Ultrafast Dynamics of Surface-enhanced Raman Scattering due to Au Nanostructures

Ikufumi Katayama,[†] Sho Koga,[‡] Ken-ichi Shudo,[‡] Jun Takeda,^{*,‡} Toru Shimada,[¶]
Atsushi Kubo,[§] Shun-ichi Hishita,^{||} Daisuke Fujita,[⊥] and Masahiro Kitajima^{*,#}

*Interdisciplinary Research Center, Yokohama National University, Yokohama, Japan, Graduate
School of Engineering, Yokohama National University, Yokohama, Japan, Fritz-Haber-Institut
der Max-Planck-Gesellschaft, Berlin, Germany, Institute of Physics, University of Tsukuba,
Tsukuba, Japan, Sensor Materials Center, National Institute for Materials Science, Tsukuba,
Japan, Advanced Nano-Characterization Center, National Institute for Materials Science,
Tsukuba, Japan, and Department of Applied Physics, National Defense Academy, Yokosuka,
Japan*

E-mail: jun@ynu.ac.jp; kitaji@nda.ac.jp

*To whom correspondence should be addressed

[†]IRC YNU

[‡]YNU

[¶]FHI

[§]University of Tsukuba

^{||}NIMS

[⊥]NIMS

[#]NDA

Abstract

Ultrafast dynamics of surface-enhanced Raman scattering (SERS) was investigated at cleaved graphite surfaces bearing deposited gold (Au) nanostructures (~ 10 nm in diameter) by using sensitive pump-probe reflectivity spectroscopy with ultrashort (7.5 fs) laser pulses. We observed enhancement of phonon amplitudes (C=C stretching modes) in the femtosecond time domain, considered to be due to the enhanced electromagnetic (EM) field around the Au nanostructures. Finite-difference time-domain (FDTD) calculations confirmed the EM enhancement. The enhancement causes drastic increase of coherent D-mode (40 THz) phonon amplitude and nanostructure-dependent changes in the amplitude and dephasing time of coherent G-mode (47 THz) phonons. This methodology should be suitable to study the basic mechanism of SERS and may also find application in nanofabrication.

Surface-enhanced Raman scattering (SERS) is one of the most intriguing effects induced by gold, silver and other metal nanoparticles, enabling ultrasensitive measurements of molecular vibrations even at the level of a single molecule,^{1,2} and having potential applications for development of sensitive bio- and nanochemical sensors.³⁻⁵ It is currently believed that local confinement and enhancement of the electromagnetic (EM) field due to surface plasmon resonance plays an important role in the enhancement of Raman-scattering cross section.⁶⁻⁹ Several authors suggest that coherent interaction between plasmons and molecules is crucial in the initial processes of the surface Raman enhancement.^{10,11} However, time-resolution in most SERS experiments is of the order of seconds, because continuous-wave (CW) lasers are generally used in Raman spectroscopy.^{2,12,13} Since the coherent interaction between plasmons and molecules occurs at a femtosecond timescale, ultrafast measurement of SERS dynamics is indispensable for studying the initial processes of the enhancement.

In the field of condensed matter physics, coherent-phonon experiments have been extensively conducted with ultrashort-pulse lasers.¹⁴⁻¹⁷ When the pulse duration of the laser is shorter than the phonon frequencies of Raman active modes in a material, the photo-excitation generates the coherent phonons, which induce macroscopic changes in the optical properties. Thus, impulsive

excitation of phonons enables us to study the dynamics of relaxation and coherent interaction of phonons with excited carriers, defects, and plasmons. It also paves the way for control of material properties through large atomic displacements induced by the strong EM field of the lasers.^{16,18,19} Coherent phonon spectroscopy, therefore, offers us the potential to observe novel aspects of SERS dynamics. Although it is of fundamental importance to understand the mechanism of SERS, the femtosecond dynamics of SERS studied by using ultrashort-pulse lasers has not been reported so far.

