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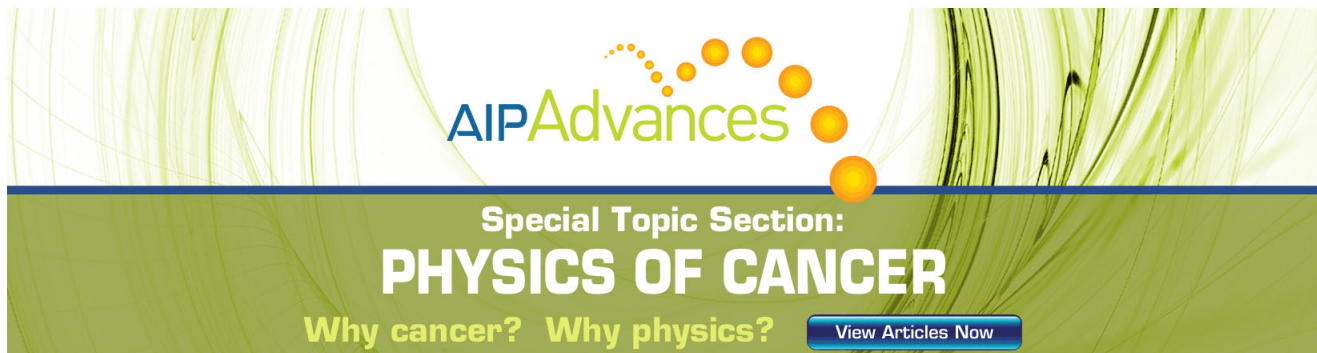
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Hyper-Raman scattering enhanced by anisotropic dimer plasmons on artificial nanostructures

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Silver nanodimers with a small gap of a few nanometers aligned on glass substrates were used to enhance hyper-Raman scattering of crystal violet dye molecules. When localized surface plasmon of the dimer array was resonantly excited along the interparticle axis, hyper-Raman intensity was significantly enhanced. Moreover, the spectral appearance was slightly different between the two excitation polarizations, suggesting a possibility of two resonance contributions at one-photon and two-photon energies. Since the plasmonic property of dimer arrays can be controlled by the dimer geometry, the dimer arrays are expected to be well-defined substrates for surface-enhanced hyper-Raman spectroscopy. © 2007 American Institute of Physics. [DOI: 10.1063/1.2786982]

The plasmonic properties of metallic nanostructures are attracting much attention from both fundamental and applied viewpoints.¹⁻⁷ When resonantly excited, localized surface plasmon can induce giant electromagnetic (EM) field enhancement, resulting in drastic enhancement of optical scattering cross section. For example, it has been reported that the enhancement factor of surface-enhanced Raman scattering (SERS) can be more than six orders of magnitude.¹⁻³ Such a huge effect has opened up a possibility of single molecule spectroscopy.⁴⁻⁶ Roughened metal substrates or metal colloid aggregates are known to exhibit huge enhancement. In these systems, however, so-called “hot” spots are found only incidentally because the enhancement factor strongly depends on their metallic nanostructures. Hence, exploration and fabrication of well-defined hot spots are currently two of the most important issues.

When two metallic nanoparticles, which nearly touch each other with a small gap of a few nanometers, are excited by polarized light parallel to the interparticle axis, the nanoparticle plasmons hybridize each other via interparticle dipole-dipole coupling, resulting in the appearance of enormous EM field around the gap.⁷⁻¹¹ Since the magnitude of EM enhancement and the resonance wavelength are controllable with the dimer geometry, metallic dimers are considered as a good candidate of well-defined hot spots. Indeed, we have already reported that the metallic nanodimer arrays, which were fabricated with an angle-resolved nanosphere lithography (AR-NSL) technique,¹² exhibited anisotropic and enormous enhancement of the SERS cross section.¹³

