Research article

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Plasmonic nanocavity enhanced vibration of graphene by a radially polarized optical field

<https://doi.org/10.1515/nanoph-2019-0553>

Received December 27, 2019; revised February 2, 2020; accepted February 2, 2020

Abstract: The combination of 2D materials and surface plasmon can produce some novel optical phenomena that have attracted much attention. Illuminated by light with different polarization states, the field distribution around the plasmonic structure can control the light-matter interaction. The interaction between graphene and light can be strongly enhanced by employing radially polarized beams in a nanocavity. Here, we study the selectively enhanced vibration of graphene in a coupled plasmonic gold nanocavity with a radially polarized optical field, and the coupling and enhancing mechanisms are investigated both experimentally and numerically. By focusing a radially polarized beam, a high z component of a localized near field in the nanocavity is provided to strongly enhance the interaction between graphene and light, which can be used to enhance the vibrational signal of the interlayer. For the in-plane vibration of graphene, a similar enhancement is obtained with a linearly and radially polarized optical field. A plasmonic nanocavity is used to enhance the vibration of graphene, which provides potential applications in studying the out-of-plane vibration mode and exploring the mechanism of the interlayer coupling of 2D materials.

Keywords: radially polarized optical field; plasmonic nanocavity; gap mode; graphene; Au nanorod.

1 Introduction

With the family developed from graphene, two-dimensional (2D) materials such as transition metal dichalcogenides, hexagonal boron nitride [1–3], and many novel 2D materials [4–7] have attracted much attention due to their extraordinary properties, which include high carrier mobility, wide range optical absorption, and atomic thickness. Such characteristics make it possible to apply 2D materials in many fields such as photoelectronics [8–10], bioscience [11, 12], environment engineering [13], catalysis [14, 15], optical effects research [16–18], and so on. The atomic thickness of 2D materials, however, hinders their ability to absorb light, which limits their application [19]. For example, for monolayer graphene, the absorption efficiency is only 2.3% [20]. Nobel metal nanostructures can confine the light to the surface of metal, which provides a strong enhancement of the electromagnetic (EM) field, thereby strengthening the weak absorption of 2D materials as well as the light-matter interaction [21–25]. Moreover, the EM field generated by plasmonic nanostructures can be designed not only by varying the size and shape of the structure but also by changing the incident optical field and polarization state [26]. The Raman spectrum is an important approach to study the characteristics of 2D materials due to its fingerprint properties. However, the Raman signal is weak, and the enhancement of such Raman signals is desirable. Therefore, the hybrid structure composed of plasmonic and 2D materials can be seen as a satisfying strategy to strengthen the interaction between 2D materials and light [27–29].

To improve Raman intensity, higher enhancement of the EM field is required. It has been proved that the EM field is stronger in the nanocavity than in the surrounding of a single nanostructure because of the existence of the “hot spot” effect [30, 31]. With decreases in the gap distance, the electric field becomes stronger, and the light can be confined in a more local area [32, 33]. In addition, the localized electric field intensity is dependent on the polarization of the excitation light [34]. Putting nanoparticles on a large enough metal plane spaced by 2D materials can produce a perfect

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plasmon nanocavity [35]. The nanogap distance of such 2D materials-plasmon nanocavity hybrid structure can be tuned by changing the interlayer number of 2D materials from sub-nanometer to several nanometers, which has been used to study the quantum effect and enhance the light-matter interaction [36–38]. The development of radially polarized beams provides more choice in the selection of polarization of excitation light [39]. In the vertical plasmonic nanogap system, the performance of radially polarized beams was better than linearly polarized beams in the previous study [40–43]. Thus, the questions we need to take into consideration are whether this excitation method is applicable to the system composed of a vertical plasmonic nanocavity and 2D materials, and if radially polarized beams perform better than linearly polarized beams.

