Terahertz emission from surface-immobilized gold nanospheres

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Received July 20, 2012; revised August 15, 2012; accepted August 19, 2012; posted August 20, 2012 (Doc. ID 172984); published September 24, 2012

Electromagnetic wave emission based on optical rectification at terahertz (THz) wavelengths was observed from surface-immobilized gold nanospheres (SIGNs) above a gold surface. Although the excitation wavelength is off-resonant with the localized surface plasmons, the THz emission field was observed to be approximately 4.8 times greater than that from a percolated gold thin film of 10 nm thickness. A theoretical calculation predicts that the light electric field is enhanced in the SIGN system, even at off-resonance wavelengths. The observed THz field amplitude was quadratic with the illumination light field, suggesting that the THz generation is due to a second-order nonlinear optical process. © 2012 Optical Society of America

Optical rectification (OR) is a second-order nonlinear optical (NLO) phenomenon that produces static dipoles by illumination with a high power laser pulse [1,2]. When ultrafast laser pulses are used, electromagnetic (EM) waves are radiated in the terahertz (THz) range because the laser pulses are rectified. A number of reports have appeared on THz generation based on OR. Kadlec et al. showed THz generation at gold and silver surfaces [3]. A metallic surface shows second-order NLO activity because of the lack of an inversion center near the surface. Later they reported OR-based THz generation in thick metal films (100–200 nm thick), and attributed the optical nonlinearity to nonlocal effects [4]. On the other hand, Ramakrishnan and Planken have reported THz emission from a thin percolated gold film of 10 nm thickness, having localized surface plasmon (LSP) hot spots [5]. Recently Ramakrishnan et al. observed THz emission from ordered NLO chromophores in a molecular monolayer at the surface plasmon resonance condition [6]. In these studies, the THz emission amplitude is quadratic in the excitation field, suggesting that the THz emission is based on the second-order NLO process.

On the contrary, Welsh et al. [7] and Polyushkin et al. [8] observed a non-quadratic dependence of the THz emission amplitude on the incident electric field. They attributed the THz emission from the metallic surface to multiphoton ionization and ponderomotive acceleration of electrons in the evanescent field produced by surface plasmons. This process may be called gindirect OR. These different observations suggest that different THz generation mechanisms are possible at gold surfaces.

In this letter, we report THz emission from surface-immobilized gold nanospheres (SIGNs) above a gold surface with a gap distance of less than 1 nm. The SIGN structure is schematically illustrated in Fig. 1(a). The gap between the SIGN and the surface is supported by an aminoundecanethiol (AUT) self-assembled monolayer (SAM). The SIGNs show an intense resonance of LSPs, as a result of the EM interaction between the SIGNs and the gold surface [9–13]. Second-order NLO optical phenomena, second-harmonic generation (SHG) [10,11], OR and the Pockels effect [12], have been observed from the SIGNs, since the SIGN structure is noncentrosymmetric. Here, THz emission was observed from the SIGNs and its amplitude was found to be quadratic in the excitation field amplitude. This indicates that the THz generation is due to a second-order NLO process.

The SIGN sample was prepared by the following procedure: As a substrate, a 100 nm thick gold film was vacuum-evaporated on a glass slide. The surface was covered with an AUT SAM, by dipping the gold substrate in an ethanol solution of AUT (Dojindo Co. Ltd., Japan) at a concentration of 1 mM for 3 h. After rinsing the substrate with ethanol, it was immersed in an aqueous colloidal gold solution containing spheres 80 nm in diameter, which was stirred for 24 h. The colloidal gold solution was purchased from Tanaka Kikinzoku K. K., Japan. The concentration was approximately 0.0068 wt%. The surface coverage of the SIGNs was evaluated to be 30.5% by scanning electron microscopy (SEM) [Fig. 1(b)]. As a reference sample, we used a thin percolated gold film of 10 nm average thickness on a glass slide, which is prepared by electron-beam evaporation of gold under high vacuum condition [5].