A nonlinear optical process would be much more sensitive to EM field enhancement because of the nonlinear dependence on excitation field.¹⁴ Hyper-Raman scattering (HRS), which is inelastic scattering in the second-order nonlinear optical process, is expected to be a useful spectroscopic technique for completing vibrational information; the

selection rule of HRS is rather similar to that of infrared (IR) absorption.¹⁵⁻¹⁷ However, HRS has extremely weak effect with scattering cross sections on the order of 10^{-65} cm⁴ s,¹⁴ and hence, enhancement of HRS signals is indispensable. In a similar manner of SERS, surface-enhanced hyper-Raman scattering (SEHRS) has been reported in metal colloid or roughened electrode systems.^{14,18-21} Then, fabrication of well-defined hot spots is awaited for further development of hyper-Raman spectroscopy.

Under these circumstances, this paper reports the enhancement of HRS by using the well-defined silver nanodimer arrays, which were fabricated with the AR-NSL technique. The uniaxially oriented dimers provide anisotropic plasmonic resonances depending on the excitation polarization: strongly hybridized dimer plasmons parallel to the axis and weakly interacting single-particle-like plasmons in the perpendicular direction.^{7-9,13} So, the focus is placed on anisotropic appearance of HRS in intensity and shape. Crystal violet, which is a trigonal conjugated cationic dye with large hyperpolarizability β ,²² was selected as the test molecule because HRS originates from hyperpolarizability modulations by nuclear vibrations of molecules.

The silver nanodimer array was fabricated onto a cover slip by the AR-NSL technique as described previously.¹³ Briefly, silver nanodots were initially formed by vapor deposition on the cover slip masked with a polystyrene nanosphere array and then second nanodots were formed near the first dots by angle-resolved deposition. A typical structure of the dimer arrays, measured by an atomic force microscope (AFM) (Nanoscope-IIIa, Digital Instruments), is shown in Fig. 1(a). As expected from the structure, the extinction of the array was anisotropic [Fig. 1(b)]. The characteristic plasmonic resonance along the interparticle axis was found to be around 800 nm. Since HRS was measured with 790 nm pulses in the present study, the polarized incidence parallel to the axis can excite the resonance accompanied with the enormously enhanced EM field around the gap. The excitation pulses with average power of 0.01 nJ pulse⁻¹ and bandwidth

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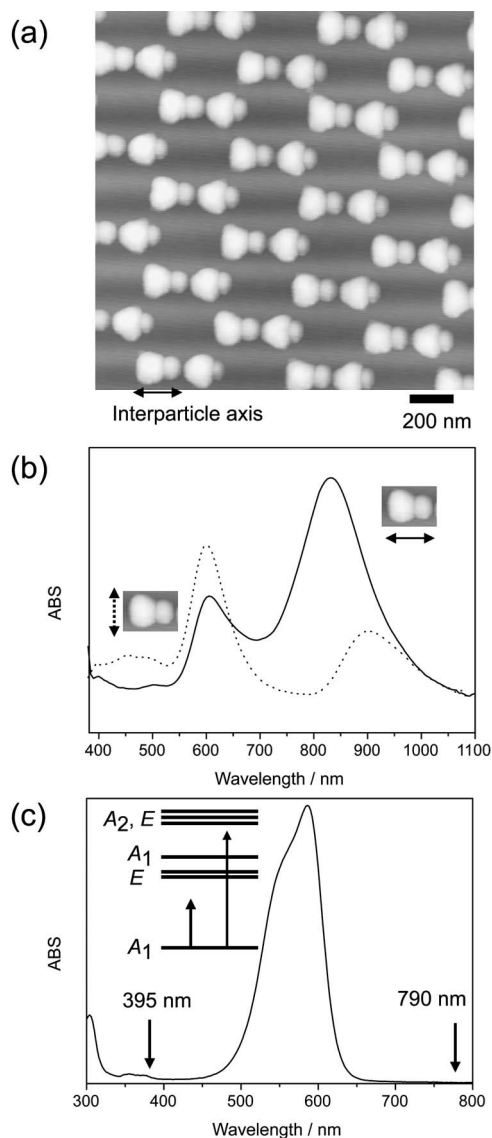