In carbon materials, SERS induced by metal nanostructures has been demonstrated in carbon nanotubes, ion-implanted graphite, and other types of defect-containing graphite.^{20–23} Recently, graphene itself was also reported to exhibit a SERS-like effect.²⁴ In usual SERS experiments, platinum or silver was deposited on the surfaces, and strong enhancement of the Raman signal was observed, depending on morphology of the metal surfaces. It is known that Au deposition surface forms nanostructures (such as hemispherical domes) near defects or edges of graphene sheets,^{25,26} which should be an effective platform for SERS. In addition, dynamical studies of surface phonons in graphite are of great interest in research on carbon-based materials such as graphene and carbon nanotubes because of the strong electron-phonon coupling due to the Kohn anomaly.^{19,27–30}

In this paper, we demonstrate for the first time that coherent atomic motions near a graphite surface can be driven to enhanced amplitude due to strong EM-field localization by metal nanostructures. We observed amplitude modulations of time-resolved reflectivity, which are associated with enhancement of coherent C=C stretching motions due to surface-localized EM field at Au-deposited graphite surfaces. Here, the surface defects preexisting on the graphite surface play the same role as the SERS-active molecules in previous SERS studies. Our results demonstrate that coherent SERS spectroscopy is indeed possible, and is a potentially powerful tool to investigate the dynamics of the interactions between metal nanostructures and lattice/molecular vibrations on surfaces.

We used highly-oriented pyrolytic graphite (HOPG) as the substrate. The cleaved surface has step edges, point defects and lattice imperfections due to fragments of graphene sheets generated

during cleavage. Figure 1 shows an image of a flat part of the graphite surfaces taken with a scanning tunneling microscope (STM), where a dislocation is indicated by red lines. We deposited Au on the cleaved graphite surfaces using the plasma sputtering deposition method. Figures 2(a) and 2(b) are surface images of the samples after the Au deposition. Hemispherical Au nanostructures ranging from several to 20 nm in diameter and a few nm in height are formed on the surface. The number of hemispheres increases with increasing deposition time and some of them coalesce.

Coherent phonons were excited with a 7.5-fs Ti-sapphire oscillator at 80 MHz repetition rate, 800 nm wavelength and 400 mW average power. The laser beam was divided into two parts; one was used as a pump beam for generating coherent phonons and the other as a probe beam for detecting vibrational coherence. The angle of incidence was about 35° for the pump beam and 25° for the probe beam. An optical shaker with the delay-scanning range of 15 ps was set in the optical path of the pump pulses and scanned at 20 Hz. Reflection of the probe pulses from the sample was analyzed with both isotropic and anisotropic (electrooptic: EO) sampling methods.^{27,31} In the isotropic sampling, the probe polarization was set parallel to the pump polarization, and the reflected probe light was detected with a photodiode. In the EO sampling, the probe polarization was tilted at 45° to the polarization of the pump pulse, and the difference between parallel ($R_{//}$) and perpendicular ($R_{\perp}$) components of the probe was detected with a balanced pair of photodiodes. The output signal was amplified with a current amplifier and collected with a computer through an analog-to-digital converter. All measurements were performed at room temperature.

Figures 3(a) and 3(b) show the transient reflectivity changes (ΔR) in the HOPG samples with and without Au deposition. Average thickness of Au deposited on the graphite surface was 1 nm. A strong electronic response arises near the time origin and diminishes within a few picoseconds. As shown in the inset of Figs. 3(a) and 3(b), coherent optical phonon oscillation with a period of 740 fs is clearly observed, which corresponds to the E_{2g1} interlayer shear oscillation in graphite (1.3 THz , 43 cm^{-1}).^{19,32,33}

Near the time origin, there are coherent phonons with much higher frequency. Figures 3(c) and 3(e) show high-frequency coherent phonons observed with isotropic and anisotropic samplings.

They were obtained by subtracting the low frequency mode and the electronic response with filtering and data-fitting in the frequency domain. The observed oscillation with a period of 21 fs is well-known in graphite and carbon-based materials as the E_{2g2} C=C stretching mode (G mode) at 47 THz (1583 cm^{-1}). Importantly, amplitude modulation with a period of 0.13 ps appears in the Au-deposited samples, as shown in Figs. 3(c) and 3(e); this is considered to reflect surface EM-field enhancement due to Au nanostructures, as discussed later.

