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1 Role of surface plasmon in second harmonic generation from gold 2 nanorods

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13 The role of surface plasmon in second harmonic generation from arrays of gold nanorod particles
14 excited by femtosecond laser pulses is investigated as a function of incident light polarization and
15 irradiation wavelength. In addition to photoluminescence, a peak of second harmonic is observed
16 and is found to depend on the polarization and wavelength of the fundamental frequency laser beam.
17 In particular, the authors found similarities between extinction spectra of the nanoparticles and
18 spectra of emitted second harmonic. This behavior can be explained by resonant excitation of
19 localized surface plasmon resonances. © 2007 American Institute of Physics.

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22 The linear optical properties of metallic nanoparticles
23 (MNs) are dominated by collective oscillations of the con-
24 duction electrons. In particular, noble MNs present localized
25 surface plasmon resonances (LSPRs) that lead to a strong
26 absorption/scattering and local field enhancement near such
27 structures.¹ The spectral position of these resonances de-
28 pends on the particles shape and size as well as on the nature
29 of the particle and the refractive index of the surrounding
30 medium.² Together with their linear properties, nonlinear op-
31 tical properties of metallic nanoparticles were studied and
32 appear promising for photonic applications.³ Because of
33 symmetry considerations, second harmonic generation
34 (SHG) is forbidden for centrosymmetric systems and thus
35 strongly depends on defects and small deviations from the
36 symmetric shape as well as from broken symmetry at inter-
37 faces. Nonlinear studies have been reported in the case of
38 metal colloids and tips through measurements of hyper-
39 Rayleigh scattering and SHG.⁴⁻⁶ SHG from nanostructures
40 with a low degree of symmetry and from noncentrosym-
41 metrical structures composed of symmetrically shaped par-
42 ticles was also investigated.⁷⁻⁹ Polarization studies have
43 shown that SHG can be enhanced via resonant excitation of
44 LSPR (Refs. 9–11) of nanoparticles. More recently, SHG
45 measurements of planar symmetrical structures were
46 achieved using non-normal incidence illumination¹² or by
47 looking at angles other than the illumination direction.¹⁰

48 So far, no spectral study of localized surface plasmons
49 on nanoparticles has been reported using SHG as a probe. In
50 this letter, we present a spectral study of SHG from periodic
51 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 gener-
ate 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 $\times 20$ microscope ob-
jective into a wide laser spot of $1.3 \mu\text{m}$ in diameter. The
pump wavelength can be tuned from 740 to 860 nm. The

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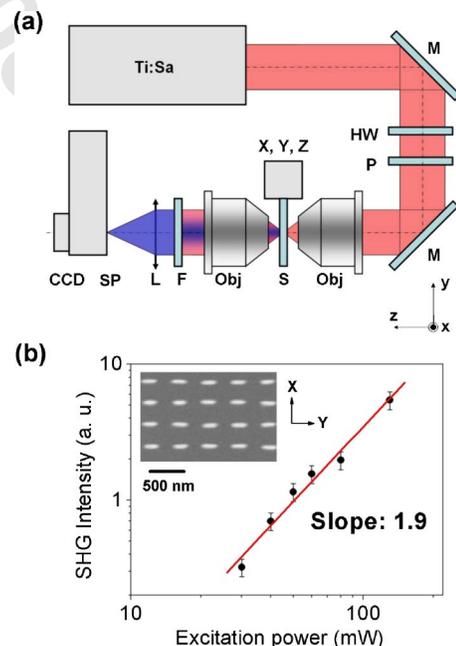


FIG. 1. (Color online) (a) Experimental setup. (b) Excitation power dependence of the detected SHG signal. The height, width, and length of the gold nanorods were equal to 60, 50, and 150 nm, respectively. Irradiation wavelength was equal to 800 nm and incident polarization was parallel to the nanoparticle 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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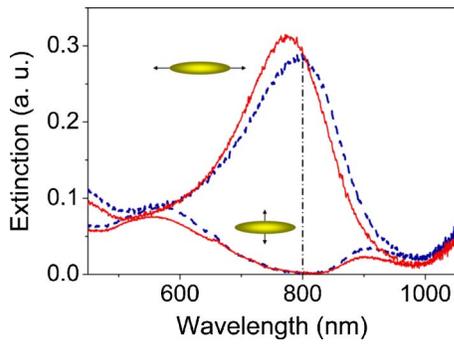


FIG. 2. (Color online) Extinction spectra from arrays of gold nanorods with long axis equal to 150 nm (solid curve) and 170 nm (dashed curve). The incident polarization used to record the spectra is schematized by arrows.