FIG. 1. (a) AFM image of the silver nanodimer array substrate fabricated with the AR-NSL technique. (b) Absorption spectra of the array parallel and perpendicular to the interparticle axis. (c) Absorption spectrum of crystal violet in methanol. Two arrows indicate the fundamental (790 nm) and doubled-fundamental (395 nm) incident energies in the SEHRS measurement. The inset diagram shows electronic ground and excited states of crystal violet.

of 14 cm^{-1} full width at half maximum were obtained from a mode-locked Ti:sapphire laser (Spectra-Physics, Tsunami) with a custom-made laser line filter (Optical Coatings Japan).²³ An inverted microscope with a $36\times$, 0.52 numerical aperture reflective objective was used to measure back-scattered hyper-Raman signal from 0.1 mM methanolic crystal violet solution dropped on the array. The anisotropic response of the array was measured by rotating the sample stage. In order to evaluate the degrees of contributions from one-photon and two-photon resonances, SERS spectra were also measured with two excitation wavelengths: 785 nm from a cw diode laser and 395 nm by second harmonic generation of the 790 nm Ti:sapphire radiation. Figure 1(c) shows absorption spectrum of crystal violet having two intense bands around 590 nm (S_0A_1 state $\rightarrow S_1E$ state) and 300 nm ($S_0 \rightarrow S_2E$ state) with a shoulder involving the first

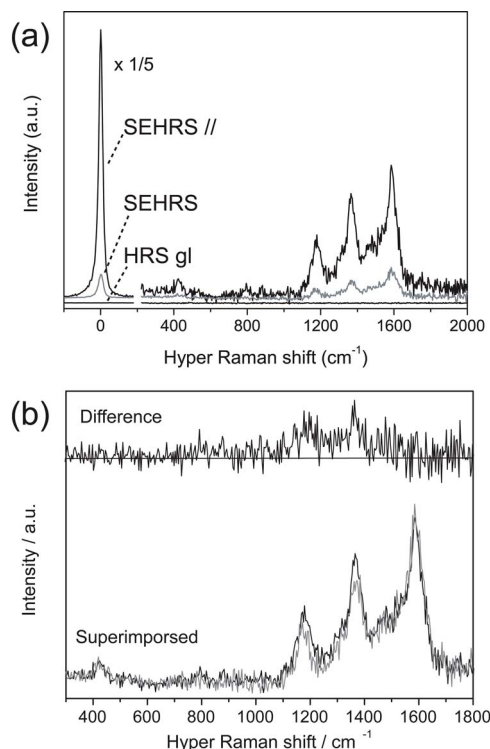


FIG. 2. (a) Three HRS spectra of crystal violet measured on glass (HRS_{gl}) and measured on the silver dimer array with parallel (SEHRS_{\parallel}) and perpendicular (SEHRS_{\perp}) excitations to the interparticle axis. Hyper-Rayleigh signal from the dimer array is scaled to one-fifth. (b) Normalized and superimposed spectra of the SEHRS_{\parallel} and SEHRS_{\perp} in (a) together with a difference spectrum showing that the two bands at 1177 and 1361 cm^{-1} were relatively weak in the case of the perpendicular excitation.

A_2 state as perturbed.^{24,25} The S_1 state consists of the delocalized orbitals involving a large contribution of the central carbon, whereas the S_2 state the localized benzenelike orbitals.²⁶ The 395 nm excitation may be in preresonance to the latter higher band.