Fourier spectra of the high-frequency components are shown in Figs. 3(d) and 3(f). A clear peak at 47 THz (G mode) is observed in samples with and without Au deposition. These spectra are consistent with the corresponding continuous-wave Raman measurements. The peak at 40 THz (1334 cm^{-1}) is strong in Au-deposited sample, while it is not observed in the absence of Au deposition. The peak corresponds to the disorder-induced mode (D-mode), which causes the amplitude modulations observed in Figs. 3(c) and 3(e). Note that these experiments were performed below the linearity threshold (below 0.3 mJ/cm^2) of the power dependence shown in the inset of Fig.3(d).

In coherent phonon measurement, the change in reflectivity R is proportional to the amplitude of coherent-phonon displacement Q as follows¹⁵

$$\frac{\Delta R}{R} = \frac{\partial R}{\partial \chi} \frac{\partial \chi}{\partial Q} Q. \quad (1)$$

Here, χ is the electric susceptibility, and $\frac{\partial \chi}{\partial Q}$ is the Raman tensor. The induced displacement Q of the collective atomic motions can also be seen in the time-resolved X-ray diffraction as changes in the diffraction efficiencies due to changes of the unit cell.¹⁷ The observed $\Delta R/R$ in Fig. 3 indicates that displacement Q of the D-mode is strongly enhanced at the graphite surface bearing Au nanostructures.

The coherent phonon signals shown in Fig. 3(c) and 3(e) can be well fitted to the summation of two damping oscillations as follows;

$$\frac{\Delta R}{R} = A_G \exp(-t/\tau_G) \sin(\omega_G t + \phi_G) + A_D \exp(-t/\tau_D) \sin(\omega_D t + \phi_D). \quad (2)$$

Here, A , ω , ϕ and τ are the amplitude, angular frequency, initial phase ($t = 0$) and dephasing time, respectively. The subscripts (G or D) indicate the G- and D modes of graphite. We performed fitting to obtain these parameters.

Hereinafter, we focus on the origin of the enhancement of D-mode coherent phonon in the Au-deposited samples. The D-mode is often observed in Raman spectra of defect-containing graphite, carbon nanotubes and graphenes.^{30,34–39} Very recently, this mode has also been observed in time-domain spectroscopy of carbon nanotubes^{27,40} and Ar⁺-ion implanted graphite with implantation doses above 10^{12} ions/cm² at 30 keV.⁴¹ The origin of the D-mode can be understood in the framework of doubly-resonant Raman scattering due to a non-zone-center ($q \neq 0$) phonon mode.^{42–44} In this model, the D-mode is generated by the second-order Raman scattering process with elastic electron scattering due to defects and inelastic scattering due to phonons. Therefore, the origin of the D-mode enhancement is related to efficient enhancement of the EM field at defect sites due to the Au nanostructures. Indeed, no coherent D-mode phonon is observed in HOPG without Au deposition, despite the existence of defects such as step edges, point defects and dislocations at the cleaved HOPG surface (Fig. 1). It should be noted that Au nanostructures on graphite are preferentially formed around defects sites,^{25,26} leading to the selective enhancement of the D-mode. Also note that because the kinetic energy of ions in sputtering deposition (~ 0.03 eV) is much lower than the energy required for defect formation (~ 30 eV),^{45,46} the Au deposition itself could not directly generate defects relevant to the D-mode.

