Enhanced optical second harmonic generation in hybrid polymer nanoassemblies based on coupled surface plasmon resonance of a gold nanoparticle array

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Enhanced optical second harmonic generation in hybrid polymer nanoassemblies based on coupled surface plasmon resonance of a gold nanoparticle array

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Effective utilization of coupled surface plasmon resonance from gold nanoparticles was demonstrated experimentally for optoelectronic applications based on second-order nonlinear optics. Hybrid polymer nanoassemblies were constructed by manipulating gold nanoparticle arrays with nonlinear optical active polymer nanosheets to investigate the second harmonic generation. The gold nanoparticle arrays were assembled on heterodeposited polymer nanosheets. The second harmonic light intensity was enhanced by a factor of 8. The observed enhancement was attributed to coupling of surface plasmons between two adjacent gold nanoparticles, thereby enhancing the surface electromagnetic field around the nanoparticles at the fundamental light wavelength (1064 nm). © 2006 American Institute of Physics. [DOI: 10.1063/1.2219086]

Localized surface plasmons have attracted much attention because of their fascinating features. Many researchers have specifically examined their enormous large molar extinction coefficient, along with the experimental and theoretical possibility of applying localized surface plasmons for chemical and biological sensors. Surface plasmon resonance appears at visible light wavelengths for silver and gold nanoparticles. Its peak positions strongly depend on the particle size, shape, surface chemistry, etc. The surface electromagnetic fields are confined to the metal nanoparticle surface. Functional molecules must be assembled in a tiny space for effective utilization of the evanescent waves as a light stimulation source.

The Langmuir-Blodgett (LB) technique is a promising tool for fabrication of well-defined and highly oriented nanoassemblies. Using these advantages, we recently demonstrated that cationic polymer nanosheets with 1.7-nm-thick monolayers act as good templates for metal nanoparticle ordering. Metal nanoparticles are immobilized on the polymer nanosheets through electrostatic interaction. They take a nanoparticle layer formation in which they are uniformly distributed. These results implied to us that hybrid nanoassemblies consisting of polymer nanosheets and a metal nanoparticle array are potentially useful for optoelectronic applications. In fact, extensive luminescence enhancement was achieved using ruthenium complex and silver nanoparticle hybridization systems. Furthermore, the LB technique provides well-defined molecular orientation. Ordered molecular orientation and dipole moment alignment can be achieved without electric poling treatment. Noncentrosymmetric dipole moment alignment, which is required for second harmonic generation (SHG), is realized by alternating the deposition of two kinds of oriented monolayers. This study demonstrates that localized surface plasmons enhance the second harmonic light of dye molecules. It is noteworthy that coupling of localized surface plasmons between two adjacent nanoparticles is extremely effective for enhancing the SH light intensity that is generated from nonlinear optical (NLO) active moieties.

We chose disperse red 1 as a NLO active moiety (DR1) and copolymerized with N-dodecyl acrylamide (DDA) through free radical copolymerization [poly(N-dodecylacrylamide-co-4’-[2-acryloyloxyethyl]ethylenoimino)-4-nitroazobenzene] (poly[DDA/DR1]). Homopolymer, poly(N-dodecyl acrylamide) (pDDA, Fig. 1) was used as an inert layer. Alternate LB film deposition was carried out with an automatically controlled LB trough (FSD-300W, USI System Co.). A glass substrate (normally 35 × 13 × 1 mm², S-0313, Matsunami) was rendered hydrophobic using octyltrichlorosilane (LS-2190, Shinetsu Chemical Co.). The surface was precoated with four-layer N pDDA nanosheets to avoid surface effects. We constructed heterostructured polymer nanosheets by transferring pDDA/DR1 (downstroke) and pDDA/Vpy (upstroke) monolayers alternately (Fig. 1). The surface was rendered hydrophobic using octyltrichlorosilane (LS-2190, Shinetsu Chemical Co.). The surface was precoated with four-layer N pDDA nanosheets to avoid surface effects. We constructed heterostructured polymer nanosheets by transferring pDDA/DR1 (downstroke) and pDDA/Vpy (upstroke) monolayers alternately (Fig. 1).

FIG. 1. (Color online) (Top) Chemical structure of pDDA/DR1, pDDA, and pDDA/Vpy. (Bottom) Schematic illustration of a hybrid nanoassembly structure.