Figure 2(a) shows three HRS spectra of crystal violet measured on glass (HRS_{gl}) and measured on the silver dimer array with parallel (SEHRS_{\parallel}) and perpendicular (SEHRS_{\perp}) excitations to the interparticle axis. The HRS cross section of free crystal violet ions was so small that the HRS_{gl} did not show any peak. On the dimer array, the cross section was substantially increased and the hyper-Raman peaks of crystal violet were clearly observed in both excitation polarizations. Especially, when excited parallel to the interparticle axis (SEHRS_{\parallel}), the enhancement was much more significant. Since the local plasmons parallel to the dimer are accompanied with so-called “gap mode,”^{9–11} this result strongly suggests that the gap worked as the hot spot in the HRS process. To our knowledge, this is the first demonstration of the well-defined plasmonic effect to the HRS enhancement. An estimate of the enhancement factor is difficult in this system because the hot spot size cannot be estimated accurately. However, even if the hot spot size were same as the dimer size, the enhancement factor of the dimer array would be three times larger than that of a common roughened surface. The observed three intense HRS peaks were assigned to be ν_9 CH in-plane bending at 1177 cm^{-1} , $\nu(\varphi\text{-N})$ stretching at 1361 cm^{-1} , and ν_8 ring stretching at 1584 cm^{-1} . (The largest

TABLE I. Principal vibrational modes of crystal violet together with frequencies and assignments (weak vibrational modes including all A_2 are omitted from the table).

Symmetry	Calc. (cm^{-1})	Raman (cm^{-1})	IR (cm^{-1}) ^a	HRS (cm^{-1})	Assignment ^b
A_1	1615	1617			8a
E	1588	1589	1584	1584	
E	1519	1518		1522	8b
A_1	1518				
A_1	1479	1475			19a
E	1477			Observed	
E	1449	1446	1442	Observed	19b
A_1	1369	1376			
E	1359		1362	1361	$\nu(\varphi\text{-N})$
E	1348				
E	1323			Observed	14
E	1284	1296	1300	Observed	
A_1	1209	1211			9a
E	1178	1178	1171	1177	9b
A_1	1171				

^aTaken from Ref. 23.^bClassified according to the normal modes of benzene (Ref. 23).

peak at 0 cm^{-1} was hyper-Rayleigh scattering from the silver dimers.) The assignments of the principal HRS modes are listed in Table I.²⁶ The vibrational modes of free crystal violet ion with propellerlike D_3 symmetry were calculated with B3LYP/6-311G**, which were classified into A_1 (Raman active), A_2 (IR active), and E (IR/Raman active) symmetries. The three HRS peaks belong to the E symmetry.

Figure 2(b) shows normalized and superimposed spectra of the SEHRS \parallel and SEHRS \perp in Fig. 2(a) together with a difference spectrum. Among the observed three HRS bands, there was an anisotropy seen in relative peak intensity; the ν_9 and $\nu(\varphi\text{-N})$ modes were less intense in the SEHRS \perp than those in the SEHRS \parallel when normalized with the ν_8 mode. A very similar appearance to the SEHRS \perp was also observed on silver monomer arrays having a plasmonic absorption band near the doubled-fundamental incidence. Hence, one can assume that the small difference is not due to the molecular orientation. It is known that the ν_9 and $\nu(\varphi\text{-N})$ modes can couple with the $S_0 \rightarrow S_1$ transition through the central carbon-phenyl displacement, and the benzenelike ν_8 mode is enhanced by the $S_0 \rightarrow S_2$ transition.^{26,27} Presumably, the observed difference is related to such contributions of different electronic excited states.

