Optical properties of nanoengineered gold blocks

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Received March 28, 2005

We report on control over the extinction spectrum of tetragonal gold nanoblocks by changing their lateral aspect ratio. Nanoblocks were patterned on a glass substrate by electron-beam lithography and were 40–400 nm in lateral dimensions and spanned from 1 to 9 in aspect ratio. This allowed us to tune the localized surface plasmon bands from 700 nm to 1.5 μm (longitudinal mode) and from 700 to 550 nm (transverse mode). Unprecedented polarization selectivity of the transverse and longitudinal plasmon bands was achieved via alignment and 3D control of the dimensions of the nanoblocks. © 2005 Optical Society of America

OCIS codes: 000.2190, 000.2690.

Nanoparticles of noble metals, such as gold and silver, exhibit characteristic bands of optical attenuation at visible wavelengths.[1,2] These bands arise due to the collective response of the metal's electrons to the incident optical radiation, leading to the formation of localized surface plasmons (LSPs).[1,2] The electromagnetic components of LSPs are predominantly concentrated within a few nanometers' distance from the surface of the nanoparticle, and in that region the electric field strength becomes enhanced. This field enhancement allows one to increase the sensitivity of the fluorescence[3,4] and Raman scattering[5–9] measurements under low excitation, which is important for the development of high-sensitivity sensors and helps elucidate the properties of molecules adsorbed on solid surfaces.

For these and other applications, it is most important to control the field enhancement and the spectral properties of the nanoparticle LSP states. This requires one to control the size, shape, density, and roughness of the nanoparticles with high fidelity. All these factors should be simultaneously controlled with high accuracy, but this has been lacking so far. During the past few years, much work has been done in achieving such control for gold nanorods synthesized by templating,[10,11] electrochemical methods,[12,13] photochemical methods,[14] etc. Due to the anisotropy of their shape and dielectric properties, nanorods have optical properties different from those of the simplest spherical nanoparticles.[15] As predicted by Gans in 1915,[16] gold nanorod extinction spectra exhibit two bands at visible and near-infrared wavelengths originating from transverse and longitudinal LSP modes. This conclusion has been confirmed by numerous experimental and theoretical investigations.[17,18]

The geometric parameters (the size, shape, roughness, and alignment) of tetragon-shaped nanoparticles can be most accurately defined by using a combination of electron-beam lithography (EBL) and sputtering. Ordered arrays of nanorods fabricated on a dielectric substrate with accuracy of a few nanometers would be an ideal platform for the study of their optical properties unhindered by various side effects due to the fluctuations in the nanorod shape, size, orientation, and density. So far, EBL has been applied for only templating circular cross-sectional patterns.[19,20] Here we report nanoengineering of tetragonal gold nanoblock (rectangular parallelepiped) patterns. The size, aspect ratio, and alignment of the nanoblocks were controlled precisely, thus facilitating spectral tuning of the transverse and longitudinal plasmon bands. The aspect ratio R is defined as the ratio of the length to the width of the oblong nanoblock in the horizontal plane. LSP modes belonging to these plasmon bands can be selectively excited by angularly tuning the linear polar-

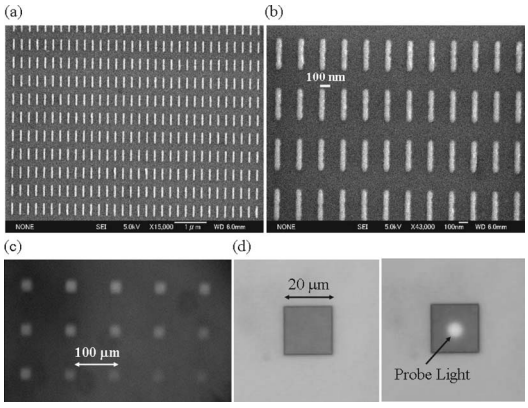

Fig. 1. SEM images of a gold nanoblock array with an aspect ratio of 9: (a) low and (b) high magnification images. Each is 40 and 360 nm in lateral dimensions and spaced 200 nm apart. Optical microscope images of Au nanoblocks: (c) nanoblock group with various aspect ratios and (d) one group of a nanoblock array without and with a probe beam of absorption microspectroscopy.

