2, where $\Delta y = N \times 0.625$ nm ($N = 0, 1...14$) is the rod length increment in the fabricated set of 15 samples (0.625 nm is the pixel size of the EBL drawing apparatus). Nanorods with a design height of $z = 30$ nm were fabricated using a lift-off technique on a 2 nm Cr buffer layer in order to achieve better adhesion. One significant advantage of this technique over synthesis from liquid solutions is the possibility to obtain large ensembles of identically oriented nanorods.[15] Figure 1(a,b) shows scanning electron microscopy (SEM) images of the nanorods with $N = 0$. Elongation of the nanorods allows distinction of longitudinal (L) and transverse (T) surface plasmon modes associated with these nanoparticles. Longitudinal (transverse) modes can be excited by radiation polarized linearly parallel to the rods' longer (shorter) axis. Length of the nanorods was chosen so as to tune their longitudinal plasmon mode to the telecommunications wavelength range near 1.5 μm, where optical measurements can be performed with ease. Simultaneously, lateral dimensions were chosen to exceed the mean-free path of Fermi electrons approximately equal to 36 nm, which ensured the electronic properties of the nanorods close to those of bulk gold. Inspection of the nanorods' size and shape was conducted using SEM. The fabricated nanorods have footprints larger than designed. These size deviations were studied systematically by detailed inspection of 30 nanorods in each sample using SEM after completing the optical characterization, because the sputtering of 2 nm Pd|Pt film was needed in order to prevent charging of glass substrate during the SEM imaging. The actual footprint of the nanorods can be approximated, with an accuracy determined by a standard deviation, as $(x = 143 \pm 3.3) \times (y = (372.5 \pm 2.7) + \Delta y)$ nm^2, where $\Delta y = N \times (1.93 \pm 0.38)$ nm. Since the SEM observation requires coating, which may alter the original shapes of the nanorods, this approximation is not necessarily accurate. The top surface of as-fabricated nanorods was inspected by atomic force microscopy and was determined to have a height of 30 nm and a roughness of about 1 nm. Separation between the rods was chosen to be large enough to prevent their dipole−dipole coupling.[16]

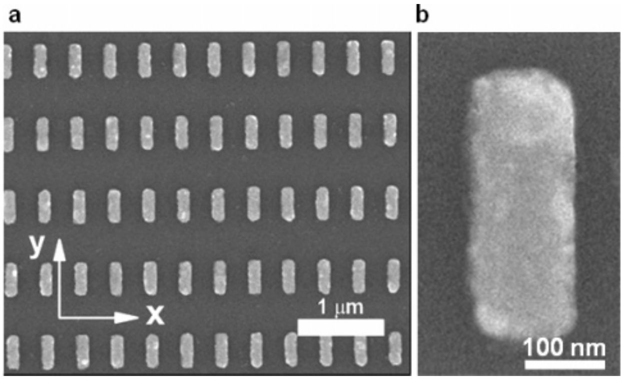

Figure 1. (a,b) Scanning electron microscopy images of the sample composed of gold nanorods with $N = 0$.

In these circumstances SEM cannot provide reliable structural characteristics of the samples despite the fact that imaging is accomplished using short-wavelength electrons in high-vacuum conditions. Interestingly, the dimensions of the nanorods can be extracted with higher accuracy from the optical extinction measurements, performed using radiation having much longer, infrared wavelength, and in an ambient environment.

To support these claims, in Figure 2(a,b) we show optical extinction spectra of as-fabricated samples (see Supporting Information for details). An area of 10×10 μm^2 comprising 312 nanorods was imaged on each sample. According to classical Maxwell electrodynamics, the peak wavelengths of these modes should roughly scale with the corresponding dimensions of the nanorods. As expected, the T modes' extinctions are identical in all samples since their transverse size is the same (Figure 3(a)). This fact illustrates the high accuracy of the fabrication procedures. On the other hand, the L modes' peaks exhibit a red-shift with the design length of the rods, as illustrated by Figure 2b. A dephasing time of $T_2 \simeq 21.5 \pm 1.5$ fs can be deduced from Lorentzian fits to the L modes' frequency-domain spectra. This value far exceeds the dephasing time in bulk gold, $T_2 = 9.1$ fs[17] and is close to the value of 18 fs found in single gold nanorods owing to drastically reduced plasmon damping.[18] In our case of multiple nanorods, some inhomogeneous broadening of the extinction peaks will lead to overestimated spectral half-width and underestimated dephasing

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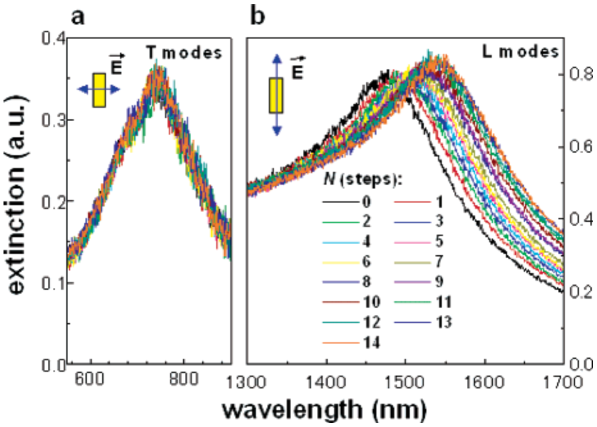

Figure 2. Extinction spectra measured in ensembles of 312 nanorods having different lengths along the *y*-axis: transverse mode (a) and longitudinal mode (b), respectively. For interpretation of the design and actual lengths see the text.

