Research article

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Graphene-coupled nanowire hybrid plasmonic gap mode–driven catalytic reaction revealed by surface-enhanced Raman scattering

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Abstract: The single-layer graphene (SLG)-coupled nanowire (NW) hybrid plasmonic gap mode (PGM)-driven molecular catalytic reaction was investigated experimentally and theoretically. First, an SLG-coupled NW was constructed, then the surface-enhanced Raman scattering (SERS) effect of graphene in the hybrid plasmonic gap was studied via the normal and oblique incidence of excitation light. The SERS peaks of the D and G of graphene are more intensely enhanced by oblique incidence than by normal incidence. Furthermore, the catalytic reaction of the dimerization of the 4-nitrobenzenethiol molecule to *p,p'*-dimercaptoazobenzene molecule driven by PGM was carried out by SERS. It was demonstrated that the efficiency of the PGM-driven catalytic reaction is much higher for oblique incidence than that for normal incidence. The mechanism of the PGM-driven catalytic reaction was studied by a finite-difference time-domain numerical simulation. When the PGM is excited by oblique incidence with $\theta = 30^\circ$, the coupling between the NW and SLG/SiO₂ substrate increases to the maximum value. This is clearly evidenced by the excitation of a vertical bonding dipolar plasmon mode under the dipole approximation. The theoretical and experimental results were consistent with each other. This research may open up a pathway toward controlling PGM-driven catalytic reactions through

polarization changes in excitation laser incidence on single anisotropic nanostructures.

Keywords: graphene; nanowire; plasmonic gap modes; plasmon-driven catalytic reaction; surface enhancement Raman scattering (SERS).

1 Introduction

Surface plasmon resonance (SPR) is the resonant collective oscillation of conduction electrons produced near the interface between a metal and a dielectric when light irradiates the metal nanostructure [1–6]. This phenomenon has been utilized in the surface plasmon-driven (SP-driven) catalytic reactions via the decay of the SP into hot carriers [7–9]. Plasmon-driven catalytic reactions have attracted considerable attention because of their higher efficiency and low energy requirements, and they have been widely applied in the fields of physics, chemistry, materials science, and solar energy [10–12]. Recently, advancements have been made in metal-catalyzed chemical reactions of single molecules [13, 14], tip-enhanced Raman spectroscopy [15], and other types of SP-driven hot electron photochemistry [16]. However, owing to the rapid relaxation process of hot carriers, efficient and stable controllable SP-driven catalytic reactions present a substantial challenge. A deep and accurate understanding of the mechanisms of the SP-driven catalytic reactions is highly essential for designing an efficient reaction system, which requires a sensitive and in-situ analysis strategy.

Owing to nondestructive optical techniques for spectral analysis, surface-enhanced Raman scattering (SERS) offers an ultrasensitive spectroscopic method reaching the single-molecular level, as well as molecular fingerprinting and rapid pretreatment [17], which can monitor the SP-driven catalytic reaction *in situ* [18–22]. For the SERS substrate, metallic nanostructures have played an important role nowadays in plasmon-enhanced spectroscopy studies because they support localized surface plasmons

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(LSPs) that can strongly confine light to the deep sub-wavelength volume to produce intense electrical fields. Hence, they can not only function as photocatalysts but also as SERS signal enhancers. Various metal nanostructures have been fabricated to enhance the SERS signal; in particular, the nanogap structure is particularly attractive because the *plasmonic gap mode* (PGM) enables more efficient light confinement than the individual particle particles, thus providing much stronger field intensities for enhanced light-matter interaction.

