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The role of surface plasmon in second harmonic generation from arrays of gold nanorod particles excited by femtosecond laser pulses is investigated as a function of incident light polarization and irradiation wavelength. In addition to photoluminescence, a peak of second harmonic is observed and is found to depend on the polarization and wavelength of the fundamental frequency laser beam. In particular, the authors found similarities between extinction spectra of the nanoparticles and spectra of emmitted second harmonic. This behavior can be explained by resonant excitation of localized surface plasmon resonances. © *2007 American Institute of Physics*.
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The linear optical properties of metallic nanoparticles (MNs) are dominated by collective oscillations of the conduction electrons. In particular, noble MNs present localized surface plasmon resonances (LSPRs) that lead to a strong absorption/scattering and local field enhancement near such structures.[1] The spectral position of these resonances depends on the particles shape and size as well as on the nature of the particle and the refractive index of the surrounding medium.[2] Together with their linear properties, nonlinear optical properties of metallic nanoparticles were studied and appear promising for photonic applications.[3] Because of symmetry considerations, second harmonic generation (SHG) is forbidden for centrosymmetric systems and thus strongly depends on defects and small deviations from the symmetric shape as well as from broken symmetry at interfaces. Nonlinear studies have been reported in the case of metal colloids and tips through measurements of hyper-Rayleigh scattering and SHG.[4–6] SHG from nanostructures with a low degree of symmetry and from noncentrosymmetrical structures composed of symmetrically shaped particles was also investigated.[7–9] Polarization studies have shown that SHG can be enhanced via resonant excitation of LSPR (Refs. 9–11) of nanoparticles. More recently, SHG measurements of planar symmetrical structures were achieved using non-normal incidence illumination[12] or by looking at angles other than the illumination direction.[10]

So far, no spectral study of localized surface plasmons on nanoparticles has been reported using SHG as a probe. In this letter, we present a spectral study of SHG from periodic arrays of gold nanorods. We demonstrate that SHG strongly depends on the incident light polarization direction and that its excitation spectroscopy unambiguously evidences the role of LSPR in the second harmonic signal enhancement.

Figure 1(a) shows the experimental setup used to generate and detect the second harmonic signals. A femtosecond Ti:sapphire laser beam (100 fs, 80 MHz repetition rate) is focused onto the nanostructures using a ×20 microscope objective into a wide laser spot of 1.3 $\mu$m in diameter. The pump wavelength can be tuned from 740 to 860 nm. The

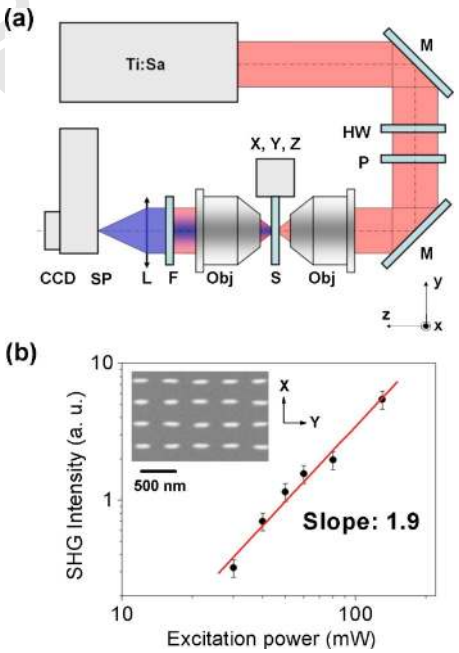


FIG. 1. (Color online) (a) Experimental setup. (b) Excitation power dependence of the detected SHG signal. The height, width, and length of the gold nanorods were equal to 60, 50, and 150 nm, respectively. Irradiation wavelength was equal to 800 nm and incident polarization was parallel to the nanoparticle long axis. The insert shows a scanning electron microscope image of gold nanorods. *X* and *Y* directions are shown with arrows.

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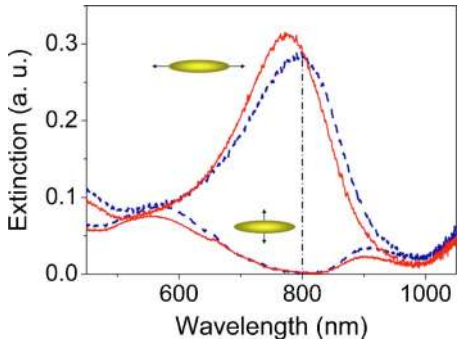


FIG. 2. (Color online) Extinction spectra from arrays of gold nanorods with long axis equal to 150 nm (solid curve) and 170 nm (dashed curve). The incident polarization used to record the spectra is schematized by arrows.

