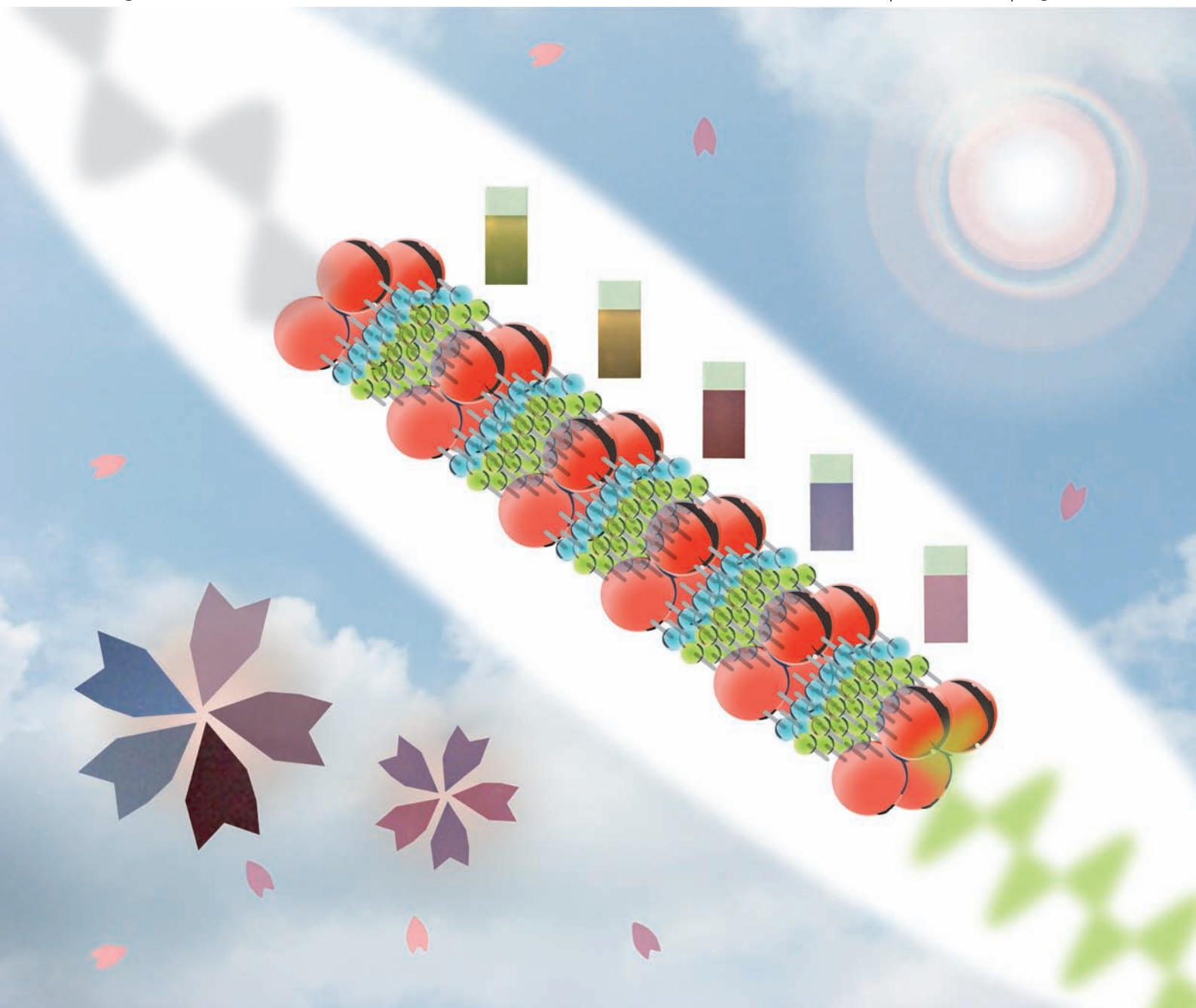


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Second harmonic generation from multilayered hybrid polymer nanoassemblies enhanced by coupled surface plasmon resonance

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We report enhanced second harmonic generation from nanostructured multilayers in combination with nonlinear optical polymer nanosheets and gold nanoparticles.