Recently, a self-assembling approach has also been used to form gap nanostructures [23]. Single-molecule optomechanics in “picocavities” [24], low-threshold nanolasers [25], plasmon rulers with subpicometer resolutions [26], and large spontaneous emission [27] have been achieved in the gap. In particular, the PGM nanostructure formed by nanowires (NWs) on film has received significant research attention and provides a promising platform for plasmon-enhanced spectroscopy and photochemistry [28]. NWs present a way to overcome the problems associated with the nanoparticle dimers [29] and possess the anisotropic merit when responding to the polarization of excitation light along the longitude or transverse direction of the NW. Furthermore, NWs tens of micrometers long can be monitored under microscopy by the naked eye. In our previous research, the polarizing effect of incident lasers on catalytic reactions driven by local SPs of an NW on silicon film were investigated [30].

However, to the best of our knowledge, PGM formed by the NW with single-layer graphene (SLG), which is the ultrathin two-dimensional novelty material, has not been reported up to now. It is expected that more unique physical properties of PGM would occur. Within the dipole approximation, a *vertical bonding dipole plasmon* (V-BDP) mode emerges when the vertically polarized nanoparticle dipole couples to its induced dipolar charges in the underlying film [31]. This study addresses several urgent problems associated with the V-BDP mode that needed to be resolved, including how the V-BDP mode can be induced using changes in the incidence angles of exciting light, how the SERS effect is enhanced by the V-BDP mode, and the efficiency of the catalytic reaction driven by the V-BDP mode.

In this study, we will first discuss the SERS effect of the PGM formed by a single NW with SLG. We will then explicate the catalytic reaction driven by the PGM. Furthermore, we studied the PGM via a finite-difference time-domain (FDTD) simulation of the single NW in a SLG/SiO₂ film system. Finally, the effect of V-BDP under different incidence angles was investigated by theoretical simulation and conclusions were drawn.

2 Materials and methods

2.1 Materials preparation

The AgNO₃ was purchased from the Sinopharm Chemical Reagent Beijing Co. Ltd. (AR, Beijing, China). The 4-nitrobenzenethiol (4NBT) reagent, and the polyvinylpyrrolidone (PVP) were purchased from Alfa Aesar (USA). The Beijing Tongguang Fine Chemical Company (Beijing, China). The SiO₂ films (300 nm thickness) were purchased from Topvender Technology Co. Ltd. (Beijing, China).

2.2 Spectroscopy and image measurement

The morphology and size of the gold structure were characterized by a scanning electron microscope (TESCAN). For the normal incidence setup, the Raman spectra were recorded using a microprobe Raman system RH13325 (R-2000) spectrophotometer. The samples were excited with 532-nm lasers with effective powers of 0.15. A 50× objective lens was used to achieve a 180° backward scattering configuration. The distance between each detection point was set at 3 μm by considering the size of the laser spot at which the diameter was approximately 1 μm. For the oblique incidence setup, the SERS measurements were taken using a commercial micro-Raman spectrometer (Horibba) with a 532-nm laser. The new designing arm was 30° from the sample platform. As a result, the polarization of the exciting light polarization was perpendicular to the NW axis. UV-visible (UV-vis) spectroscopy was performed using a Shimadzu UV 2401 PC instrument. A ready-made solution of Ag NW was placed in 5 mL quartz cells, which were then placed on the sample table of a UV-visible spectrophotometer for measurements. For scanning electron microscope (SEM) analysis, one drop of solution was placed on a Si film and left to dry in the atmosphere. The SEM images of the NWs were obtained using a Hitachi S-4800 microscope.

2.3 Synthesis of graphene

SLG was prepared via a chemical vapor deposition (CVD) method [32] using the instrument G-CVD-50 (Y2K2) system with methane as the carbon source, argon as the shielding gas, and a small amount of injected hydrogen. The copper foil used in the experiment was purchased from the Alpha Company (0.127 mm thick), with a purity of approximately 99.99%. We cut the copper foil, pressed it flat, and folded it into a copper box; then we put it into the heating area in the furnace body of the instrument, near the thermocoupler. The formation of graphene was divided into four stages, and the parameters for each growth stage of the graphene are set. The first was a heating stage during which the furnace temperature rose from 0° to 1030° in 30 min. The hydrogen gas had an inlet rate of 10 standard cubic centimeters per min (sccm). The second was an annealing stage during which the temperature and hydrogen inlet rate remained unchanged for 10 min. The third was a growth stage during which methane had a 10 sccm passage rate for 60 min while hydrogen had a 10 sccm passage rate. The temperature remained unchanged. The last one was a cooling stage during which the heating was stopped and the furnace body was pushed away from the thermocoupler position, keeping the hydrogen and methane inlet rates unchanged. Graphene growth was completed when the furnace body was naturally cooled to 400°. When the copper