In this paper, the coupling effects are studied by employing Raman signal through a hybrid system composed of an Au nanorod and Au microplate spaced by graphene under a radially- and linearly-polarized-beam excitation. The coupling and enhancing mechanisms are investigated both experimentally and numerically. Comparing the hybrid system excited by a linearly and radially polarized beam, the results show that the difference between the enhancement effect under different polarization states is small due to the mismatch of the Raman vibration mode and the plasmon mode. The dependence of the Raman vibration mode and the plasmon mode is discussed in detail. This work suggests that the radially polarized beam can be more suitable for investigating the out-of-plane vibration mode of 2D materials, such as the interlayer vibration. It may provide potential application in exploring the superconductivity mechanism of twisted 2D materials.

2 Experimental section

2.1 Sample preparation

In this experiment, all reagents were used without further purification, and deionized (DI) water was used. Chloroauric acid (HAuCl_4), hexadecyltrimethylammonium bromide (CTAB), sodium borohydride (NaBH_4), and sodium oleate (NaOL) were purchased from Sigma Aldrich (Shanghai, China). Hydrochloric acid (HCl), ammonium persulfate, polyvinyl pyrrolidone (PVP), polymethyl methacrylate (PMMA) and acetone solution were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Monolayer graphene was purchased from 6carbon Technology (Shenzhen, China).

The Au nanorods were synthesized by the seed-mediated wet-chemical method we reported [44]. The

single-crystal Au microplates were synthesized by a wet-chemical method [45]. Gels of HAuCl_4 -PVP (with molar ratios $\text{PVP}/\text{Au}=200\text{--}300$) were obtained at 50°C by mixing HAuCl_4 solution (1.5 ml, $[\text{HAuCl}_4]=0.04\text{ M}$) with PVP (K30). The gels were kept at 50°C for a 24 h period. Then the gels were transferred to an environment with temperature lower than 5°C . Finally, the single-crystal Au microplates were obtained by placing the gels at temperatures less than 50°C over a long period of time.

Graphene was transferred by a wet-chemical etching method. The monolayer graphene was cut into small pieces and PMMA was coated uniformly by spin-coating followed by heating for 1 min at 180°C . Then the PMMA/graphene layer on the Cu foil was transferred into the persulfate solution to etch the Cu foil. After the Cu foil was etched off, the PMMA/graphene layer was rinsed several times in DI water and gathered by a substrate. After blow drying in a nitrogen atmosphere, the sample was heated at 130°C for 20 min and soaked in an acetone solution several times to remove the PMMA layer. The bilayer graphene can be obtained by repeating the above steps.

2.2 Characterization and measurement

The scanning electron microscope (SEM) images were obtained by an FEI-Nova Nano SEM 450 (Hillsboro, OR, USA) operating at a voltage of 10 kV, and the automatic force microscope (AFM) images were collected from the Nanowizard Ultraspeed (JPK, Berlin, Germany). The UV-visible extinction spectra were measured by using a Perkin Elmer Lambda 950 spectrometer (Waltham, MA, USA). The Raman spectrum was collected from a LabRam HR Evolution Raman system (HORIBA Jobin Yvon, PAR, FRA).

During the experiment, considering the spot size of the 532 nm laser, the concentration of Au nanorod colloid was optimized to ensure that the area of interest has only one nanorod. To avoid damage induced by laser heating, the excitation laser power was set to 0.6 mW. By adding an extra vortex retarder ($m=1$), the linearly polarized 532 nm laser can change to a radially polarized beam. After being tightly focused by a $100\times$ microscope objective ($\text{NA}=0.9$), the 532 nm radially polarized beam is illuminated to the sample vertically.

2.3 Simulation

The numerical simulations were performed using the finite-element method with COMSOL Multiphysics (COMSOL, STO, SWE). The model of the hybrid system of the Au nanorod-graphene-Au microplate was built

according to the experimental geometry, which was put on the silicon substrate. A linearly and radially polarized beam of 532 nm was used to excite the hybrid system. The permittivity of the Au is from the data by Johnson and Christy [46].