Hybrid nanomaterials, consisting of inorganic and organic compounds, offer great potential for use in various applications. Nanosized inorganic materials exhibit unique properties. In particular, noble metal nanoparticles of gold and silver have attracted much attention in the past decade.¹ One interesting feature is surface plasmon resonance.² The approach of combining surface plasmon resonance and functional molecules is expected to create fascinating optical properties. It is important to assemble nanoscale functional molecules around the metal nanoparticle for effective utilization of surface plasmon resonance.³ Numerous reports have described hybrid nanoarchitectures, comprising metal nanoparticles and functional molecules. However, most of them are limited to a two-dimensional field. Three-dimensionally-controlled nanomaterials are anticipated for wider use in hybrid nanomaterials.

Recently, we reported the effective utilization of surface plasmon resonance for optically-enhanced second harmonic generation (SHG) from nonlinear optical (NLO) polymer nanosheets.⁴ Coupled surface plasmon resonance, generated from two adjacent Au NPs in a Au–NP monolayer, locally enhanced fundamental light (incident light at 1064 nm), thereby achieving an eight-fold enhancement of the SH light (532 nm) over that of NLO polymer nanosheets. This Communication presents vastly enhanced SHG from multilayered hybrid polymer nanoassemblies. The multilayered hybrid polymer nanoassemblies show a clear linear relationship between the square root of the second harmonic (SH) light intensity and the number of assembly cycles, reflecting a well-defined hybrid nanostructure with highly oriented polymer nanosheets and uniformly distributed Au NPs in respective monolayers. This structure was confirmed using atomic force microscopy (AFM).

Hybrid polymer nanoassemblies were prepared as follows. We used the Langmuir–Blodgett (LB) technique for preparing hybrid polymer nanoassemblies.⁵ Poly(*N*-dodecylacrylamide) (pDDA) has a good ability to form stable LB films (polymer nanosheet).⁶ We chose disperse red 1 (DR1) as an SH active dye. The DR1 moieties were copolymerized with DDA

through free radical copolymerization (poly(*N*-dodecylacrylamide-*co*-4'-[2-(acryloyloxy)ethyl]ethylamino}-4-nitroazobenzene) (p(DDA/DR1))), $M_n = 7.5 \times 10^3$, $M_w/M_n = 1.78$, 28 mol% DR content (M_n and M_w are number-averaged and weight-averaged molecular weights, respectively). We fabricated two types of hybrid polymer nanoassemblies (Fig. 1). Firstly, two-layer cationic poly(*N*-dodecylacrylamide-*co*-4-vinylpyridine) (p(DDA/VPy)) nanosheets were deposited on a glass substrate. The substrate was immersed in a Au NP (Au NPs 30 nm diameter) aqueous solution for 12 h. The Au NPs were adsorbed uniformly on the p(DDA/VPy) nanosheets through electrostatic interactions and formed a monolayer.^{7†} Secondly, we constructed heterostructured NLO polymer nanosheets on Au NP arrays by transferring pDDA as an SH inert layer and p(DDA/DR1) as an SH active layer, alternately; this was designated as a single-layer structure. Furthermore, two-layer p(DDA/VPy) nanosheets were deposited on the single-layer structure, and again immersed in a Au NP aqueous solution; this was denoted as a sandwich structure. Next, SHG measurements were carried out using a Q-switched Nd:YAG laser (5 ns, 10 Hz, 1064 nm). The sample was set on a rotating stage to monitor the frequency-doubled light as a function of the angle of incidence (p-light); the p-light component of the SH light was detected using a photomultiplier.