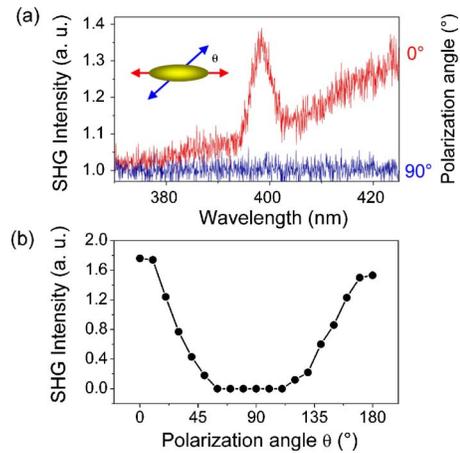


FIG. 3. (Color online) (a) Second harmonic spectra from arrays of 150 nm long axis gold nanorods. (b) Integrated second harmonic intensity from arrays of 150 nm long axis gold nanorods for different incident polarization angles θ . The irradiation time and power used to record the spectra were equal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

long axis, as indicated in the insert of Fig. 3(a). The maxi- 108
 mum intensity of the second harmonic generation signal is 109
 obtained when the incident light polarization direction is paral- 110
 lel to the nanorod long axis ($\theta=0^\circ$), i.e., when the LSPR 111
 associated with the long axis of the nanoparticles is excited. 112
 On the contrary, when the polarization angle is equal to 90° , 113
 no second harmonic signal is detected. The spectrum corre- 114
 sponding to $\theta=0^\circ$ contains, in addition to the SHG signal, 115
 the beginning of a broad peak centered at a higher wave- 116
 length falling outside of our detection window. This corre- 117
 sponds to the photoluminescence of the nanoparticles under 118
 two-photon excitation and has been already observed. 119

SHG intensity $I_{(2\omega)}$ is proportional to the squared second 120
 order nonlinear polarization $P^{(2)}$ and, in the case of metallic 121
 nanoparticles, $I_{(2\omega)}$ is proportional to 122

$$I_{(2\omega)} \propto f_{(\omega)}^4 f_{(2\omega)}^2 I_{(\omega)}^2, \quad (1) \quad 123$$

where $f_{(\omega)}$ is the local field enhancement factor at the funda- 124
 mental frequency, $f_{(2\omega)}$ the local field enhancement factor at 125
 the second harmonic frequency, and $I_{(\omega)}$ the pump beam in- 126
 tensity. In the case of nanorods, $f_{(\omega)}$ can result from both 127
 LSPR and off-resonance electromagnetic singularities 128
 (lightning rod effect). On the other hand, $f_{(2\omega)}$ is expected to 129
 result only from lightning rod effects because no resonance 130
 is observable for these particles at such a wavelength due to 131
 gold interband transitions. Figure 3(b) shows the influence of 132
 the incident polarization on the second harmonic signal. The 133
 second harmonic intensity is calculated by fitting each spec- 134
 trum with a Lorentzian intensity distribution and then integrat- 135
 ing it. The second harmonic intensity $I_{(2\omega)}$ is found to 136
 strongly depend on the incident light polarization direction, 137
 which indicates that the SHG is resonantly enhanced by 138
 LSPR in nanoparticles preferentially excited when the light 139
 polarization is oriented along the long axis of the nanorods. 140
 Additionally, this polarization allows electromagnetic singu- 141
 larities to be excited at the rod extremities. Given the poly- 142
 crystalline nature of the samples, which is found to be glo- 143
 bally isotropic, the orientational dependence of the frequency 144
 doubling cannot be related to crystal structure. 145