In order to examine the enhancement of the EM field near the Au nanostructures on graphite, we used the finite-difference time-domain (FDTD) method⁴⁷ to calculate the electric-field distribution around hemispherical Au nanostructures on a graphite surface. The nanostructures shown in Fig. 2 (hemispheres on graphite) are different from the structures normally employed in localized EM field calculations (spheres in a dielectric).^{48–52} For simplicity, we simulated EM-field distribution for an Au dimer on a graphite substrate, as in Fig. 4, because dimer typically shows a strong SERS effect in molecular systems.^{1,4} In this calculation, the size of the Au structures (10 nm in diameter) was set comparable to that observed in STM images (Fig. 2). The incident electric field

was assumed to be a Gaussian pulse with the central wavelength and pulse duration of 800 nm and 10 fs, respectively. The spectrum of the incident field covers a very broad wavelength range from 630 nm to 1000 nm. We used Drude dispersions for refractive indices of both graphite and gold, whose parameters set to reproduce the reported dispersions near 800 nm.^{53–55}

Figure 4(a) shows the calculated spatial distribution of electric-field amplitude at an air/graphite interface in the presence of Au hemispheres. The electric field near the graphite surface is strongly enhanced around Au, and the electric field near the edges of the Au nanostructures at the surface becomes much stronger than that in the bulk part. This can be regarded as representing confinement of the EM field on a nanometer scale. The characteristic length-scale of this enhancement was around 1 nm in the calculation, which is considerably smaller than the penetration depth of the laser in bare graphite (40 nm). Since coherent phonon displacement Q is proportional to the square of the electric field,^{15,56} it should be strongly enhanced near the edges of the Au nanostructures, as shown schematically in Fig. 4(b). As Au nanostructures grow preferentially around defect sites,^{25,26} SERS of graphite becomes very sensitive to surface defects. In the case of D-mode, the elastic electron scattering required for the double resonance^{42,43} might also be enhanced by this nanoscale electric-field distribution.

Figures 5(a) and 5(b) show the dependences of the coherent phonon amplitudes A_G and A_D in Eq. (2) on the average thickness. The thickness was estimated from the amount of Au deposition, assuming that the same amount of Au is homogeneously deposited on the graphite surface. Note that peak frequencies of E_{2g1} , G- and D- modes were independent of the average thickness. The amplitude of the D-mode increases rapidly up to 0.3 nm with an initial slope of $1.5 \pm 0.5 \times 10^{-5}$ /nm as indicated by the black solid line in Fig. 5(b), and then approaches saturation with further increase of Au thickness. Above 0.3 nm the G-mode amplitude decreases with increasing Au thickness, whereas the D-mode does not show any decrease below the thickness of 10 nm. This difference indicates that the D-mode and G-mode signals originate from different regions of graphite: one is from the surface and the other is from the bulk, as suggested from the FDTD calculation. The thickness dependence can be understood as follows; in the case of thickness less than 0.3

nm, many Au nanostructures such as monomers, dimers and trimers are formed separately on the graphite surface, as shown in Fig. 2(a). They enhance the local EM field to increase the D-mode amplitude. At medium Au thickness around 5 nm, coalescence of Au hemispheres starts to occur. However, because the sizes of the nanostructures are still in the range of several nanometers (see the inset in Fig. 2(b)), the electric field near the surface is still enhanced. When the sufficient Au is deposited to form a flat layer on the graphite surface (>10 nm), the D-mode intensity starts to decrease as a function of the thickness (not shown).

The thickness dependence of the G-mode is different from that of the D-mode, mainly because the G-mode has a very strong bulk signal. Average thickness dependence of the bulk signal can be calculated with the multiple reflection model by considering the absorption of pump and probe beams by a flat Au layer.^{54,55,57} The result (green solid line in Fig. 5(a)) reproduces quite well the tendency for thickness dependence of the G-mode.

