Plasmon excitation in MoS$_2$/graphene van der waals heterostructures

DAN-DAN LIU$^{1,*}$, ZHI-YIN ZHANG$^2$, PENG GUO$^1$ and JIAN-JUN WANG$^1$

$^1$College of Science, Zhongyuan University of Technology, Zhengzhou 450007, China
$^2$Institute of Applied Mathematics, Zhengzhou Shengda University of Economics, Business and Management, Zhengzhou 451191, China
*Corresponding author. E-mail: dandanliu@zut.edu.cn

MS received 27 May 2021; revised 19 August 2021; accepted 23 August 2021

Abstract. We have carried out a study of collective excitations for MoS$_2$/graphene van der Waals heterostructures (vdWHs) using time-dependent density function theory (TDDFT). The resonance absorption spectra of the structures were analysed to determine the polarisation direction in the $X$-, $Y$- and $Z$-axes. We found that the resonance intensities in MoS$_2$/graphene structures were larger than the bilayer graphene structures in high-energy resonance, and the resonance peak of the graphene/MoS$_2$/graphene heterostructure almost annihilated at the low-energy resonance band became broadened at the high-energy resonance band. We studied Fourier-induced charge density of MoS$_2$/graphene structures and found that they have dipole-like characteristics in the low-energy region.

Keywords. Plasmon resonances; Van der Waals heterostructures; transition metal dichalcogenides.

PACS Nos 73.20.Mf; 73.21.-b

1. Introduction

Since the discovery of graphene in 2004 [1], two-dimensional (2D) materials have created a revolution in materials science due to their unique physical/chemical properties and great potential for applications in electronic devices [2–7]. In graphene, the carbon atoms are arranged in a honeycomb lattice with Dirac cones, permitting electrons to flow freely across its surface with low scattering. The special electronic structure features of graphene give rise to the uncommon properties of plasmon resonances that have a relatively long propagation length and do not decay easily [8–12]. Plasmons in single/multilayer graphene nanostructures were studied by Zhang and coworkers [13,14]. The plasmon structure of bilayer graphene was investigated in the framework of ab-initio time-dependent density-functional theory (TDDFT) at the level of the random-phase approximation (RPA) [15]. While a rich harvest of results has been collected from most of the ‘low-hanging graphene fruits’ in the graphene field, the applications of graphene for the fabrication of logical circuits have been limited because of its lack of a band gap.

Now, researchers have started to pay more attention to other 2D crystals, such as transition metal dichalcogenides (TMDS), hexagonal boron nitride (hBN) and phosphorene. For example, single-layer MoS$_2$ with a naturally occurring parent layered material has been successfully synthesised. The single-layer MoS$_2$ exhibits relatively large free charge carrier mobilities and has a relatively sizable band gap, revealing the viability of using MoS$_2$ for controlling the on and off currents in electron devices [7,16,17]. N-type transistors based on single-layer MoS$_2$ show good performance with a $I_{on}/I_{off}$ ratio of $\sim$108, a high drain current of up to several hundred mA/mm and a subthreshold swing down to 74 mV/dec [18,19]. In the present work, researchers considered the generation of plasmons in MoS$_2$ that were accommodating massive electrons and had relatively low carrier concentrations of $10^{12}$–$10^{14}$. The plasmon resonances of MoS$_2$ were theoretically studied, and only the modes with relatively low frequencies in the far-infrared and terahertz regimes were found [20]. The intraband plasmons of six different metallic monolayer TMDs were explored by first-principles TDDFT in RPA calculations [21]. The existence of one-
dimensional (1D) plasmons along the metallic edges of MoS$_2$ nanoribbons was revealed by first-principles calculations [22].