3 Results and discussion

The schematic diagram with the corresponding morphology characterization of the hybrid nanocavity-2D material system is shown in Figure 1. As shown in Figure 1A, the Au nanorod and Au microplate spaced by the bilayer graphene constitute a plasmonic nanocavity. The incident light shines on the sample vertically from the top side with the change in its polarization. A corresponding diagram applied in the experiment is shown in Figure 1B. Figure 1C shows the AFM image of the synthesized Au microplate, with the height of the profile of the microplate equal to approximately 35 nm. Through the SEM image of the Au nanorods and absorption spectrum (Figure 1D), one can see that the length of the nanorods is ~ 50 nm, the width is ~ 15 nm, and absorption peaks are at 516 nm and 656 nm, which correspond to the transverse and longitudinal

mode, respectively. Moreover, the narrow peak at 656 nm can reveal that the sizes of the Au nanorods are uniform. The structure can be seen from the AFM image in Figure 1E, the interested area is zoomed in, and the corresponding profile along the blue line is shown in the lower side of the image. (For the corresponding SEM images please see Figure S1.)

We first studied the near field optical response probed by the bilayer graphene Raman signal in the nanocavity coupled with a radially polarized beam. Figure 2A shows the Raman signals excited by the 532 nm radially polarized beam with graphene on the Si substrate, graphene on the Au microplate, and graphene in the nanocavity. Compared with the graphene on the Si substrate (black line), the G peak and 2D peak of the graphene in the nanocavity (blue line) are both enhanced with the radially polarized beam due to the strong gap mode. The Raman signal of the graphene on the Au microplate (red line) was also measured, from which we can see that there also exists enhancement compared with the graphene on the Si substrate. By comparison, we can see that the Raman enhancement in the nanocavity was obviously far higher than the Raman on the Au microplate, which can illustrate the enhancement mainly contributed to the

Figure 1: Schematic diagram and characterization of the Au nanorod-graphene-Au microplate hybrid system.

(A) The scheme of the Au microplate-graphene-Au nanorod sandwich plasmonic structure. (B) Diagram of the nanocavity structure applied in experiment. (C) AFM image of the synthesized Au microplate with its corresponding height profile. (D) SEM image of the synthesized Au nanorods with the absorption spectrum. (E) AFM image of the whole plasmonic nanocavity structure, with the Au nanorod profile in the lower side.

Figure 2: Raman spectrum of the Au nanorod-graphene-Au microplate hybrid system under different optical field excitations.

(A) Raman spectrum of the graphene on the Si substrate (black line), on the Au microplate (red line), and in the gap between the Au nanorod and the Au microplate (blue line), respectively, excited by the 532 nm radially polarized beam. (B) Raman spectrum of the graphene in the gap of the Au nanorod and the Au microplate excited by the 532 nm linearly polarized beam. The black line and red line represent the Raman spectrum measured at the $\theta = 0^\circ$ and $\theta = 90^\circ$, as shown in the inset. (C) Polarization dependence of the G peak (black line), 2D peak (red line), and D peak (blue line) in polar coordinates.

coupling between the nanocavity and the incident light. From the changed Raman spectrum, we found that the enhancement of different Raman peaks follows the order $EF_D > EF_G > EF_{2D}$, which is similar to previous report [47]. This phenomenon can be explained by the electromagnetic mechanism of surface-enhanced Raman scattering (SERS) [48]. Because the wavelengths of the three peaks follow the order $\lambda_D > \lambda_G > \lambda_{2D}$, the Raman scattered photons of the D band can match the localized surface plasmon of the nanorod better than the G band and the 2D band, which leads to the change of the graphene Raman.

The graphene Raman signals with the linearly polarized beam illumination are also measured to compare with the radially polarized beam. Figure 2B shows the polarization dependence of the graphene Raman signal in the nanocavity. θ is set as the angle between $\mathbf{E}$ and the long axis of the Au nanorod. The maximum Raman intensity (red line) is obtained when $\mathbf{E}$ is parallel to the long axis ($\theta = 0^\circ$) of the Au nanorod. The minimum Raman intensity (black line) is obtained when $\mathbf{E}$ is vertical to the long axis of the Au nanorod ($\theta = 90^\circ$), where the corresponding SEM image is shown in the inset image. A more vivid polarization dependence relationship in polar coordinates is shown in Figure 2C. By comparing the Raman signal obtained from the radially polarized beam and the linearly polarized beam excitation, one can see that the enhancement difference between the maximum Raman intensity with a radially and linearly polarized beam excitation is small. To determine the reason, further study on the coupling effect in the nanocavity is necessary.