Fig. 2 shows SH light fringe patterns as a function of the incident angle (p-light) from the two types of hybrid polymer nanoassembly. The black (dashed) line shows an SH fringe pattern from one-bilayer NLO polymer nanosheets for

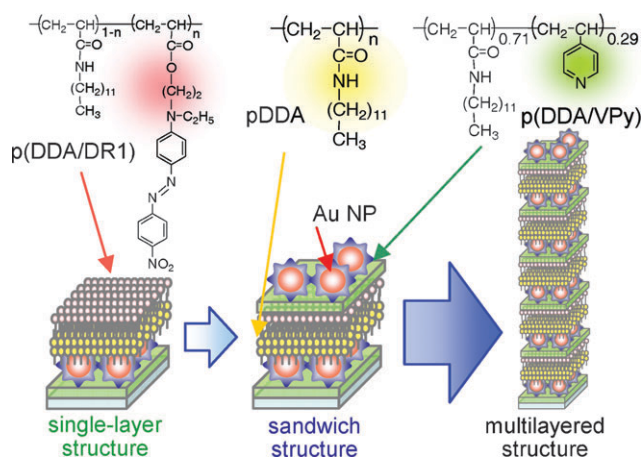


Fig. 1 Chemical structure and schematic illustration of hybrid polymer nanoassemblies using Au NPs (30 nm diameter).

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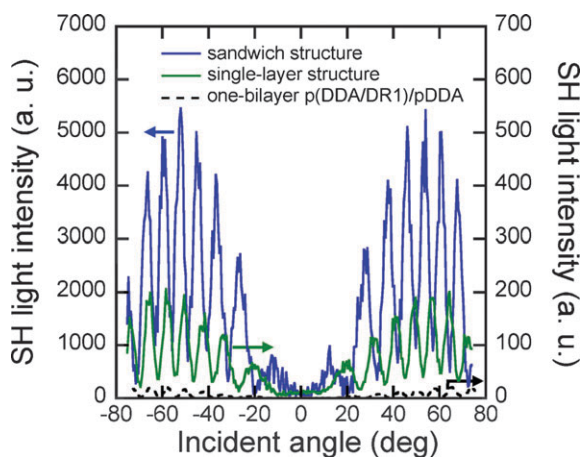


Fig. 2 SH light interference patterns as a function of the incident angle: one-bilayer p(DDA/DR1)/pDDA nanosheets without Au NPs (dashed line), single-layer structure (green line), and a sandwich structure (blue line).

comparison. These fringe patterns result from interference between the SH signal derived from the front and back layers. The clear fringe pattern indicates that Au NPs were immobilized uniformly in hybrid polymer nanoassemblies, and underwent no aggregate formation, which would affect light coherence and scattering. The Au NPs produced no observable SH signal in the absence of NLO polymer nanosheets. We achieved 8-fold and 288-fold SH light intensity enhancement, respectively, for the single-layer structure and the sandwich structure, in comparison with one-bilayer NLO polymer nanosheets. After a 12 h immersion time, adjacent Au NPs appeared, along with isolated Au NPs. These adjacent Au NPs could mutually interact electromagnetically and generate surface plasmon coupling.⁸ The surface plasmon coupling yields an electromagnetic field enhancement at 1064 nm and generates enhanced SH light intensity from the NLO polymer nanosheet at 532 nm. Interestingly, the SH light intensity of the sandwich structure was enhanced much more than that of the single-layer structure. Considering that the monolayer thicknesses are 1.4 nm for p(DDA/DR1) and 1.7 nm for pDDA, the distance between the bottom and top Au NP is approximately 8.2 nm in the sandwich structure. Consequently, interlayer surface plasmon coupling can occur in hybrid polymer nanoassemblies, as it does in intralayer surface plasmon coupling.