box was removed from the furnace, graphene grew on copper foil. We cut the copper foil and pressed it flat, applied PMMA glue to the inside of the copper foil with a glue homogenizer, placed it in a solution of ammonium persulfate with a mass fraction of 0.03% until the copper was dissolved, then we transferred it to a silicon wafer. After that, we put it in a 150° drying oven for 1 h and then put it in a solution of acetone for 12 h to wash off the PMMA glue, yielding a clean single layer of graphene on the silicon wafer.

2.4 Synthesis of Ag nanowires

The silver NW (Ag NW) was synthesized via a wet-chemistry polyol reduction method [33]; 10 mL of ethylene glycol was placed in a glass beaker on a magnetic stirrer and then 700 mg of PVP and 1000 mg of AgNO₃ were slowly added and stirred until fully dissolved. The PVP thickness is about 3 nm which coated the Ag NW surface (see the Supplementary material, the TEM image of the Ag NW coated by the PVP part). Next, the mixed solution was placed in a sealed Teflon reactor, which was heated at 160 °C for 90 min. The reactor was then allowed to cool, and the product was washed with acetone and alcohol, centrifuged (2000 rpm, 10 min), and redispersed in ethyl alcohol (10 mL). Finally, a highly pure solution of silver NWs was obtained. The high-quality silver NWs were approximately $20 \pm 5 \mu\text{m}$ in length and $300 \pm 20 \text{ nm}$ in diameter per SEM observations.

2.5 Sample preparation

To ensure that a monolayer molecule was deposited on the silicon film, the films were immersed in a $5 \times 10^{-6} \text{ M}$ solution of 4NBT in ethanol for 3 h. The films were washed with ethanol for 5 min and dried with N₂ gas. Finally, a Ag NW was deposited on graphene/SiO₂ film by spin-coating to form the graphene-coupled NW hybrid plasmonic gap system.

2.6 Theoretical simulation

The theoretical simulations in this study were conducted using the FDTD method with Lumerical FDTD Solutions 8.0 software [34]. The NW systems configured here consisted of one Ag NW located 3 nm above the SLG/SiO₂ substrate. The Palik dielectric data for SiO₂ was used. The single NW used for simulation was a long cylinder 300 nm in diameter and 6 μm in length placed along the *x* direction on the *x-y* plane. A 532-nm incident laser with a Gaussian beam profile was used (waist radius: 500 nm). The Johnson–Christy dielectric data for Ag were used, and a vacuum with a real refractive index of 1 was selected for the background medium. The NW model was excited using a Gaussian beam wave with an electrical field amplitude of 1.0 V/m. A perfectly matched layer boundary condition was introduced to avoid the reflection and backscattering of the electric field from the pre-selected boundary. The duration of all simulations was fixed at 500 fs to ensure full electric field convergence. The simulation mesh size was 2 nm; fine meshes 1 nm in resolution were used to describe the gap between the NW and the silicon substrate. For the SLG, it is simulated as a surface conductivity material model [35, 36] (see the Supplementary material of “The Single-Layer Graphene Simulation Model” part). Finally, the FDTD boundary conditions were set as perfectly matched layers to absorb all incident light.