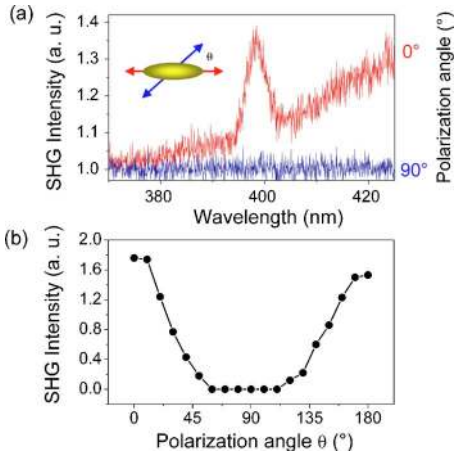


FIG. 3. (Color online) (a) Second harmonic spectra from arrays of 150 nm long axis gold nanorods. (b) Integrated second harmonic intensity from arrays of 150 nm long axis gold nanorods for different incident polarization angles $\theta$. The irradiation time and power used to record the spectra were equal to 5 s and 50 mW, respectively. Irradiation wavelength was set to 800 nm.

incident polarization direction and power are controlled with a half-wave plate and a Glan-Taylor polarizer. The sample is moved in the focal plane of the first objective microscope using three-dimensional microdisplacement. The SHG signal is collected in transmission through the sample with a second $\times 20$ microscope, and a BG 39 Schott filter is used to eliminate the fundamental beam. The SHG spectra are measured by a spectrometer and a charge coupled device. The insert in Fig. 1(b) shows a scanning electron microscope image of the nanostructures fabricated by electron beam lithography through the lift-off method.[6] Spacing between the ellipses is kept constant and equal to 200 nm both in the $x$ and $y$ directions. We chose this edge to edge distance so that no strong near-field coupling nor any grating effect (i.e., far-field coupling) are observed in the extinction spectra. Because of this, and also because of the homogeneity in size and shape of the patterned area, we trust the extinction spectra to reflect the optical properties of one particle and believe that we are probing a single particle response. The long axis length is varied from 150 to 190 nm, whereas the short axis and the height of the nanostructures are equal to 50 and 60 nm, respectively. Figure 1(b) shows the excitation power dependence of the SHG signals measured on gold nanorods by fitting a Lorentzian to a series of spectra. The linear fit of the variation of the emitted signal versus pump power in a logarithmic scale shows that the second harmonic signal has a nearly quadratic dependence on the excitation intensity (slope: 1.9), a characteristic of second order nonlinear processes. The extinction spectra were recorded using a spectrometer coupled to a microscope by means of an optical fiber.

Figure 2 shows the extinction spectra from arrays of nanorod particles. The maxima that peak at 776 and 795 nm correspond to nanoparticles with long axes of 150 and 170 nm, respectively, and are associated with the long axis resonance mode of the nanostructures. As can be observed, the peak of the LSPR associated with the nanorod long axis is tuned to the laser wavelength at 800 nm. The resonance features in the extinction spectrum along the short axis at wavelengths greater than 800 nm cannot be attributed to a plasmon resonance and even though their origin has not been clearly established yet, they do not reflect any particular physical property of the nanoparticle themselves.

Figure 3(a) shows the typical spectra obtained when illuminating gold nanorods of 150 nm long axis with the femtosecond 800 nm pump beam. The polarization angle $\theta$ of the incident laser beam is defined with respect to the nanorod long axis, as indicated in the insert of Fig. 3(a). The maximum intensity of the second harmonic generation signal is obtained when the incident light polarization direction is parallel to the nanorod long axis ($\theta=0°$), i.e., when the LSPR associated with the long axis of the nanoparticles is excited. On the contrary, when the polarization angle is equal to 90°, no second harmonic signal is detected. The spectrum corresponding to $\theta=0°$ contains, in addition to the SHG signal, the beginning of a broad peak centered at a higher wavelength falling outside of our detection window. This corresponds to the photoluminescence of the nanoparticles under two-photon excitation and has been already observed.[13,14]

SHG intensity $I_{(2\omega)}$ is proportional to the squared second order nonlinear polarization $P^{(2)}$ and, in the case of metallic nanoparticles, $I_{(2\omega)}$ is proportional to[15]

$$I_{(2\omega)} \propto f_{(\omega)}^4 f_{(2\omega)}^2 I_{(\omega)}^2, \quad (1)$$

where $f_{(\omega)}$ is the local field enhancement factor at the fundamental frequency, $f_{(2\omega)}$ the local field enhancement factor at the second harmonic frequency, and $I_{(\omega)}$ the pump beam intensity. In the case of nanorods, $f_{(\omega)}$ can result from both LSPR and off-resonance electromagnetic singularities[16] (lightning rod effect). On the other hand, $f_{(2\omega)}$ is expected to result only from lightning rod effects because no resonance is observable for these particles at such a wavelength due to gold interband transitions. Figure 3(b) shows the influence of the incident polarization on the second harmonic signal. The second harmonic intensity is calculated by fitting each spectrum with a Lorentzian intensity distribution and then integrating it. The second harmonic intensity $I_{(2\omega)}$ is found to strongly depend on the incident light polarization direction, which indicates that the SHG is resonantly enhanced by LSPR in nanoparticles preferentially excited when the light polarization is oriented along the long axis of the nanorods. Additionally, this polarization allows electromagnetic singularities to be excited at the rod extremities. Given the polycrystalline nature of the samples, which is found to be globally isotropic, the orientational dependence of the frequency doubling cannot be related to crystal structure.