The LB technique using polymer nanosheets enables fabrication of controlled nanoassemblies, not only as 2-D products but also as 3-D products.⁹ We constructed multilayered hybrid polymer nanoassemblies by repeating the polymer nanosheet and Au NP assembly cycle. In this case, the immersion time was 6 h for each Au NP adsorption. In the one-layer Au NP extinction spectrum (Fig. 3a, dashed line), the band peak at 520 nm corresponds to the surface plasmon band, which is attributable to a dipole-type electric field oscillation from single Au NPs. The AFM image in Fig. 4a shows a Au-NP monolayer immobilized on p(DDA/VPy) nanosheets. After a 6 h immersion time, Au NPs were separated from each other, consequently generating no intralayer surface plasmon coupling. The extinction spectra of the multilayered hybrid poly-

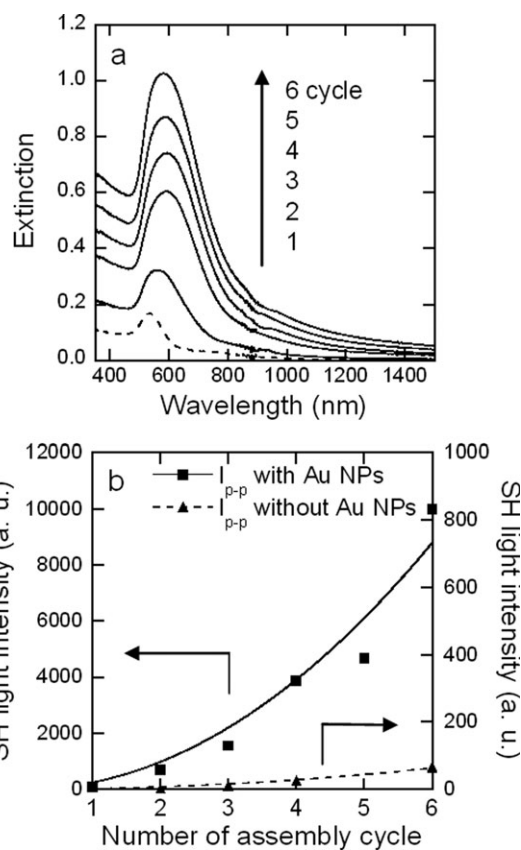


Fig. 3 (a) Extinction spectra of multilayered hybrid polymer nanoassemblies as a function of the number of assembly cycles, N . (b) SH light intensity (arbitrary unit) from hybrid polymer nanoassemblies with Au NPs using the p-polarized fundamental light (solid line), and p(DDA/DR1)/pDDA nanosheets without Au NPs using the p-polarized fundamental light (dashed line) as a function of the number of assembly cycles, N .

mer nanoassemblies as a function of the number of assembly cycles reflect the uniform Au NP adsorption in each layer (Fig. 3a). In a multilayered structure, the surface plasmon peak shifts towards a longer wavelength, and the extinction is enhanced. The surface plasmon resonance band broadened to approximately 1800 nm. This broadened band is attributable to the dipole-like interlayer surface plasmon coupling band.¹⁰

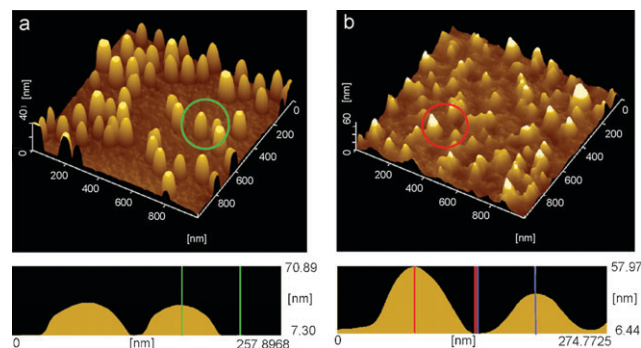


Fig. 4 AFM images of the two types of hybrid polymer nanoassemblies: (a) Au NP arrays on p(DDA/VPy) nanosheets, and (b) two-layer Au NPs in a sandwich structure. The immersion time was 6 h.