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pDDA (upstroke) alternately at the surface pressure and temperature of 30.0 mN/m for pDDA, 15.0 mN/m for p(DDA/DR1), and 20.0 °C. The respective transfer ratios of the p(DDA/DR1) and pDDA were 0.85 and 1.0. Two-layer cationic polymer nanosheets, p(DDA/Vpy) (Fig. 1) at 35 mN/m and 15.0 °C, were deposited on the heterodeposited polymer nanosheets. The substrate was immersed in a gold nanoparticle aqueous solution.6

Optical second harmonic generation measurements were carried out using a Q-switched Nd:YAG (yttrium aluminum garnet) laser (1.1 mJ per pulse, 5 ns pulse width, λ = 1064 nm). Briefly, the sample was set on a rotation stage to monitor the frequency-doubled light as a function of the angle of incidence. The fundamental light beam was polarized in the plane of incidence (p light) and the p-light component of the SH light was monitored using a photomultiplier. Figure 2 shows the SH light interference pattern obtained from one-bilayer film of p(DDA/DR1) and pDDA coated on both sides of the glass substrates (Fig. 2, dashed line). Dependence of the SH light intensity with respect to the incident angle shows a well-contrasted fringe pattern resulting from interference between the emitted light produced by the front and back layers. Interestingly, the SH light intensity is enhanced drastically under gold nanoparticle arrays (Fig. 2, solid line). The clear SH light interference pattern also indicates that the gold nanoparticle arrays are immobilized uniformly on the heterostructured polymer nanosheets and thereby produce a nanoparticle layer, engendering no aggregate formation that would affect the light coherence and scattering.9

Figure 3(a) shows UV-vis absorption spectra of hybrid polymer nanoassemblies as a function of immersion time. The strong absorbance band at ca. 520 nm corresponds to the localized surface plasmon band that is attributable to dipole-type electric field oscillation from single gold nanoparticles. As the immersion time increased, the number of gold nanoparticles immobilized on the polymer ultrathin film surface increased. Nearer gold nanoparticles generate a coupled surface plasmon electromagnetic field, resulting in a redshift of the absorption band broadened to 1500 nm. Figure 3(b) shows the absorbance at 1064 nm and the SH light intensity of hybrid polymer nanoassemblies with different immersion times. Interestingly, no remarkable SH light intensity enhancement was observed below 8 h, and eightfold enhancement was achieved at 12 h immersion time. The change in SH light intensity is closely coincident with that in absorbance at 1064 nm. As the immersion time becomes greater than 6 h, the gold nanoparticles increase so that they interact electromagnetically with each other. Figure 4 shows an environmental scanning electron microscopy (ESEM) image of gold nanoparticle arrays after 12 h immersion. Some of the adjacent gold nanoparticle arrays are highlighted by oval (inset, Fig. 4). The electromagnetic field enhancement at 1064 nm is attributable to the dipolelike coupled surface.
plasmon mode generated between adjacent gold nanoparticles. This is a plausible reason for the SH light intensity enhancement. It is noteworthy that no considerable SH light intensity was obtained from gold nanoparticle arrays alone. These results strongly imply that gold nanoparticle ordering for creating coupled surface plasmon electromagnetic field and hybridization of NLO active molecules with gold nanoparticle arrays at the nanometer scale are important for SH light intensity enhancement based on surface plasmon resonance.

In conclusion, hybrid polymer nanoassemblies were prepared for second harmonic generation. The SHG active layer, pDDA/DR1 nanosheet was alternated with the inactive layer, pDDA nanosheet by alternate LB film deposition and coupled with a gold nanoparticle monolayer. Interestingly, gold nanoparticles yield widely various surface plasmon modes that occur not only at isolated gold nanoparticles but also among adjacent gold nanoparticles. The surface plasmon electromagnetic field generated from dipolelike oscillation among adjacent gold nanoparticles enhanced the SH light intensity from the pDDA/DR1 nanosheet. That electromagnetic resonance is slightly but markedly overlapped with the fundamental frequency (1064 nm), as confirmed using UV-vis absorption spectra. To our knowledge, this is the first example to use coupled surface plasmon resonance for SH light enhancement from dye molecules. It is worth mentioning that more than 12 h immersion in gold nanoparticle aqueous solution affects the film quality, decreasing the SH light intensity. In other words, 12 h immersion is the optimal time for our experimental condition. Furthermore, the effect of surface plasmons at 532 nm on the SH light intensity remains to be clarified. Detailed analyses are now in progress.

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1See, e.g., P. N. Prasad, Nanophotonics (Wiley, New Jersey, 2005), p. 129.