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ARTICLE

Raman Enhancement Effect on Thin GaSe Flake and Its Thickness Dependence

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Chemical enhancement is one of the important mechanisms in surface-enhanced Raman spectroscopy, however, its origin is still under debate. Recently, two dimensional (2D) layered material is thought to be a strong candidate to investigate the chemical mechanism of Raman enhancement because it has flat surface, well defined structure and is without the interference of electromagnetic enhancement. Herein we report the systematic studies of Raman enhancement effect on the gallium selenide (GaSe) flake by using copper phthalocyanine (CuPc) molecule as a probe. It is found that the Raman signal of CuPc on the monolayer GaSe can be significantly increased by one order of magnitude than that on the SiO_2/Si substrate. Moreover, the enhancement effect is found to decrease with increasing the thickness of GaSe flake. The origin of Raman enhancement is attributed to the chemical mechanism resulted from the charge transfer between the GaSe flake and the detected molecules. The supposition is further verified by investigation of the quenching photoluminescence of GaSe as well as the Raman enhancement effect of CuPc with different thicknesses on the GaSe flake. Our work will shed more light on the understanding of the chemical mechanism for Raman enhancement and expand more practical applications of GaSe.

Introduction

Surface-enhanced Raman scattering (SERS) is one of the promising techniques among various spectroscopic methods owing to its ultrahigh sensitivity, molecular specificity and exceptionally analytical capability.[1, 2] Although the origin of SERS effect has been paid great attention for several decades, the most accepted mechanisms are generally classified to electromagnetic mechanism (EM) and chemical mechanism (CM).[3, 4] In theoretical and experimental studies, EM is believed to be related to the enhancement of the excited local electromagnetic fields around metallic structures.[3] By contrast, the underlying mechanism of chemical enhancement is less understanding. This is because that the CM enhancement is many orders of magnitude smaller than that of the EM, leading to that the Raman signal enhanced by the CM is covered up by the EM inevitably.[5] Therefore, it is highly important to explore a new nonmetallic substrate that can only support the CM without the EM.

Two dimensional (2D) materials have attracted much academic

attention for the application in SERS recently, owing to their unique structures and ease of processing.[6, 7] It has been reported that graphene can be used as a CM substrate to enhance the Raman signal of absorbed molecules, which is now designated as the graphene-enhanced Raman scattering (GERS).[8] Moreover, the facile surface modification through either physical or chemical possessing makes the graphene as an ideal substance to deeply study of the mechanism of chemical enhancement.[8] On the one hand, due to its non-polar monolayer structure,[6, 9] the mechanism of Raman enhancement of pristine graphene is generally attributed to the charge transfer.[8, 10] On the other hand, we had previously shown that the enhanced Raman scattering can also be observed on both the graphene oxide and the graphene nanomesh substrate, in which the underlying mechanism is considered to be related to the dipole-dipole interaction between the intrinsic dipoles existed on the substrate surface and the detected molecules.[11, 12] This dipole related mechanism for the Raman enhancement is further demonstrated by h-BN 2D material,[13] because the dipole-dipole interaction can occur on the highly polar monolayer while its insulating character is unable to support the charge transfer process.[14] Besides the graphene and the h-BN, considerable effort has also been put into other 2D materials to understand the CM of Raman enhancement effect. Recently, MoS_2, a semiconducting transition metal dichaldogenide (TMD) composed of S-Mo-S three atomic layers structure, is also found to show the Raman enhancement, and the mechanism is ascribed to the chemical

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enhancement through both the weak charge transfer and dipole–dipole interaction.[13, 15]

In this work, using copper phthalocyanine (CuPc) molecule[16] as a probe, we report for the first time the systematic investigation of Raman enhancement effect on gallium selenide (GaSe), an important p-type 2D semiconducting chalcogenide. With its unique Se-Ga-Ga-Se four-layer structure,[17] it is hopeful to understand more clearly the cause of Raman enhancement by CM. The GaSe flakes with different thickness were prepared through the mechanically exfoliated method and the CuPc molecules were deposited on the GaSe and the SiO_2/Si substrate by the thermal evaporation. We found that, as compared to the SiO_2/Si substrate, the monolayer GaSe can significantly increase the Raman signal of CuPc by as large as fourteen-fold, meanwhile the enhancement effect decreases with increasing the thickness of the GaSe flake. Moreover, we also observed the "first layer effect"[10] behaviour by studying the Raman enhancement of CuPc with different thicknesses on the GaSe flake. Along with the observation of quenching photoluminescence of GaSe, the enhancement effect is attributed to the chemical mechanism resulted from the charge transfer between the GaSe flake and the CuPc molecules. This finding can deepen our understanding of the chemical mechanism for Raman enhancement and strengthen the application of 2D materials.