3 Results and discussion

3.1 Construction of the nanogap

NWs possess the merit of a well-defined anisotropy in the transverse and longitudinal directions; this can be used as a benchmark system for studying the polarization-dependent local surface plasmon resonance (LSPR) properties [30]. As shown in Figure 1(C), a uniform high-quality NW with a diameter of approximately 150 μm was prepared [33] with a fivefold twinned crystal structure and a pentagonal cross section with five smooth planar surfaces. The hybrid system of the NW and the graphene/SiO₂ substrate had two stable parallel flat surfaces: the bottom facet of the pentagonal NW and the graphene film. Thus, the system formed a well-defined nanogap perpendicular to the surface. The gap plasmons were excited inside the nanogap when the NW interacted with the electromagnetic image induced under the substrate graphene film. Figure 1(A) and (B) shows schematic diagrams of an NW under a microscope for SERS measurement with normal incidence ($\theta = 90^\circ$) and oblique incidence ($\theta = 30^\circ$) on the surface of an SLG/SiO₂ substrate. θ is the angle between the wave vector *K* of excitation light and the surface of substrate. It is noted that the polarization direction of the excitation laser *E* is normal for the longitudinal direction of the NW in the all cases. This is because SP polaritons are transverse magnetic waves at the metal-dielectric interface, the electric field of PGMs should be polarized perpendicular to the NW long axis [37]. A single NW on SLG/SiO₂ substrate viewed under a Zeiss microscope is shown in Figure 1(D). The UV–vis absorption spectroscopy of the NW solution shows a maximum peak at 418 nm and a long SP absorption tail extending to the infrared region. The scattering spectroscopy simulated by FDTD was shown in Supplementary material (SM, Figure S1). The calculated LSPR band of the Ag NW was located at 610 nm with the full-width half-maximum (FWHM) of 150 nm. Thus, this can be used as a good SERS plasmonic substrate at 532 nm as shown in Figure 1(E).

The edge of the SLG prepared by the CVD method (see the Section 2.3 Synthesis of graphene) could be clearly viewed under a microscope and highlighted by the rectangle in 1(D), and the Raman spectroscopy of the pristine SLG is shown in Figure 1(F). The prominent *G* and *G'* peak are well-defined Lorentz lineshapes with the FWHM of 13.17 and 32.17 cm^{-1} . The intensity ratio of *G'*/*G* was 5.06 which indicates the graphene is a well-defined SLG [38]. It is noted that the *G* peak (1580 cm^{-1}) is the only fundamental Raman mode with the doubly degenerate (iTO and LO)

Figure 1: Schematic diagram of a graphene-coupled Ag nanowire (NW) hybrid nanostructure under a microscopy and SERS measurement with normal incidence (A) ($\theta = 90^\circ$) and oblique incidence of the laser on the Ag NW and graphene/SiO₂-substrate (B) ($\theta = 30^\circ$). The polarization direction E of the laser is along the transverse cross section of the NWs. Here θ is the incidence angle between the propagation direction K and the surface of the substrate. (C) Scanning electron microscope (SEM) image of Ag NWs; the insets show the top view of vertically standing NWs clearly demonstrating their pentagonal cross sections highlighted in the rectangle. (D) A single NW deposited on the single-layer graphene (SLG) image was viewed under a Zeiss microscope. The blue color part under the NW is the SLG. The edge of the SLG is highlighted by the rectangle. (E) UV-visible absorption spectrum of the Ag NWs sample. (F) The Raman spectrum of the SLG prepared by CVD method. The scalar bars shown in C and D are 1 and 20 μm , respectively.

phonon mode at the Brillouin zone center. While the D peak is associated with the defects or the edge, and G' is the overtone of the D peak. In fact, in accordance with double resonance theory [39, 40], the D peak originates from a second-order process involving one iTO phonon and one defect, whereas the $2D$ peak originates from a second-order process involving two iTO phonons near the K point. This means that if the detecting position was at the center part of the SLG, the D peak could not be observed, but the G' peak could be observed. This phenomenon has been reappeared in our experimental shown in Figure 2(D) and (F).