Even in data taken at the same average thickness, considerable variations are observed in both A_D and A_G (Figs. 5(a) and 5(b)), possibly due to inhomogeneous distribution of Au nanostructures on the surface. Figure 5(c) shows that A_G and A_D are highly correlated at various positions of a sample with the average thickness of 0.4 nm. Similar correlations were seen at other average thicknesses. Indeed, the ratio of D-mode and G-mode amplitudes (A_D/A_G) shows less variation, as can be seen in Fig. 5(d). The correlation of amplitudes A_D and A_G suggests that coherent G-mode phonons have a component that is generated by the Au nanostructures

The key advantage of coherent phonon spectroscopy compared with CW Raman measurements is that it can provide dynamical information about the coherent lattice motions, such as displacement, dephasing time and time-dependent frequency shift (phonon chirping) in the time domain. Upon pulse laser irradiation of Au nanostructures, the coherent polarization of the collective motion of electrons (surface plasmons) in the nanostructures produces a localized electromagnetic field, which strongly and coherently couples with the atomic displacement of the phonons in the femtosecond timescale. Finally, the coherent oscillations are attenuated by dephasing while interacting with the excited electrons. Therefore, the temporal traces of coherent phonons during the

generation and decay processes directly reflect the electron-phonon interaction.

First, to clarify the characteristics of coherent phonon spectroscopy, we attempted to estimate the order of magnitude of the phonon displacement from the optical reflectivity change. Because Bi (a semimetal similar to graphite) is the only substance for which the proportionality constant between Q and reflectivity change is experimentally known, we used this value for the estimation. The displacement for the coherent vibration is $Q = 0.02$ nm at about 6 mJ/cm^2 (from time-resolved X-ray diffraction),¹⁷ and the transient optical reflectivity change ($\Delta R/R$) under similar experimental conditions is 0.012.^{17,18,58} The observed $\Delta R/R$ in our experiments was 5×10^{-6} , as shown in Fig. 3, leading to an estimated displacement of ~ 8 fm. Because the characteristic depth (1 nm) at which the EM field is enhanced (Fig. 4) is 40 times smaller than the absorption length of graphite (40 nm), we obtain the displacement at the top surface as ~ 320 fm. Such a strong enhancement of the displacement for D-mode appears as modulations in the reflectivity change. Quantitative estimation of the induced displacement is of great significance in examining the potential application of the SERS for coherent control of molecules and nanomaterials.

Figure 6(a) shows the observed dephasing times of G-mode and D-mode as a function of the Au thickness. Figure 6(a) indicates that the dephasing time of the D-mode shows slight increase with average thickness. Because the dephasing times of both modes decrease with higher defect density (the dephasing rates increase) due to defect scattering,⁵⁹ the observed dependence of the D-mode dephasing time suggests that the density of defects is not increased with Au deposition. Therefore, the D-mode signal for the Au-deposited sample presumably originates from the defects existing on the cleaved surface prior to Au deposition. The increase in the dephasing time might originate from the change in defect conformation due to the increased Au deposition. On the other hand, the dephasing time of the G-mode decreases until 0.3 nm, and then decreases with a slower slope as a function of the Au thickness. Because the dephasing time of the G-mode at the surface is shorter than that in the bulk due to the existence of surface defects,⁵⁹ the thickness dependence can be understood in terms of the increasing ratio of the surface contribution to the bulk G-mode signal. The formation of Au nanostructures and the slow decrease of the bulk G-mode signal above 0.3

nm shorten the dephasing time. Therefore, the enhanced local EM field near the Au nanostructures contributes not only to the D-mode, but also to the G-mode. It is worth noting that the obtained dephasing times are slightly shorter than those estimated from the spectral width of continuous-wave Raman spectra, possibly because of the higher sensitivity to the dephasing.¹⁶

Experimental information on phonon chirping can be obtained from the time-resolved coherent vibrations. Figure 6(b) shows the results for G- and D-modes analyzed with the time-windowed Fourier transform of the transient reflectivity response.¹⁹ The G-mode appears at higher frequency at the time origin and then gradually downshifts to the CW Raman frequency. On the contrary, the shift of D-mode is much larger than that of G-mode. At $t = 0$, it appears at lower frequency than the CW Raman frequency, showing a positive chirp. The D-mode chirp behaviors are also observed in graphene layers, implying that the coherent phonons originate from the topmost graphene layers of graphite.⁶⁰ In graphene, the chirping is attributed to the bond-softening effect owing to excited carriers, or the dispersive nature of the D-mode.⁶⁰

In addition, coherent phonon measurement has high sensitivity to low-frequency modes. A strong reduction of the phonon amplitude for the E_{2g1} mode (interlayer shear oscillation of graphene sheets, dephasing time ~ 6 ps) was observed with increasing Au thickness, as shown in Figs. 3(a) and 3(b), and this is in interesting contrast to the amplitude enhancement of the G- and D-modes; this behavior suggests that localized enhancement of the EM field at nanometer scale may not effectively excite the E_{2g1} mode. Further theoretical consideration is required to understand the mechanism.