Graphene combined with different 2D materials such as hBN and the TMDs can form the basis for artificially layered van der Waals heterostructures (vdWHs), the study of which has followed closely on the heels of the development of the 2D materials. The advances in vdWHs have created a new touchstone in materials science, unveiling unusual properties and new phenomena that differ from those found in the corresponding monolayer structures [23–26]. Conventional heterostructure fabrication methods involve complex and expensive ultrahigh-vacuum techniques to epitaxially grow the single-crystalline layers. Additionally, vdWHs can be stacked in ambient conditions with no requirements of lattice matching. Furthermore, the weak interlayer bonding in vdWHs leads to clean and atomically well-defined interfaces, reducing the detrimental interface scattering effects [27,28]. In addition, van der Waals stacking of different 2D metals opens up the possibilities of controlling plasmons on the atomic length scale and of creating deep-subwavelength metamaterials with unique optical properties that cannot be either found in nature or achieved with conventional heterostructures. For example, the higher degree of confinement and the longer lifetimes of vdWH plasmons accessed in graphene-encapsulated BN crystals [29–31] have stimulated intense efforts to study such collective excitations triggered by the prospect of paving the way for the fabrication of nanophotonic and nanoelectronic devices and components.

We calculate the optical response of MoS$_2$/graphene vdWHs using time-dependent density functional theory (TDDFT). The method successfully predicted the plasmon excitation on the time evolution of the system subject to any external perturbation [13–15,21,32–35]. For example, using TDDFT, Marinopoulos et al [32,33] studied the anisotropic dielectric response of graphite and the optical and loss spectra of carbon nanotubes. The studies of optical spectra in terms of the absolute peak positions and anisotropy effects are consistent with the experiment. Yan et al [34,35] successfully predicted the existence and nature of the end and central plasmon resonances in linear sodium and silver chains. In our study, we focussed on the plasmon excitation in the directions parallel and perpendicular to the MoS$_2$/graphene plane. In our structures, all dangling bonds at the edges are passivated by hydrogen atoms. To obtain experimentally relevant results, the size of the calculated systems should be quite large at approximately 300 atoms. The studied systems have rectangular geometries. The impact of the number of layers on plasmon excitation in graphene was analysed at van der Waals interactions distance of 3–5 Å. Then, we calculate the effect of MoS$_2$ on the collective excitation at the same interlayer distance and compare the results of full first-principles calculations for 1–3 layers.

2. Computational details

All calculations have been carried out using a real-space and real-time TDDFT code. The theoretical foundation of TDDFT calculation have been presented elsewhere [36–38]. The electron–ion interaction was described by norm-conserving Troullier–Martins pseudopotentials. The exchange correlation was treated with Perdew–Burke–Ernzerhof (PBE) formulation of the generalised gradient approximation (GGA) in both the ground state and the plasmon excited state calculations [39,40]. We obtained the information regarding the excitations from the dipole strength function and analysed the excitation spectrum using the Fourier transformation of the dipole strength. The numerical parameters used in the calculations are as follows: the simulation zone was defined by assigning a sphere centred around each atom with a radius of 6 Å and a uniform real-space mesh grid of 0.35 Å, the time step was 0.003 h/eV and the total number of the propagation steps was 6000.

3. Results and discussion

3.1 Plasmon resonances in graphene

We first investigated the plasmon resonances of graphene in our calculations, where we fix the atoms in the XY-plane using Cartesian coordinates. Figure 1 shows the schematic diagram of the rectangular graphene structures, with the top view of the monolayer presented in figure 1a and the side view of the bilayer/trilayer presented in figures 1b and 1c. The armchair edge is parallel to the $X$-axis, while the zig-zag edge is perpendicular to the $X$-axis. To identify the plasmon resonances of the simulated heterostructures, the AA stacked method was used for graphene structures. The induced densities were located in the planes above the top layer of graphenes at a distance of 1.0 Å.