When the NW was deposited on the SLG/SiO₂ substrate, the nanogap is formed in the space between the NW and the SLG/SiO₂ substrate. Owing to the presence of a surfactant polymer (cetyltrimethylammonium bromide) coating on the surface of the NW together with the SLG, an estimated gap distance of approximately 3 nm is formed at

Figure 2: (A) Surface-enhanced Raman scattering (SERS) spectra of a single-layer graphene (SLG) in the graphene/SiO₂ film-coupled nanowire (NW) hybrid nanogap by oblique incidence with $\theta = 30^\circ$ (as shown in Figure 1(B)) at difference points away from the center of axis of the NW. (B) The Raman intensities of D , G , and G' SERS peaks shown in A; (C) The Raman shifts of D , G , and G' SERS peaks shown in A; (D) The SERS spectra of SLG in the graphene/SiO₂ film-coupled NW hybrid nanogap by normal incidence with $\theta = 90^\circ$ (as shown in Figure 1(A)) at difference points away from the center of axis of the NW. (E) The Raman intensities of D , G , and G' SERS peaks shown in D; (F) The Raman shifts of D , G , and G' SERS peaks shown in D.

the NW and the SLG contacting surface. Here, the SLG was not only acted as the reflecting “mirror” to form the plasmonic gap with the NW (see the details discussion in the simulation part) but also as the large SERS probe located in this plasmonic gap. It is noted that the plasmonic gap was formed by NW/SLG/SiO₂; here the contribution of graphene to the plasmonic gap mode is more important than that gap formed only by NW/SiO₂ without graphene (please see the detail describing of contribution of graphene in Supplementary material “The Plasmonic Gap Formed By Ag NW/SiO₂” part).

3.2 The SERS enhancement of SLG by PGM

As shown in Figure 2(A), the SERS of the SLG in this nanogap had an oblique incidence excitation of 532 nm (as shown in Figure 1(B)) at different distance points crossing the gap center. The reason for this oblique incidence experimental design is to enhance the intensity of the PGM. Here a , b , c , d , e , and f represent the measurement positions of 0, 0.5, 1, 1.5, 2, and 2.5 μm , respectively, away from the gap center (which is also the axis center of the

NW). The positions *a* to *f* are schematically shown in Figure 1(A) and (B), and also labeled them in Figure 1(D). The SERS intensity of the *D* and *G* peaks of graphene shown in Figure 2(B) were drastically enhanced when the detecting position approached the gap center. It is shown that the *f* position was less affected by PGM; however, the *a* position was mainly enhanced by the PGM. The ratio of the SERS intensity of the *G* peak of position *a* versus position *f* was approximately 2.4×10^6 , and that of the *D* peak was approximately 3.7×10^6 . Meanwhile, the Raman shifts of both peaks were redshift. The *G* peak gets redshift about 9 cm^{-1} and the *D* peak gets redshift about 43 cm^{-1} . For comparison, the SERS spectroscopy for normal incidence is shown in Figure 2(D). Both the intensity (as shown Figure 2(E)) and the Raman shifts (as shown Figure 2(F)) of *G* and *G'* were not considerably affected by the PGM so much. However, the NW deposited on the SLG surface induced curvature in the SLG, which is linked to edge defects, so when the detecting position approached the NW center from *f* to *a*, the *D* band was pronounced (see Supplementary material, Figure S2).