61 incident polarization direction and power are controlled with
 62 a half-wave plate and a Glan-Taylor polarizer. The sample is
 63 moved in the focal plane of the first objective microscope
 64 using three-dimensional microdisplacement. The SHG signal
 65 is collected in transmission through the sample with a second
 66 $\times 20$ microscope, and a BG 39 Schott filter is used to elimi-
 67 nate the fundamental beam. The SHG spectra are measured
 68 by a spectrometer and a charge coupled device. The insert in
 69 Fig. 1(b) shows a scanning electron microscope image of the
 70 nanostructures fabricated by electron beam lithography
 71 through the lift-off method.⁶ Spacing between the ellipses is
 72 kept constant and equal to 200 nm both in the x and y direc-
 73 tions. We chose this edge to edge distance so that no strong
 74 near-field coupling nor any grating effect (i.e., far-field cou-
 75 pling) are observed in the extinction spectra. Because of this,
 76 and also because of the homogeneity in size and shape of the
 77 patterned area, we trust the extinction spectra to reflect the
 78 optical properties of one particle and believe that we are
 79 probing a single particle response. The long axis length is
 80 varied from 150 to 190 nm, whereas the short axis and the
 81 height of the nanostructures are equal to 50 and 60 nm, re-
 82 spectively. Figure 1(b) shows the excitation power depen-
 83 dence of the SHG signals measured on gold nanorods by
 84 fitting a Lorentzian to a series of spectra. The linear fit of the
 85 variation of the emitted signal versus pump power in a loga-
 86 rithmic scale shows that the second harmonic signal has a
 87 nearly quadratic dependence on the excitation intensity
 88 (slope: 1.9), a characteristic of second order nonlinear pro-
 89 cesses. The extinction spectra were recorded using a spec-
 90 trometer coupled to a microscope by means of an optical
 91 fiber.

92 Figure 2 shows the extinction spectra from arrays of na-
 93 norod particles. The maxima that peak at 776 and 795 nm
 94 correspond to nanoparticles with long axes of 150 and
 95 170 nm, respectively, and are associated with the long axis
 96 resonance mode of the nanostructures. As can be observed,
 97 the peak of the LSPR associated with the nanorod long axis
 98 is tuned to the laser wavelength at 800 nm. The resonance
 99 features in the extinction spectrum along the short axis at
 100 wavelengths greater than 800 nm cannot be attributed to a
 101 plasmon resonance and even though their origin has not been
 102 clearly established yet, they do not reflect any particular
 103 physical property of the nanoparticle themselves.

104 Figure 3(a) shows the typical spectra obtained when il-
 105 luminating gold nanorods of 150 nm long axis with the fem-
 106 tosecond 800 nm pump beam. The polarization angle θ of
 the incident laser beam is defined with respect to the nanorod