Reflection absorption spectroscopy was carried out using a MCPD-3000 spectrometer (Otsuka Electronics, Japan). Light from a halogen lamp was guided to the

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Fig. 1. (a) Schematic structure, (b) SEM image, and (c) reflection absorption spectra of SIGN.

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sample using a quartz bundle optical fiber (0.4 mm in diameter) and was incident on the sample at 45° angle of incidence, after choosing a polarization using a film polarizer. A lens was used to focus the incident beam on the sample surface. Light reflected at the sample was detected by the spectrometer using another bundle optical fiber (0.4 mm in diameter).

The THz emission was measured using the optical geometry, described in previous papers [5,6]. As the light source, a Ti:sapphire oscillator (Scientific XL, Femtolasers) was used, generating pulses of 50 fs duration, at a central wavelength of 800 nm at a repetition rate of 11 MHz. The average output power from the laser was 800 mW at maximum. The laser beam was split into two arms (80% for pump and 20% for probe). The pump beam was sent to an in-plane retro-reflector mounted on a loudspeaker oscillating at 50 Hz, and was focused on the sample surface at an angle of incidence of 45°. The THz radiation from the sample was collected in the reflection direction, using off-axis parabolic mirrors, and was focused on an electro-optic crystal [500 μm thick ZnTe (110)]. The synchronized, co-propagating sampling pulse was also focused on the crystal. The generated THz electric field elliptically polarizes the sampling beam to an extent proportional to the instantaneous THz electric field. The ellipticity of the sampling beam was measured by a differential detection setup consisting of a quarter wave plate, a Wollaston prism, and a differential detector.

Figure 1(c) shows p- and s-polarized reflection absorption spectra of the SIGN sample. Two absorption LSP bands were observed in the p-polarized spectrum: one at 520 nm (first peak) and the other at 660 nm (second peak). The first peak is attributed to LSPs in isolated gold nanoparticles without any EM interactions. The second peak originates from the SIGN-surface interaction, which causes the mirror effect by the surface second-order susceptibility of the SIGN surface, $\chi^{(2)}$, as shown in Fig. 4(b). The synchronized, co-propagating sampling pulse was also focused on the crystal. The generated THz electric field elliptically polarizes the sampling beam to an extent proportional to the instantaneous THz electric field. The ellipticity of the sampling beam was measured by a differential detection setup consisting of a quarter wave plate, a Wollaston prism, and a differential detector.

Figure 2 shows the measured p-polarized THz electric field generated by p-polarized illumination from the SIGN sample, together with that from the thin percolated gold film used as a reference. While both samples absorb about 46% of incident pump power at 800 nm, the maximum peak-to-peak THz field from the SIGN sample was approximately 4.8 times greater than that from the thin percolated gold film. Somewhat weaker THz generation by s-polarized excitation was also observed as shown in Fig. 3. The ratio between the peak to peak values of the emitted THz electric fields for p- and s-polarized excitation is $\sim$2.

Interestingly, there are hints of spectral reshaping in the THz pulses suggesting an additional spectral function involved in the THz generation process, which can depend on the geometries of the sample on the nanoscale. However, considering the poor signal to noise ratio in the present results, such a detailed study of the THz generation process is beyond the capability of the current study.

The THz emission comes from the enhancement of the light electric field. Here we show that greatly enhanced local electric fields are produced at the SIGN surface, even at the off-resonant wavelengths of 800 nm, according to the theoretical calculation based on the quasi-static approximation [9,10,13]. Figure 4(a) shows the calculated amplitude of the local electric field component normal to the SIGN surface, $E_{loc}$, as a function of the polar angle $\theta$ along the meridian at the azimuthal angle $\phi = 0°$ from the $x$ axis, when a $p$-polarized unit electric field, $E_0 = 1$, is applied at an angle of incidence of 45°. The gap distance of 0.74 nm for AUT SAM with a dielectric constant of 2.25 was used for the calculation [10]. The largest electric field of about 80 is produced at around $\theta = 0°$, which corresponds to the gap region between the SIGN and the substrate surface. This enhancement at an off-resonance wavelength is due to two reasons: the low-Q (quality factor) LSP resonance from the imaginary part of the dielectric constants of gold and the large absolute polarizability of the SIGN ascribed to the large dielectric constants of gold. With increasing $\theta$, the electric field decreases to zero at $\theta = 120°$, and then it increases to 5 at the top region of the SIGN, $\theta = 180°$. Although the large enhancement factor 80 is calculated in the gap region, the large amplitude does not fully contribute to the OR-based THz generation. This is because the electric field with similar amplitude is also produced on the substrate surface just below the SIGN, as shown in Fig. 4(b), in which local electric field on the surface is plotted along the $x$ axis. Both polarizations from OR cancel each other mostly, since the sign of the surface second-order susceptibility of the SIGN surface is opposite that of the substrate surface [11]. Hence, the largest contribution mainly comes from the local electric fields at the upper region of the SIGN.