We analysed the resonance absorption spectra of the bilayer graphene nanostructures in the polarisation direction of the $X$-, $Y$- and $Z$-axes, as shown in figures 2. Figure 2b shows an enlarged image of the low-energy resonance region in the shaded area of figure 2a. As observed from figure 2b, the resonance energy does not move with the increase in the layer spacing and the intensity of the resonance absorption
spectrum is almost the same in the low-energy resonance region, indicating that the electrons participating in the resonance do not change with the variation in the layer spacing. The absorption intensity at the layer spacing of 3.0 Å is lower in high-energy resonance region shown in figures 2a and 2b. This is due to the strong electron coupling with small spacing between the two layers that limits the number of electrons that participate in the collective resonance. Near the resonance region of 6 eV, the energy of the resonance increases and is blue-shifted with the increase in the layer spacing. This is marked with circles where resonance energies for layer spacings of 3.0, 4.0 and 5.0 Å are 5.31, 5.64, 5.7 eV and the resonance intensity values are 18.20, 23.4, 26.2(1/eV), respectively. This is because the electron coupling between the layers becomes weaker with the increasing interlayer spacing and the number of electrons participating in the collective excitation increases. However, if the interlayer spacing keeps increasing, the resonance strength will tend to become saturated. At the polarisation direction perpendicular to the graphene plane, the resonance intensity is relatively small and is less than 20(1/eV). It was also found that in the low-energy resonance region, the resonance energy presents a red-shift and the intensity of the resonance absorption spectrum decreases continuously with the increase in layer spacing, indicating that the number of participating resonance electrons decreases with the increase in layer spacing. We also found that the strength of the resonance absorption peak of bilayer graphene (spacing at 5.0 Å) is more than twice that of the monolayer graphene in the same polarisation direction (X/Y-axis).

To better understand the influence of the number of layers on the plasmon resonance of graphene, we also simulated the plasmon resonance of trilayer graphene. The spacings in trilayer graphenes are 3.0 and 4.0 Å, respectively. Figure 3a shows the resonance absorption spectrum for the polarisation direction parallel to the X-axis, while figure 3b shows the spectrum for the polarisation direction parallel to the Y-axis. The intensity of resonance absorption spectrum of the trilayer graphene is more than three times higher than that of the monolayer graphene, indicating that more electrons participate in resonance as the number of layers increases. Comparison of the results for 3.0 and 4.0 Å layer spacing for the polarisation direction in the X(Y)-axis shows that the resonance energy and intensity in the low-energy resonance region are almost unchanged, indicating that the number of electrons participating in the plasmon resonance is almost the same and the layer spacing does not affect the low-energy resonance mode. In the high-energy resonance region, the resonance intensity for 4.0 Å spacing is larger than that for 3.0 Å spacing, indicating that the number of resonance electrons for 4.0 Å spacing is larger than that for 3.0 Å spacing. This can be explained as due to the strong coupling between the electrons limiting the number of electrons participating in the resonance at 3.0 Å spacing. Compared with the polarisation direction in the X-axis, the resonance intensity of the polarisation direction of the Y-axis is higher, and this is related to the boundary configuration.

Figure 4 shows the Fourier-induced charge density for the resonance of bilayer graphene with a layer spacing of 4.0 Å. The induced charge density plane is parallel to the graphene nanostructure for the plane located at a distance of approximately 1.0 Å from the graphene surface. The induced charge distribution obtained using the Fourier transform is given by

$$\Delta \rho(r, \omega) = \frac{1}{T} \int_0^T [\rho(r, t) - \rho(r, 0)] e^{i\omega t} dt,$$

where $T$ is the total evolution time of the wave function and $\omega$ is the resonance frequency. Figures 4a–4c show the induced charge density diagrams for resonance frequencies of 3.65, 5.64 and 16.64 eV when the impulse excitation is polarised in the X-axis. Figures 4d–4f show the induced charge density diagrams for resonance frequencies of 2.19, 5.13 and 16.59 eV when the impulse excitation is polarised in the Y-axis. We found that the induced charge density is mainly distributed in the edge.
Figure 2. Dipole resonance absorption spectra of monolayer and bilayer graphene with different spacings. (a) The polarisation direction parallel to the \(X\)-axis, (c) the polarisation direction parallel to the \(Y\)-axis, (d) the polarisation direction parallel to the \(Z\)-axis and (b) the enlarged image of the low-energy resonance region in the shaded area of (a).