3.3 The catalytic reaction driven by PGM

The aforementioned observations demonstrate that the SERS signal of SLG was significantly influenced by the incident angle θ . To answer further questions about how the incident angles affect the catalytic reaction efficiency and the physical origin, we perform molecular catalytic reactions by SERS using the same method. It is well known that, for the plasmon-driven catalytic reaction, the reactant 4NBT molecule can be dimerized into the product *p,p'*-dimercaptoazobenzene (DMAB) molecule. The essence embodied in this kind of plasmon-driven reduction reaction is the plasmonic hot electron decay from SPR. On one hand, this decay process may provide the electrons needed for the reduction reaction; on the other hand, it could afford a large amount of kinetic energy to overcome the potential energy barrier [13]. We again choose 4NBT as the model reactant molecule to study the PGM-driven catalytic reactions. The SERS of the experimental and the simulated spectra of the 4NBT reactant and DMAB product was given in our previous research [30]. There, $\nu_1 = 1081 \text{ cm}^{-1}$, $\nu_2 = 1338 \text{ cm}^{-1}$, and $\nu_3 = 1572 \text{ cm}^{-1}$ are characteristic Raman modes of the reactant 4NBT molecule, and $\nu_4 = 1141 \text{ cm}^{-1}$, $\nu_5 = 1386 \text{ cm}^{-1}$ and $\nu_6 = 1432 \text{ cm}^{-1}$ are characteristic Raman modes of the product DMAB molecule. The Raman mode of ν_2 is attributed to NO-stretching of 4NBT, and ν_6 to the NN-stretching of DMAB [10].

The SERS spectrum of the 4NBT catalytic reaction driven by PGM at different incidence angles θ was shown in Figure 3. The trends of the SERS intensities of 4NBT are

Figure 3: (A) Surface-enhanced Raman scattering (SERS) spectrum of 4-nitrobenzenethiol (4NBT) in the single-layer graphene (SLG)-coupled nanowire (NW) hybrid plasmonic gap by oblique incidence with $\theta = 30^\circ$ at difference points away from the center of axis of the NW with 532 nm wavelength excitation. (B) SERS spectrum of 4NBT in the graphene-coupled NW hybrid plasmonic gap by normal incidence with $\theta = 90^\circ$ at difference points away from the center of axis of the NW with 532 nm wavelength excitation. (C) Coverage of the 4NBT reactant and the *p,p'*-dimercaptoazobenzene (DMAB) product at difference points in A; (D) Coverage of the 4NBT reactant and the DMAB product at difference points in B.

similar to that of SLG shown in Figure 2. First, for normal incidence (Figure 3(B)), the SERS profiles of 4NBT from the *i* to *e* detection points away from the center of the plasmonic gap were identical to those from the Raman spectra of pristine 4NBT molecule, which are mainly Raman peaks of ν_1 , ν_2 , and ν_3 . As the detecting position approached the center of plasmonic gap, as in curves *d* to *a*, three new Raman peaks ν_4 , ν_5 , and ν_6 , which are attributed to DMAB, appeared gradually. At the *a* position, the center of the gap, the three new SERS peaks increased to a maximum. This observation demonstrated that 4NBT molecule was gradually catalyzed to DMAB molecule by the PGM. To estimate the relative surface coverage of 4NBT and DMAB during the reaction, we analyzed the intensities of the SERS peaks at $\nu_2 = 1338 \text{ cm}^{-1}$ (4NBT) and $\nu_6 = 1435 \text{ cm}^{-1}$ (DMAB) in accordance with the study by Choi et al. [13]. The intensities of ν_2 and ν_6 arose from 4NBT and DMAB, respectively. Here, by assuming similar SERS enhancement factors for ν_2 and ν_6 , the surface coverage of the product versus the reactant species can be weighted by the SERS intensities (I_{ν_6} , I_{ν_2}). The surface coverage can be derived from Eq. (1)

$$\begin{pmatrix} I_{\nu_2} \\ I_{\nu_6} \end{pmatrix} = \begin{bmatrix} \sigma_{4\text{NBT}, \nu_2} & 0 \\ 0 & \sigma_{\text{DMAB}, \nu_6} \end{bmatrix} \begin{pmatrix} \mu_{4\text{NBT}} \\ \mu_{\text{DMAB}} \end{pmatrix} \quad (1)$$

where $\mu_{4\text{NBT}}$ and μ_{DMAB} are the surface coverage of 4NBT and DMAB, respectively, and $\sigma_{4\text{NBT}, \nu_2}$ and $\sigma_{\text{DMAB}, \nu_6}$ are the corresponding Raman scattering cross sections of solid species (the values are taken from reference [13]). From Eq. (1), the surface coverage rate is written as