We also calculated the amplitude of local electric field at the SIGN surface as a function of the polar angle $\theta$. Figure 3 shows the calculated amplitude of local electric field as a function of the polar angle $\theta$. The calculation is based on the theoretical calculation based on the quasi-static approximation [9,10,13]. Figure 4(a) shows the calculated amplitude of the local electric field component normal to the SIGN surface, $E_{loc}$, as a function of the polar angle $\theta$ along the meridian at the azimuthal angle $\phi = 0°$ from the $x$ axis, when a $p$-polarized unit electric field, $E_0 = 1$, is applied at an angle of incidence of 45°. The gap distance of 0.74 nm for AUT SAM with a dielectric constant of 2.25 was used for the calculation [10]. The largest electric field of about 80 is produced at around $\theta = 0°$, which corresponds to the gap region between the SIGN and the substrate surface. This enhancement at an off-resonance wavelength is due to two reasons: the low-Q (quality factor) LSP resonance from the imaginary part of the dielectric constants of gold and the large absolute polarizability of the SIGN ascribed to the large dielectric constants of gold. With increasing $\theta$, the electric field decreases to zero at $\theta = 120°$, and then it increases to 5 at the top region of the SIGN, $\theta = 180°$. Although the large enhancement factor 80 is calculated in the gap region, the large amplitude does not fully contribute to the OR-based THz generation. This is because the electric field with similar amplitude is also produced on the substrate surface just below the SIGN, as shown in Fig. 4(b), in which local electric field on the surface is plotted along the $x$ axis. Both polarizations from OR cancel each other mostly, since the sign of the surface second-order susceptibility of the SIGN surface is opposite that of the substrate surface [11]. Hence, the largest contribution mainly comes from the local electric fields at the upper region of the SIGN.
along the meridian at $\phi = 90^\circ$, when a $s$-polarized unit electric field is induced, at a 45° angle of incidence. A large electric field of $\sim 10$ is also produced in the gap region, as shown in Fig. 4(c). The electric field monotonically decreases with increasing $\theta$, and it becomes zero at the top $\theta = 180^\circ$. The light electric field is generated on the surface as shown in Fig. 4(d), in which the electric field at the substrate surface is plotted. Similarly to the $p$-polarization, the THz fields generated in the gap region are mostly canceled, and the enhanced electric field in the upper region of the SIGN is the cause of the THz generation.

Finally, we show the $p$-polarized THz emission field amplitude as a function of the $p$-polarized illumination intensity in Fig. 5. The linear relation is obtained up to the incident pump laser power of 400 mW. The linear relation indicates that the THz emission process is due to the OR effect of second-order NLO, as previously observed for the percolated gold film [5].

In summary, we observed THz emission from SIGNs above a gold surface. Although the excitation wavelength (800 nm) is off-resonant with the LSPs, the emission was observed to be approximately 4.8 times greater than that from a percolated gold thin film of 10 nm average thickness. We showed that the light electric field can be enhanced even at off-resonance wavelengths, in the SIGN system, by theoretical calculations based on the quasi-static approximation. The observed THz field amplitude was found to be quadratic in the excitation field, indicating that the THz generation is due to a second-order NLO process.

P. C. M. P. thanks the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO) and the Stichting voor Technische Wetenschappen (STW) for the financial support in the form of a Vici grant.

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