Figure 3. Dipole resonance absorption spectra of trilayer graphene at 3.0 and 4.0 Å layer spacings. (a) Polarisation direction is parallel to the \(X\)-axis and (b) polarisation direction is parallel to the \(Y\)-axis.
Figure 4. The Fourier-induced charge density for the resonance of bilayer graphene with a layer spacing of 4.0 Å. The resonance frequencies are 3.65 eV (a), 5.64 eV (b) and 16.64 eV (c) for the polarised direction in the X-axis. The resonance frequencies are 2.19 eV (d), 5.13 eV (e) and 16.59 eV (f) for the polarised direction in the Y-axis.

region of the graphene nanostructure. This phenomenon is in agreement with the results of Mishchenko et al [41], who studied the plasmon resonance of graphene nanostructures based on the hydrodynamic approach. They indicated that plasmons in graphene nanostructures are limited and are distributed in the edge region of the nanostructures due to the spatially separated electrons and holes in graphene. It is observed from the figure that the direction of the induced charge density resonance is the same as the polarisation direction. When polarised along the X-axis, the direction of the collective excitation of the electron is horizontal, while for the excitation along the Y-axis, the direction of the collective excitation of the electron is also along the vertical direction. It is also found that the induced charge density distribution corresponding to the plasmon resonance mode in the low-energy region has the characteristics of a dipole-like resonance. We attribute this mainly to the fact that the plasmon resonance in the low-energy region is a long-range charge-transfer excitation. Thus, electrons can resonantly oscillate over a long distance along the direction of excitation.

3.2 Plasmon resonances in MoS2/graphene

It is known that vdWHs are different from the conventional heterostructures that are manufactured using two-dimensional materials based on the epitaxial growth technique and where lattice matching is required. The vdWHs are formed by the weak interactions between the layers and do not require lattice matching. It is often possible to form a heterostructure simply by placing one 2D-dimensional material layer directly onto another layer. It was found that the stacking method has little effect on the plasmon resonance. The MoS2/graphene structures used for these calculations are shown in figure 5. We passivated the dangling bonds at the edges with H atoms. The polygonal MoS 2 nanoflakes are already experimentally achievable. Figure 5 shows MoS2/graphene vdWHs used in this study. The plane of the structures is parallel to the x-y plane in the Cartesian coordinates. The grey, white, yellow and blue spheres represent the C, H, S and Mo atoms, respectively. Figure 5a shows the side view and 5b shows the top view of graphene/MoS2 vdWH structures. The sizes of MoS 2 and graphene nanoflakes are nearly the same, and van der Waals force is applied to their interlayer interactions for the interlayer spacings in 3–5 Å.

Figure 6 shows the dipole resonance absorption spectra of bilayer graphene and graphene/MoS2 at 3.0 Å (figures 6a and 6d), 4.0 Å (figures 6b and 6e) and 5.0 Å (figures 6c and 6f) layer spacings, where the upper plane is for the polarisation direction parallel to the X-axis, and the lower plane is for the polarisation direction parallel to the Y-axis. It is observed from the results that there are two plasmon bands in graphene/MoS2 that are located in the high-energy spectral region. The first resonance band is observed at approximately 7.5 eV with a narrow and weak resonance intensity, while the other band is located at energy close to 15 eV with a wide and high resonance intensity. From figures 6a–6c, the resonance energy shows a blue shift for the
Figure 5. (a) The side view and (b) top view of graphene/MoS$_2$ vdWH structures.

Figure 6. Dipole resonance absorption spectra of bilayer graphene and graphene/MoS$_2$. The layer spacings are 3.0 Å (a), 4.0 Å (b) and 5.0 Å (c) in the polarisation direction parallel to the $X$-axis. The layer spacings are 3.0 Å (d), 4.0 Å (e) and 5.0 Å (f) in the polarisation direction parallel to the $Y$-axis.