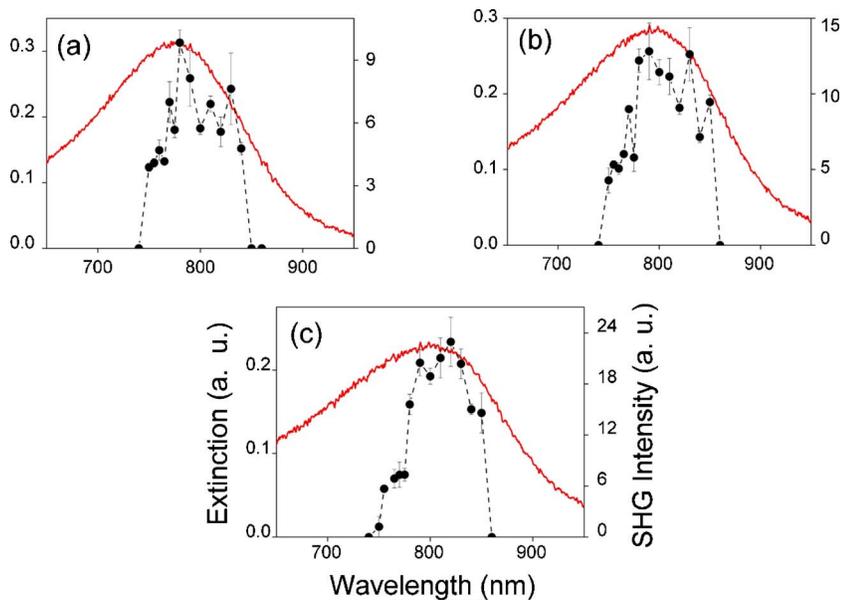


FIG. 4. (Color online) Second harmonic generation enhancement (circles) from arrays of gold nanorods with (a) 150 nm, (b) 170 nm, and (c) 190 nm long axis (the dashed line serves as a guide for the eyes). The extinction spectrum (solid line) is shown for comparison. The irradiation time and power used 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.

146 The results presented in Fig. 3 suggest the possible in-
 147 fluence of plasmon resonance on second harmonic genera-
 148 tion from the nanostructures. In Fig. 4, the study of the in-
 149 fluence of the irradiation wavelength on the second harmonic
 150 generation process confirms the role of the plasmon reso-
 151 nance. Results from excitation spectroscopy of SHG from
 152 150, 170, and 190 nm long axis gold nanorods are presented
 153 in Fig. 4. The light polarization used to illuminate the struc-
 154 tures and to record the extinction spectra is oriented parallel
 155 to the nanorod long axis in order to maximize the SHG sig-
 156 nal. It can be observed that whatever the long axis size, the
 157 second harmonic signal follows the extinction spectrum
 158 (solid line) of the nanoparticles and thus clearly demon-
 159 strates the role of the LSPR in the SHG process. At the
 160 half-width, the extinction spectrum peak is broader than the
 161 one corresponding to the SHG intensity. This can be ex-
 162 plained by the fact that the second harmonic signal is much
 163 more sensitive to the field enhancement than extinction. In-
 164 deed, nonlinear processes are particularly sensitive to these
 165 local resonances due to their quadratic dependence on the
 166 intensity. According to Eq. (1), $I_{(2\omega)}$ is proportional to the
 167 fourth power of the field enhancement at the fundamental
 168 frequency, which originates from LSPR excitation. A small
 169 variation in the plasmon resonance intensity thus leads to
 170 strong variations in second harmonic intensity, as observed
 171 in Fig. 4. The wavelength dependence studies may also sug-
 172 gest that the second harmonic signal has a dipolar electric
 173 origin rather than a quadripolar electric one.⁸ Although the
 174 SHG is theoretically forbidden in centrosymmetrical sys-
 175 tems, we make the assumption that, in our case, due to the
 176 lithographic fabrication process, the nonlinear generation
 177 process may arise from a deviation of the shape of the nano-
 178 particles from that of a perfect symmetrical nanorod as well
 179 as from the broken symmetry at the air-metal and metal-
 180 substrate interfaces. Defects in the crystalline structure of
 181 gold nanoparticles also have to be considered. Finally, it
 182 should also be pointed out that due to the large range of wave-
 183 vectors produced by confined plasmon excitation, depolariza-
 184 tion effects can be induced; i.e., vertical component of the
 185 near-field appears, making asymmetry discussion nontrivial.
 186 In conclusion, our polarization and spectroscopic studies
 187 demonstrate that second harmonic generation from

metallic nanoparticles strongly depends on their dipolar plas-
 188 mon resonance. Resonance enhancement of the second har-
 189 monic intensity has been observed while tuning the polariza-
 190 tion of the pump beam from parallel to perpendicular to the
 191 long axis of nanoparticles. We also observed a strong varia-
 192 tion in the wavelength dependence of the second harmonic
 193 generation intensity when the irradiation wavelength is tuned
 194 towards the extinction peak. This further highlights the influ-
 195 ence of the field enhancement from resonance plasmon exci-
 196 tation in the second harmonic generation process from met-
 197 tallic nanoparticles. 198

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