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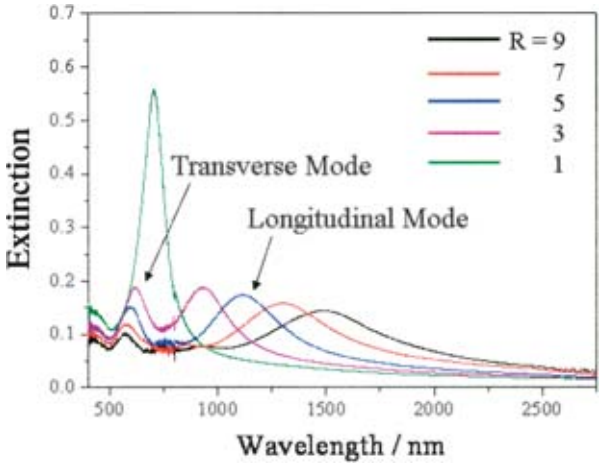

Fig. 2. Absorption spectra of gold nanoblocks with different aspect ratios R under nonpolarized irradiation.

ization of the incident light with respect to the orientation of the nanoblocks.

The gold nanoblocks were fabricated on glass substrates with high-resolution EBL on a scanning electron microscope (SEM, ELS-7700, Elionix Co. Ltd., Tokyo, Japan) at a 100 kV accelerating voltage and lift-off of a 2 nm Cr/60 nm Au bilayer deposited by sputtering. A typical SEM image of the nanoblocks is shown in Fig. 1(a). The precision of the positioning and dimensions of the nanoblocks is better than 2 nm. Hence, identical nanoblocks are patterned [Fig. 1(b)]. The structures have dimensions of 40 nm $\times$360 nm$\times$60 nm and are spaced 200 nm from each other. Nine 20 μm$\times$20 μm size areas containing from 3000 to 4000 gold nanoblocks with different aspect ratios (varied from 1 to 9) are separated by a 100 μm interval, as illustrated in Fig. 1(c). For transmission measurements in the visible region (400–800 nm), a halogen light beam was passed through a pinhole (diameter of 200 μm) and introduced to an optical microscope (Nikon Co., Optiphot 2), where it was focused on the sample by a ($\times$20, N.A.=0.4) microscope objective. By focusing a quasi-parallel probe beam, a waist of about 8 μm was attained at the focus, as shown in Fig. 1(d). The transmitted beam was collected by a multichannel photodetector (Hamamatsu Photonics Co., PMA-11), which recorded its spectrum normalized to the spectrum of the incident beam. Infrared extinction spectra (800–2750 nm) were measured by a Fourier-transform infrared spectrometer with a microscope attachment (IRT-3000).

The nonpolarized extinction spectra of gold nanoblocks with various aspect ratios are shown in Fig. 2. For $R=1$, absorption spectra exhibit a single peak near the 700 nm wavelength. For higher values of R, a distinct branching into two bands can be seen in the visible region from 620 to 550 nm and in the near-infrared region from 930 to 1500 nm. These bands represent the transverse and longitudinal plasmons. It is noteworthy that longitudinal peaks are redshifted, whereas transverse peaks are blueshifted, with the shift magnitude strongly dependent on the aspect ratio. This behavior is in agreement with experimental results obtained earlier for gold nanorod structures.[17,18]

The measured spectra indicate that transverse and longitudinal modes of identical and parallel nanoblock arrays can be selectively excited by controlling the orientation of the linear polarization of the incident light. Figure 3 shows the extinction spectra measured for light polarized perpendicular and parallel with respect to the direction of the rectangular blocks' elongation. In these cases the spectra have only one dominating peak corresponding to either transverse or longitudinal LSPs. Note that for all aspect ratios except $R=1$, the magnitudes of the peaks are twice as large as those of the corresponding peaks in the nonpolarized spectra shown in Fig. 2. This circumstance indicates that proper choice of polarization leads to selective excitation of either transverse or longitudinal LSPs in these nanoengineered gold blocks with a high-fidelity suppression of the other band. The fidelity factor can be defined as a ratio of extinction coefficient $\kappa_{T,L}$ into the corresponding mode (T or L) at the wavelength where it has the maximum (here, the bandwidth of the plasmon bands is not taken into account): $f_{T,L}(R)=A_{T,L}(\lambda^{\max},R)/A_{L,T}(\lambda^{\max},R)$. The baseline corrected fidelity factor for the $R=9$ nanoblocks was larger than 10 and 17 for the longitudinal and transverse modes, respectively. Such high selectivity of LSP excitation was achieved due to control over the alignment and dimensions of the nanoblocks with a precision better than 2 nm. By choosing an angle of the linear polarization of the incident light with the nanoblock's orientation, it is possible to obtain any desired ratio of extinction into the longitudinal and transverse modes. Identical spectra were obtained from nanoblock patterns [Fig. 1(c)] with separation between nanoblocks larger than 20 nm. Hence, there were no interactions between