In order to investigate the anisotropic behavior of SEHRS on the dimer array, SERS excited by the fundamental and doubled-fundamental incident energies were compared with the SEHRS. Figure 3(a) shows the SERS spectrum excited by the 785 nm cw polarized radiation parallel to the interparticle axis together with theoretically calculated Raman-active modes (the spectrum excited perpendicularly was not obtained because of the weak signal intensity). The observed Raman peaks are in good agreement with the calculated result; the 1617 cm^{-1} peak having A_1 symmetry was much more intense than the theoretically estimated intensity of the free molecule, indicating that crystal violet is attached flat on the silver surface (that is, C_3 axis is normal to the surface).²⁸ In the SERS spectra excited by the 395 nm pulses, on the other hand, the ν_8 mode with E symmetry was

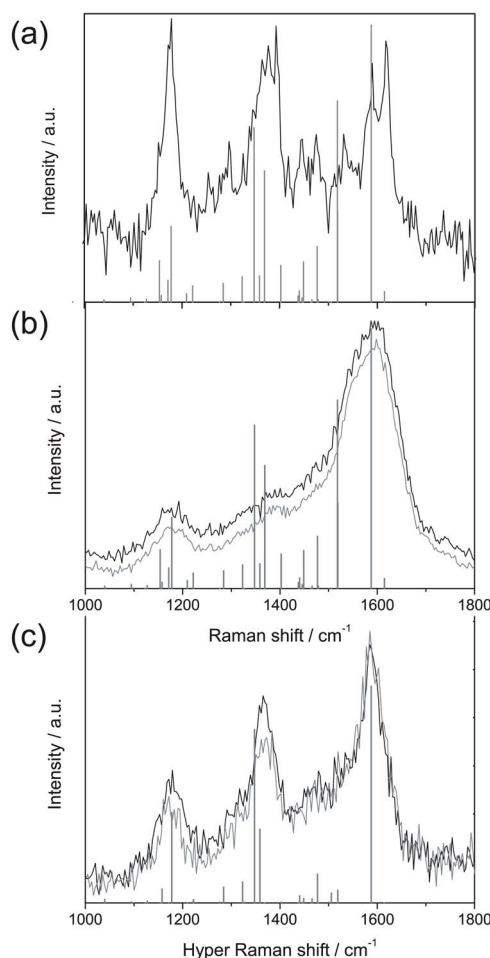


FIG. 3. SERS spectra of crystal violet onto the silver dimer arrays excited (a) by the 785 nm cw together with calculated Raman-active modes and (b) by the 395 nm pulses. (c) SEHRS spectrum excited by the 790 nm pulses together with calculated IR active modes. Black and gray colors represent parallel and perpendicular excitations, respectively.

most intense as shown in Fig. 3(b).²⁹ Note that there was no difference seen between the parallel and perpendicular excitations. This result suggests that the ν_8 mode was, as expected from Fig. 2(b), coupled with the S_2 state. Finally, Fig. 3(c) shows the SEHRS spectrum together with the theoretically calculated IR modes. The present SEHRS should be in preresonance to the S_2 state same as the 395 nm excited SERS because of the noncentrosymmetry of crystal violet. In the vibronic theory for resonant hyper-Raman scattering by Chung and Ziegler *et al.*,³⁰ Franck-Condon-type transition dominantly contributes to the hyperpolarizability β in a non-centrosymmetric system, meaning that resonant hyper-Raman spectrum and resonant Raman spectrum excited by the doubled photon energy gain intensity through the same electronic excited state. Therefore, it is expected that the ν_8 mode enhancement was closely related to the two-photon resonance with the S_2 state of crystal violet, while the other modes were mainly enhanced by the plasmonic resonances. If this is true, the anisotropy of the dimer plasmons can lead to the relative intensity change of these modes.

In summary, the silver nanodimer array exhibited significant enhancement of the HRS signal intensity when the hybridized dimer plasmons were resonantly excited. The degree of enhancement should be improved further by tuning the dimer geometry, e.g., the gap distance and the particle shape. Furthermore, the detailed comparison of the SEHRS spectra between the parallel and perpendicular excitations showed the difference of the relative intensity between the three intense HRS modes. As long as SEHRS is induced by conventional metal nanostructured systems with a variety of plasmonic resonances, such spectral information would disappear by averaging. The utilization of artificial nanostructures having well-defined plasmon resonances is the key to all of the information in SEHRS spectra obtained in the present study.

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