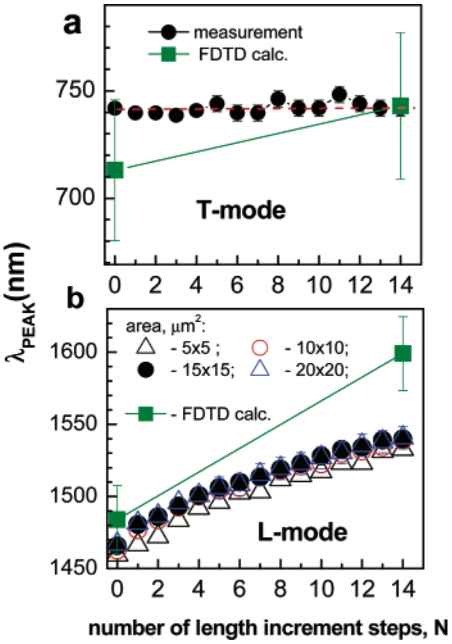

Figure 3. Spectral position of the extinction peaks of transverse (a) and longitudinal (b) modes versus Δy. In panel b, comparison among areas of different sizes, corresponding to 78, 312, 703, and 1250 nanorods is given. The green squares represent the values obtained from FDTD calculations, for $N = 0$ and 14; the error bars reflect systematic error due to non-normal incidence. The solid lines between the points are linear extrapolations.

time. Thus, dephasing in a single nanorod may be even slower than found from an ensemble of nanorods. On the other hand, the obtained value indicates negligible inhomogeneous broadening and confirms a high quality of the samples.

The spectral positions of the L modes' extinction peaks are shown in Figure 3b. These positions were determined with accuracy better than 0.5%. The peaks exhibit a pronounced red-shift with *N*. Notice that rod length increase by a single step leads to an easily detectable spectral shift of the peak by about 5 nm. In order to verify the possible statistical influence of inhomogeneous broadening in the samples, extinction in areas of different size comprising different numbers of nanorods was measured. These data are also presented for comparison in Figure 3b (see caption for explanation). As can be seen, essentially the same results were reproduced regardless of the area probed, although some blue-shift with respect to other datasets developed when the area shrunk to 5 × 5 μm^2 (78 nanorods). The experimentally observed trends were compared with predictions of theoretical finite-difference time-domain (FDTD) calculations (see Supporting Information for details about calculations and interpretation of their results). The modeled optical extinction peak positions for gold nanorods with $N = 0$ and $N = 14$ are shown in Figure 3 (only the extreme values of *N* were used as the intermediate length steps became indistinguishable under spatial discretization step of 5 nm used in the modeling). The calculations show the same trends as the experimental data; some difference in the peaks' position can be explained by factors neglected in the theoretical model, like the presence of finer features in the shapes of the nanorods, variations in their local dielectric environment (e.g., due to unintentional contamination), and non-normal incidence of the probing radiation in the experiments.

Altogether, the above data demonstrates the high sensitivity of the longitudinal plasmon extinction resonance on the design length of the nanorods. Although this dependence and its accuracy still have to be evaluated in order to enable calibrated length measurements, the actual nanorod length step size should fall into the range between the design value of 0.625 nm and the value of 1.93 nm inferred from the SEM observation. This means that length can be determined with accuracy corresponding to the thickness of about ~4 to 12 atomic layers of gold.

In conclusion, we have fabricated large ensembles of gold nanorods arranged into arrays, which exhibit plasmonic extinction bands highly sensitive to the rod length variations. The strong red-shift of longitudinal plasmon resonance with nanorod length occurs in the telecommunications spectral range near 1.5 μm wavelength. The length change by an amount comparable to the thickness of a few gold atomic layers can be easily detected, demonstrating the possibility of performing quantitative measurements of the absolute dimensions of nanoparticles with atomic-scale precision in an ambient environment using optical techniques.

Supporting Information Available: Details of optical transmission measurements and FDTD modeling. This material is available free of charge via the Internet at http://pubs.acs.org.

Note Added after ASAP Publication. The description of the supporting information available was omitted in the version of this paper published ASAP on October 18, 2006. It was added on October 25, 2006.

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JA0645786