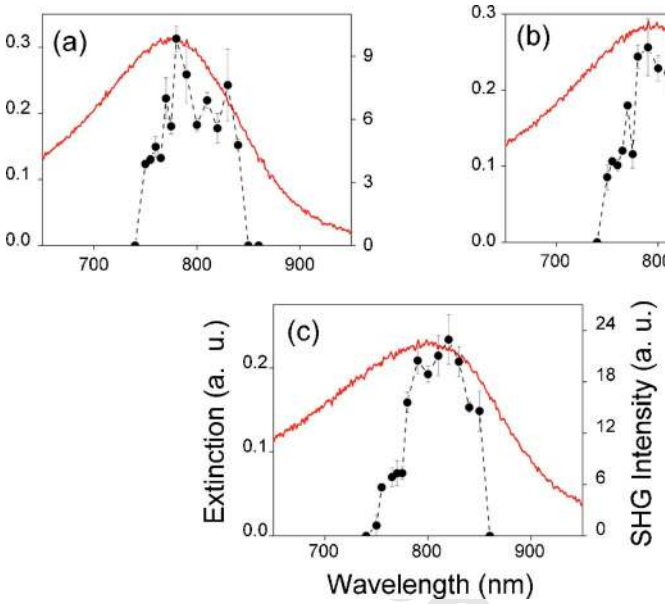


FIG. 4. (Color online) Second harmonic generation enhancement (circles) from arrays of gold nanorods with (a) 150 nm, (b) 170 nm, and (c) 190 nm long axis (the dashed line serves as a guide for the eyes). The extinction spectrum (solid line) is shown for comparison. The irradiation time and power used to record the second harmonic signal were equal to 5 s and 50 mW, respectively. The incident polarization was set parallel to the nanoparticle long axis.

The results presented in Fig. 3 suggest the possible influence of plasmon resonance on second harmonic generation from the nanostructures. In Fig. 4, the study of the influence of the irradiation wavelength on the second harmonic generation process confirms the role of the plasmon resonance. Results from excitation spectroscopy of SHG from 150, 170, and 190 nm long axis gold nanorods are presented in Fig. 4. The light polarization used to illuminate the structures and to record the extinction spectra is oriented parallel to the nanorod long axis in order to maximize the SHG signal. It can be observed that whatever the long axis size, the second harmonic signal follows the extinction spectrum (solid line) of the nanoparticles and thus clearly demonstrates the role of the LSPR in the SHG process. At the half-width, the extinction spectrum peak is broader than the one corresponding to the SHG intensity. This can be explained by the fact that the second harmonic signal is much more sensitive to the field enhancement than extinction. Indeed, nonlinear processes are particularly sensitive to these local resonances due to their quadratic dependence on the intensity. According to Eq. (1), $I_{(2\omega)}$ is proportional to the fourth power of the field enhancement at the fundamental frequency, which originates from LSPR excitation. A small variation in the plasmon resonance intensity thus leads to strong variations in second harmonic intensity, as observed in Fig. 4. The wavelength dependence studies may also suggest that the second harmonic signal has a dipolar electric origin rather than a quadripolar electric one.[8] Although the SHG is theoretically forbidden in centrosymmetrical systems, we make the assumption that, in our case, due to the lithographic fabrication process, the nonlinear generation process may arise from a deviation of the shape of the nanoparticles from that of a perfect symmetrical nanorod as well as from the broken symmetry at the air-metal and metal-substrate interfaces. Defects in the crystalline structure of gold nanoparticles also have to be considered. Finally, it should also be pointed out that due to the large range of wave vectors produced by confined plasmon excitation, depolarization effects can be induced; i.e., vertical component of the near-field appears, making asymmetry discussion nontrivial.

In conclusion, our polarization and spectroscopic studies have shown that second harmonic generation from metallic nanoparticles strongly depends on their dipolar plasmon resonance. Resonance enhancement of the second harmonic intensity has been observed while tuning the polarization of the pump beam from parallel to perpendicular to the long axis of nanoparticles. We also observed a strong variation in the wavelength dependence of the second harmonic generation intensity when the irradiation wavelength is tuned towards the extinction peak. This further highlights the influence of the field enhancement from resonance plasmon excitation in the second harmonic generation process from metallic nanoparticles.

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