graphene/MoS$_2$ heterostructure from 5.0 eV at 3.0 Å spacing to approximately 7.5 eV at the 5.0 Å spacing (labelled in the circle). This may be due to the large carrier mobility of MoS$_2$ that allows its electronic behaviour to be tailored. Therefore, the electrons of the surface dangling bonds of the S atom transferred from MoS$_2$ to graphene because the work function of MoS$_2$ is smaller than that of graphene. Compared with bilayer graphene, the resonance energy in the MoS$_2$/graphene structures is red-shifted to approximately 15 eV and the resonance intensity become stronger at 3.0/4.0 Å layer spacing, while the resonance intensity of the two resonance bands of the two systems is almost unchanged at 5.0 Å layer spacing. This phenomenon indicates that
the electrons in MoS$_2$ flow into graphene at 3.0 and 4.0 Å layer spacings, and the delocalised electrons in MoS$_2$ also participate in the $\pi + \sigma$ plasmon resonance. Meanwhile, fewer electrons in graphene transfer at the interface, as the spacing is increased, and the unique resonance mode is maintained at nearly the same energy at 5.0 Å spacings. For the polarisation direction parallel to the $X$-axis, the resonance intensities of the MoS$_2$/graphene structures are almost the same at 4.0 and 5.0 Å layer spacings and are greater than that of the 3.0 Å layer spacing. It is also found that the resonance intensity in the MoS$_2$/graphene structures was larger than that for bilayer graphene at 3.0 and 4.0 Å spacings but is almost the same at 5.0 Å layer spacing. Near the resonance region of 5 eV, the resonance strength of graphene/MoS$_2$/graphene heterostructure is reduced compared to those of bilayer graphene. The introduction of monolayer MoS$_2$ changes the environmental dielectric and effective Fermi level of graphene which is in accordance with the results reported in [42].

The relationship between the resonance frequency and the dielectric constant of the environment is according to the equation: $\omega_{sp} = \omega_p/\sqrt{1 + 3\varepsilon_m}$, where $\varepsilon_m$ is the dielectric constant of the environment.

Figure 7 shows the dipole resonance absorption spectra of trilayer graphene and graphene/MoS$_2$/graphene. The layer spacings are 3.0 Å (a) and 4.0 Å (b) for the polarisation direction parallel to the $X$-axis. The layer spacings are 3.0 Å (c) and 4.0 Å (d) for the polarisation direction parallel to the $Y$-axis.

Figure 8 shows the Fourier-induced charge density for the resonance of MoS$_2$/graphene with a layer spacing of 4.0 Å. The induced charge density plane is parallel to the nanostructure at a distance of approximately 1.0 Å from the graphene surface. The resonance frequency
Figure 8. Fourier-induced charge density for the resonance of MoS$_2$/graphene with a layer spacing of 4.0 Å. The resonance frequencies are 5.64 eV (a), 7.76 eV (b) and 15.5 eV (c), respectively, for the polarised direction in the $X$-axis. The resonance frequencies are 5.13 eV (d), 7.54 eV (e) and 17.0 eV (f), respectively, for the polarised direction in the $Y$-axis.

is 5.64 eV (figure 8a), 7.76 eV (figure 8b) and 15.5 eV (figure 8c), respectively, for the polarised direction in the $X$-axis. The resonance frequency is 5.13 eV (figure 8d), 7.54 eV (figure 8e) and 17.0 eV (figure 8f) for the polarised direction in the $Y$-axis. It is observed that the charge distribution is also consistent with the polarisation direction of our external field and the low-energy resonance region also presents dipole-like characteristics. Comparison of the resonance frequency values of 5.64 and 5.13 eV observed in figure 4 indicates that the amount of electrons involved in the resonance at 5.64 and 5.13 eV in MoS$_2$/graphene is significantly enhanced which is consistent with the analysis described above.

4. Conclusions

A systematic study of plasmon resonance of bilayer and trilayer graphene (MoS$_2$/graphene) based on TDDFT was performed. In graphene structures, the absorption spectra, the absorption structures, the absorption spectra of bilayer/trilayer graphene are almost the same as the monolayer graphene in the low-energy region. We also found that the strength of the resonance absorption peak of bilayer graphene with 5.0 Å layer spacing is more than twice that of the monolayer graphene in the high-energy region. Meanwhile, in the MoS$_2$/graphene structures, two main resonance bands are located in the higher-energy region. The resonance intensity of these bands becomes higher. This is because the electrons in MoS$_2$ flowed into the surface of graphene, leading to a much greater number of electrons participating in the resonance. The induced charge density distribution corresponding to the plasmon resonance mode in the low-energy region has the characteristics of a dipole-like resonance. Our study provides a firm theoretical basis for future experimental observations.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant Nos 11647091 and U1604131).

References