Figure 4: (A–G) The finite-difference time-domain (FDTD) simulation of the electromagnetic field distributions on x-y plane of the surface of section ($z = 0$) for the graphene-coupled NW hybrid gap structure with different incidence angle $\theta = 0^\circ, 15^\circ, 30^\circ, 45^\circ, 60^\circ, 75^\circ$ and 90° , respectively. The ranges of the x-axis and y-axis are -200 to 200 nm. (H) The light incidence configuration for the FDTD simulation.

$$\eta = \frac{\mu_{\text{DMAB}}}{\mu_{4\text{NBT}}} = \frac{I_{v_6}}{I_{v_2}} \times \frac{\sigma_{4\text{NBT}, v_2}}{\sigma_{\text{DMAB}, v_6}} \quad (2)$$

As is clearly shown in Figure 3(D), as the detecting position approaches the gap center (from i to a), the coverage of the reactant 4NBT calculated in accordance with Eq. (2) decreases and that of the product DMAB increases. This demonstrated that more DMAB is produced because of the hot electron decay from the PGM of the plasmonic gap. When the laser irradiates directly on the NW axis such that the local surface plasmonic resonance reaches a maximum, it not only enhances the SERS signal but also creates more hot electrons, driving more 4NBT to dimerize to DMAB [30]. If the NW/graphene substrate is excited by a laser with an oblique angle of $\theta = 30^\circ$, what will

happen? As shown in Figure 3(A), the aforementioned conclusions via normal incidence could also reappear. However, the efficiency of catalytic reaction is enhanced more. The coverage of reactant 4NBT and product DMAB is shown in Figure 3(B); when the detecting position is approaching gap center a , the reactant 4NBT is dimerized completely (100%) to the product DMAB.

3.4 The PGM enhancement in nanogap by FDTD

The results of both experimental configurations (normal and oblique incidence) have interestingly similar trends.

However, they are quite different in their surface coverage rate η by Eq. (2), for normal incidence is only $\eta = 20\%$, whereas the maximum ratio for oblique incidence is $\eta = 100\%$. There must be some essential physical differences between them. To address the differences, the FDTD method was used to calculate local electric field intensity distributions E and the induced charge density around the hybrid plasmonic gap. Figure 4(A–G) shows the near electromagnetic field distribution on the x - y plane of the surface of section ($z = 0$) on the plasmonic gap with different incidence angles $\theta = 0^\circ, 15^\circ, 30^\circ, 45^\circ, 60^\circ, 75^\circ$, and 90° , respectively. The light incidence configuration for the FDTD simulation is shown in Figure 4(H). It is clearly shown that the intensities of electric field E in the gap formed by NW and the graphene/SiO₂ are extraordinarily strong in the all cases from A to F. Such significant field localization results in strong light absorption and scattering. As the incidence angles θ are changing from 0° to 90° , the intensities of electric fields in the gap also change. At $\theta = 30^\circ$ (Figure 4(C)), the intensities of electric fields in the gap approach the maximum value. This indicates that the PGM is excited more intensely by oblique incidence at $\theta = 30^\circ$ than that by normal incidence at $\theta = 90^\circ$. This explains the reason why the experimental SERS signal for graphene shown in Figure 2(A) is more considerably enhanced by the oblique incidence at $\theta = 30^\circ$ than that by normal incidence at $\theta = 90^\circ$.

3.5 The V-BDP gap mode revealed by FDTD

To further study the essence of the PGM and the coupling of NW with graphene, we also simulated the induced charge density distributions of the graphene-coupled NW hybrid gap with different incidence angles. Within the dipole approximation, a V-BDP mode emerges when the vertically polarized NW dipole couples to its induced dipolar charges in the underlying graphene layer. Likewise, the transversely polarized NW dipole would induce an image dipole underlying the graphene but with the opposite polarity, resulting in a transverse bonding dipole plasmon mode with suppressed radiation [31], or called the dark mode. Similar to the film-coupled nanosphere structure, the hybridization of the plasmonic resonances of PGM would lead to symmetric and antisymmetric resonances [41]. However, the symmetric resonance is related to a horizontal electric dipole in the nanosphere and an induced electric dipole in the film. Antisymmetric resonance is then characterized by a vertical bonding dipole in the nanosphere and an induced electric dipole in the film, which add up and produce an even larger vertical electric dipole.