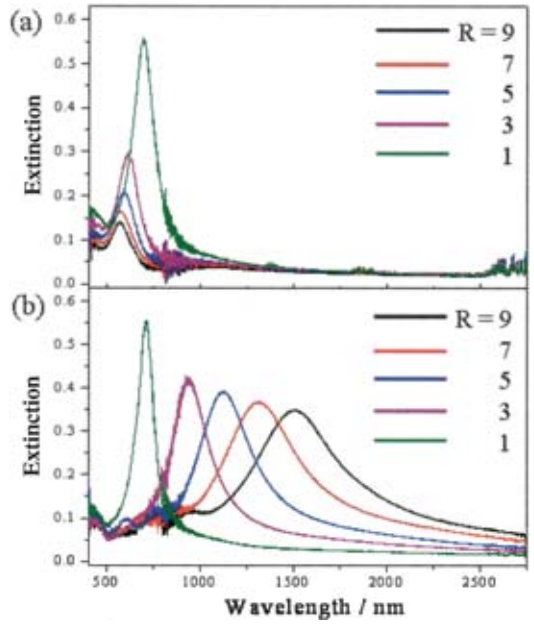

Fig. 3. Extinction spectra of gold nanoblocks with different aspect ratios R for light polarized (a) perpendicular and (b) parallel to the direction of the rectangular blocks' elongation.

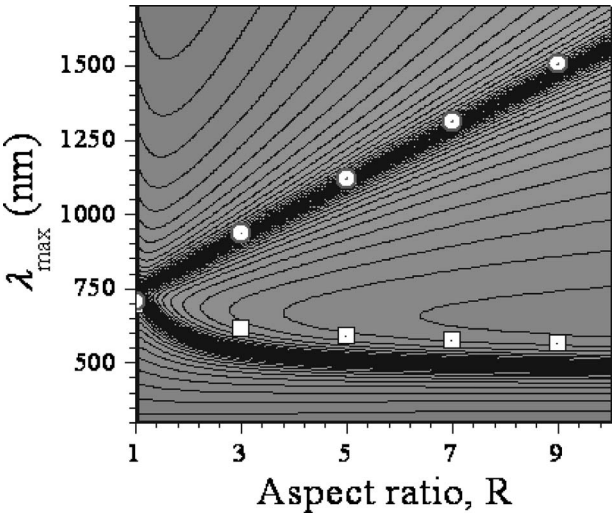

Fig. 4. Dependence of the maximum wavelength of the transverse (squares) and longitudinal (circles) plasmon versus the aspect ratio R of the 60 nm thick Au nanoblocks. The background shows the contour plot of the calculations by the Gans dipole approximation.

the LSP modes of the adjacent blocks. This also proves that there are no other uncontrolled parameters, e.g., thickness, roughness, and mass density of gold, and generic properties of LSPs can be investigated.

Figure 4 shows the dependence of the plasmon peak wavelength on the aspect ratio. For the longitudinal plasmons the dependence is linear. These data can be compared with Gans's theory based on the simple dipole approximation.[17] For the longitudinal branch, the best fit is obtained by adjusting the dielectric constant of the medium surrounding the nanoblocks to the value of $\varepsilon_m = 0.8/R + 0.17$ and is shown in Fig. 4. Similar functional dependence of ε_m was established earlier for liquid solutions of nanorods.[17] Such phenomenological dependence accounts for the fact that the higher-aspect-ratio nanoblocks are more surrounded by air than by glass, which contacts the 3D nanoblock from only one side. The transverse branch fits the experimental data only qualitatively, because the theory considered cylindrical nanowires instead of tetragonal blocks. For the simulations we implemented the bulk gold parameters: The electron density was calculated as the atomic number density, and the effective optical mass of the electron was taken as $m_{\text{eff}} = 0.99$.[21] These parameters can differ for the nanostructured material. Overall, an adequate correspondence was observed between predictions of dipole approximation and experimentally measured spectra of nanoblocks of gold (for a width from 40 to 120 nm and a length from 120 to 360 nm at a fixed 60 nm thickness).

In conclusion, we have shown control of the localized surface plasmon band from visible to telecommunication wavelengths by the aspect ratio of gold nanoblocks. Due to the high precision of the size, shape, and alignment control of the nanoblocks, their plasmon bands can be selectively excited by appropriately tuning the polarization of the incident light. The control of spectral properties is a promising application for optical filters, optical sensors, and near-field optics.

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