To understand the coupling effects of the nanocavity with incident light, a simulation was generated. The

schematic diagram of the sandwich nanostructure is shown in Figure 3A. The charge distribution within the nanocavity with different polarized beam excitations is shown in Figure 3B, where the top and bottom representing the radially and linearly polarized excited systems, respectively. One can see that under a radially polarized beam excitation, the charge distribution in the nanocavity is different with a linearly polarized excitation. Figure 3C and D show the electric field distribution of the nanocavity area under different polarization light excitations. The variation of the electric field intensity with different gap distances in the nanocavity is shown in Figure S6. When the system is excited by the radially polarized beam, the electric field in the nanocavity is highly enhanced, with the strongest field confined to the middle area of the Au nanorod (Figure S4). On the other hand, under the linearly polarized beam excitation, the strongest fields are concentrated on the two ends of the nanorod (Figure S5). As we know, the G peak and 2D peak correspond to the in-plane vibration mode [49]. The Raman mode can be enhanced selectively by different $\mathbf{E}$ components in different directions. In the radially polarized beam configuration, the z -component of the electric field makes a major contribution to the field enhancement. However, the z -component rarely contributes to the in-plane Raman vibration mode [50]. For the Raman signal enhancement in this study, the x - y components of the electric field dominate the enhancement. Combining the results from both simulation and experiment, it can be inferred that the small intensity difference between the Raman signal excited by the linearly and radially polarized beams can own to the similar contribution of the x - y components between radially and

Figure 3: Simulation of the Au nanorod-graphene-Au microplate hybrid system.

(A) Diagram of the simulation configuration of the sandwich structure. (B) Charge distribution when the nanocavity is excited by the radially polarized beam and the linearly polarized beam with the $\mathbf{E}$ vector parallel to the long axis of the Au nanorod. (C) Distribution of $\lg(|\mathbf{E}|/|\mathbf{E}_0|)^4$ with the nanocavity excited by the radially polarized beam. (D) Distribution of $\lg(|\mathbf{E}|/|\mathbf{E}_0|)^4$ with the nanocavity excited by the linearly polarized beam.

Figure 4: Graphene Raman signals on the Si substrate (black line) and in the nanocavity (red line).

linearly polarized excitations. Therefore, for the 2D materials-nanocavity system, the radially polarized beam is more effective at exciting the out-of-plane vibration mode than the in-plane vibration mode.

Commonly, the accepted mechanisms of SERS are the electromagnetic field enhancement and charge transferring theory. We believe that charge transfer between the graphene, Au microplate, and Au nanorod also attributed to the enhancement of the Raman intensity to a certain

degree. Further, we observed a small red shift (higher wave-number) at the 2D peak of the graphene on the nanocavity contrasted with the graphene on the Si substrate as shown in Figure 4. Note that the Raman spectrum of the graphene on the Si substrate is scaled up by 50 times for comparison with the enhanced Raman spectrum of the graphene in the nanocavity. Here we think that the small shift may be led by the charge transfer between the graphene and the surrounding Au microplate and Au nanorod, which is similar to a previous report [51].

4 Conclusions

In conclusion, a radially polarized optical field is used to excite the plasmonic nanocavity in which the Raman signal of graphene is enhanced. The Raman signal enhancement effects are similar under linearly and radially polarized fields, which is due to the contributions of the electric field components on x - y direction are comparable. Moreover, a small red shift of graphene Raman at the 2D peak has also been observed, which may attribute to the charge transfer between the graphene and the surrounding Au nanorod. As an efficient method to excite the vertical plasmon mode in a nanogap composed of nanoparticles and a metal plane, it can provide a potential

suggestion for exploring the inner mechanism of the inter-layer coupling of 2D materials.

Acknowledgments: This work was supported by the National Natural Science Foundation of China (Grant No. 11574190, Funder Id: <http://dx.doi.org/10.13039/501100001809>), the Natural Science Foundation of Shaanxi Province (Grant Nos. 2019JQ-142 and 2019JM-441), and the Fundamental Research Funds for Central Universities (Grant Nos. GK201903013 and GK201701008).

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Supplementary Material: The online version of this article offers supplementary material (<https://doi.org/10.1515/nanoph-2019-0553>).