The optical density at the fundamental light (1064 nm) increases linearly with the number of assembly cycles, implying a well-defined multilayered structure. In theory, the SH light intensity from a thin film shows a quadratic increase with increasing film thickness (Fig. 3b, dashed line).¹¹ The SH light intensity, as a function of assembly cycle, shows a good quadratic dependence, even for hybrid polymer nanoassemblies (Fig. 3b, solid line). This result shows that hybrid polymer nanoassemblies maintain the NLO property, despite the great difference in size between the Au NPs and the nanosheet thickness. The quadratic dependence suggests that effective surface plasmon coupling occurs between interlayers, and that the DR orientation is maintained for each successive layer. Fig. 4b shows an AFM image of the two-assembly cycle of hybrid polymer nanoassemblies. The Au NPs in the second layer are stacked on top of those in the first layer, not embedded in them. No change in the root mean square (RMS) value was observed through respective cycles. After a 12 h immersion time, the quadratic dependence was not apparent. The surface coverage of the Au NP monolayers was determined to be 4.4% (6 h) and 25.7% (12 h). Qualitatively, intralayer and interlayer interaction of multiple Au NPs is possible with increasing amounts of Au NPs. The surface plasmon coupling with multiple Au NPs (more than two) will lower the maximum electromagnetic field enhancements.¹² In other words, interlayer surface plasmon coupling between two Au NPs is very effective for SHG enhancement in 3-D NLO active nanoarchitectures. We achieved a 150-fold SH light enhancement from a six-assembly cycle over that of six-bilayer NLO polymer nanosheets without Au NPs. Detailed analyses are now in progress.

In conclusion, we have constructed hybrid polymer nanoassemblies comprising of NLO polymer nanosheets and Au NPs based on the LB technique for SH generation. The SH light intensities of two types of hybrid polymer nanoassembly, a single-layer structure and a sandwich structure, were greatly enhanced over those of NLO polymer nanosheets without Au NPs. We achieved significant SH light enhancement from multilayered hybrid polymer nanoassemblies using surface plasmon coupling. The quadratic dependence of the SH light intensity on the deposition cycle reveals the uniform polymer nanosheets' deposition and Au NP adsorption, which indicates that hybrid polymer nanoassemblies are helpful to elucidate interactions between surface plasmon and dye molecules. They are anticipated for use in small, inexpensive and high efficiency optoelectronic devices.

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Notes and references

† Gold nanoparticles (Au NP) were synthesized using the sodium citrate reduction method. The Au NP diameter was confirmed as 30 nm using scanning electron microscopy. The glass substrate was rendered hydrophobic using octyltrichlorosilane (LS-2190; Shin-Etsu Chemical Co.). Two-layer cationic p(DDA/VPy) (29 mol% VPy content) polymer nanosheets were deposited on the glass substrate at 35 mN m⁻¹ and 15.0 °C, then immersed in a Au NP aqueous solution for 12 h. After immersion, the substrate was washed with distilled water and dried using nitrogen gas. In these processes, Au NPs were immobilized uniformly on the p(DDA/VPy) nanosheets through electrostatic interactions. Heterostructured NLO polymer nanosheets were constructed on a Au NP monolayer by transferring pDDA (upstroke) as an SH inert layer and p(DDA/DR1) (downstroke) as an SH active layer at a surface pressure and water temperature of 30 mN m⁻¹ and 20.0 °C for pDDA, and 15 mN m⁻¹ and 20.0 °C for p(DDA/DR1). This structure was termed a single-layer structure. Furthermore, two-layer p(DDA/VPy) nanosheets were deposited on a single-layer structure and then immersed in a Au NP aqueous solution for 12 h. This structure was designated as a sandwich structure. By repeating this assembly cycle, we easily constructed multilayered hybrid polymer nanoassemblies.

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