Figure 5: (a–g) The finite-difference time-domain (FDTD) simulation for charge density distribution on xy plane of the surface of section ($z = 0$) of the film-coupled NW hybrid gap structure with different incidence angles $\theta = 0^\circ, 15^\circ, 30^\circ, 45^\circ, 60^\circ, 75^\circ$, and 90° , respectively. The ranges of the x - and y -axis are $(-92, -82 \text{ nm})$ and $(-100, 100 \text{ nm})$, respectively. (h) The case of $\theta = 30^\circ$ with enlargement ranges of the ranges of the x - and y -axis are from -200 to 200 nm , respectively.

Figure 5(a–g) shows the charge density distributions of the hybrid gap with different incidence angles. When the component of the electric field along the direction of the y axis changes as a results of different incidence angles, the vertical dipole charges sensitively. It is noted that the vertical dipole charges are directly related to the V-BDP gap mode. As is the degree of the coupling between the NW and the SLG. The vertical dipole charges distributed on the two lateral surfaces of the plasmonic gap are shown in Figure 6. The charges reach their maximum value when the incidence angle $\theta = 30^\circ$. With obligation incidence, the V-BDP gap mode can be efficiently excited and enhanced, as can the SERS and the catalytic reaction efficiency. Hence, we may conclude that the excitation of the V-BDP gap mode can be monitored by changing the polarization of the exciting electric field. This could play a very important role

Figure 6: Integrated vertical dipole charge on x-y plane of surface of section ($z = 0$) of graphene-coupled NW hybrid gap structure with different incidence angles.

in the enhancement of the Raman scattering process and plasmon-driven catalytic reactions in plasmonic nanogaps.

4 Conclusion

We have investigated PGM-driven catalytic reactions in the plasmonic gap formed by the space between a single NW and the SLG/SiO₂ substrate via SERS spectroscopy. The excitation of PGM could be tuned by changing the incidence angle of excitation light with the substrate. The PGM in the gap can be used in plasmon-enhanced Raman spectroscopy and plasmon-driven catalytic reactions. When the incidence light is normal on the surface of the graphene/SiO₂ substrate, not only the SERS peaks of graphene as probe is not enhanced but also the Raman peaks of the catalytic reaction product DMAB driven by the gap mode was not prominent. By changing the laser incidence angle from normal (90°) to obliquation (30°), the SERS peaks of graphene were drastically enhanced. Furthermore, the dimerization of 4NBT to DMAB became more efficient. This intense catalytic reaction was due to more hot electrons being decayed by the PGM as the incidence angle changed. For further investigation of the physical attributes of PGM, the near electric field distribution in the gap was calculated using FDTD methods. It was demonstrated that the intensities of near the electric fields in the gap changed as the incidence angle θ varied from 0° to 90°. At $\theta = 30^\circ$, the intensities of the electric fields in the gap approached their maximum values. In addition, the calculated vertical dipole charges distributed on the two lateral surfaces of the plasmonic gap were subject to the incidence angles and

would reach the maximum value when the incidence angle $\theta = 30^\circ$. This hinted that the V-BDP mode was excited by oblique incidence, which results in the strong coupling of the NW with the semiconductor substrate. The theoretical and experimental results were consistent with each other. This research may pave the way for controlling PGM-driven catalytic reactions by changing the polarization of an excitation laser incident on single anisotropic nanostructures such as a single NW. Future studies should determine the mechanism of hot electron transfer from the NW to the reactant and methods through which to exactly control the catalytic reactions in the plasmonic gap.

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