In summary, we have demonstrated amplitude enhancement of coherent phonons due to the local EM field around Au nanostructures for the first time. FDTD calculations indicate that hemispherical Au nanostructures with the average size of 10 nm formed on the graphite surface confine the local EM field at nanometer scale (~ 1 nm), resulting in enhancement of the coherent lattice motions in the vicinity of the surface. The experimental results show that the amplitude of D-mode coherent phonons is strongly enhanced in the presence of Au nanostructures. The different dependences of the G- and D-mode amplitudes on the average Au thickness indicate that the G-mode

coherent phonons have an increasing contribution of the enhanced surface component. The coherent observation of enhanced phonons enables us to obtain dynamical information about the lattice motions due to the Au nanostructures in the time domain. Our results indicate that coherent phonon measurement on surfaces bearing metal nanostructures using an ultrashort pulse laser is a powerful method for investigating the dynamical properties of nanomaterials and coherent interactions between surface phonons (or adsorbed molecules) and plasmons.

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Figure 1: Surface image of cleaved HOPG measured with a scanning tunneling microscope. The lines are added to indicate the atomic arrangements and dislocations.

Figure 2: HOPG surface with Au deposition of 0.1 nm at different spatial resolutions ((a) and (b)). The inset of (b) is a cross section of a nanoparticle on graphite, showing the steps at the surface of the nanoparticle.

Figure 3: Transient reflectivity changes of HOPG with and without (w/o) Au deposition (1 nm) measured with (a) isotropic and (b) anisotropic (EO) samplings. The observed low-frequency oscillation is also shown in both figures after subtraction of electronic response. (c) Extracted high-frequency coherent phonons from the data shown in (a) with isotropic sampling. (d) The Fourier transformation of (c). (e) The high-frequency coherent phonons observed in EO sampling. (f) The Fourier transformation of (e). The inset of (d) shows the pump power dependence of the coherent phonon amplitudes in HOPG with Au deposition.

Figure 4: (a) Spatial distribution of the electric field amplitude calculated with the FDTD method. The optical pulse with the pulse duration of 10 fs is applied to the Au nanostructures on the graphite substrate. The polarization of the incident electric field is set parallel to the dimer axis. Colors indicate the absolute value of the electric field amplitude at each point. (b) A schematic illustration of our experiment and the amplitude enhancement of surface phonons in graphite due to the Au nanostructures.

Figure 5: Thickness dependences of the (a) G-mode and (b) D-mode amplitudes. The solid line in (a) is the calculated thickness dependence of the bulk component due to the transmittance of the Au thin layer. The solid line in (b) is added simply as a guide to the eye. (c) The correlation between D-mode and G-mode amplitudes at the deposited Au thickness at 4 nm. (d) Thickness dependence of the ratio of the amplitudes of D-mode and G-mode coherent phonons. Note that the horizontal axes of (a), (b) and (d) consist of linear and logarithmic scales in order to show the data on graphite with various Au thicknesses including 0 nm. The thickness is only an average, and does not indicate the formation of a flat Au layer having the indicated thickness. Solid lines in (b)-(d) are included simply as a guide to the eye.

Figure 6: (a) Dephasing times of G-mode and D-mode. Note that the horizontal axis consists of linear and logarithmic scales in order to show the data on graphite with various Au thicknesses including 0 nm. Solid and dashed lines are shown simply to guide the eye. (b) Time dependence of the G-mode and D-mode resonant frequency. Green circles refer to graphite without Au deposition and blue triangles to graphite with Au deposition (1 nm).