Results and discussion

The bulk GaSe was prepared with high-purity Ga_2Se_3 (99.99%, Alfa Aesar Company) and Ga (>99.99%, Sigma Aldrich Company) at the molar ratio of 1:1 in an evacuated quartz tube at 950°C.(Detail information is described in the experiment section). The X-ray diffractometer (XRD) result of GaSe and the schematic of its structure are shown in Figure 1a and the inset, respectively. As seen from Figure 1a, the dominant (004) diffraction peak, along with small peaks of (002), (110), (0010) and (0014), indicates that the GaSe is a standard hexagonal phase with high crystalline. Additionally, the lattice constants of the structure can be deduced to a~0.377 nm and c ~ 1.591 nm, the values are well agreement with the previous reports.[18, 19] Figure 1b is the scanning electron microscope (SEM) image of GaSe crystal, from which the layer feature can be observed. The few-layer GaSe flakes with various thicknesses were prepared by the mechanical exfoliation method from GaSe crystal using Scotch tape and transferred onto the SiO_2/Si substrate under vacuum conditions. Figure 1c shows a typical morphology of the GaSe flake observed by atomic force microscope (AFM). As seen, the flake has a smooth surface and its thickness is determined to be about 2.8 nm (inset), corresponding to about 3 layers of GaSe. The structure of few-layer GaSe was further characterized by a transmission electron microscope. As shown in Figure 1d, both the high resolution scanning transmission electron microscopy (STEM) image and the selected area electron diffraction (SAED) pattern further confirm the good crystal quality of the GaSe flake. The lattice

constant of (1 0 0) plane is measured to be ~0.38 nm, also consistent with the XRD result of 0.377 nm. Moreover, with the help of STEM image, the GaSe is determined to be ε-GaSe structure (Supporting Information, Figure S1). In addition, the composition of GaSe flake is determined by the energy dispersive X-ray spectra (EDX) and the atomic ratio of Ga to Se is found to approach to 1 (Supporting Information, Figure S2), indicating the flake has a good stoichiometry.
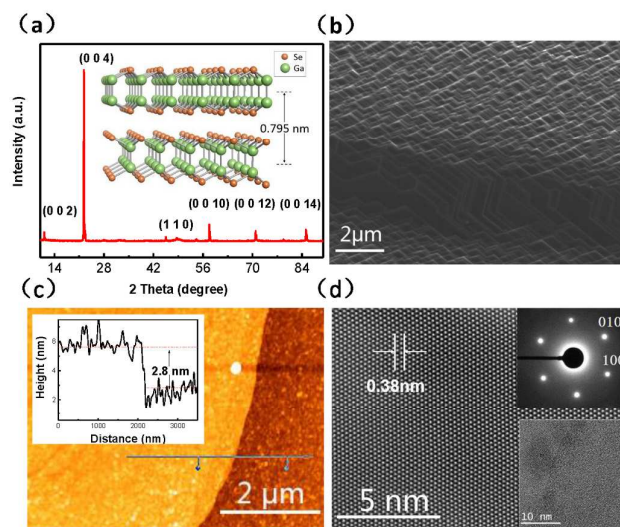

Figure 1. (a) XRD pattern of the GaSe crystal. Inset shows the schematic layer structure of GaSe and the thickness for monolayer. (b) SEM image of GaSe layer structure. (c) AFM image along with a cross-section height profile of few-layer GaSe flake. The height of the flake is about 2.8 nm, corresponding to 3 layers of GaSe. (d) High-resolution STEM image of few-layer GaSe. The lattice constant of (100) plane is ~0.38 nm. Insets are the SAED (top right) and HRTEM image (bottom right).

Figure 2a shows the comparative Raman spectra of GaSe bulk and the flakes with different thickness. The flake thickness was confirmed by AFM (Supporting information, Figure S3). As seen, two out-plane vibration Raman modes of A^1_{1g} (131.4 cm^{-1}) and A^2_{1g} (305.3 cm^{-1}) as well as an in-plane mode of E^1_{2g} (209.3 cm^{-1}) can be observed from the bulk GaSe, which are in agreement with other reports.[20, 21] As the flake thickness decreases, the intensities of A^1_{1g}, E^1_{2g}, and A^2_{1g} modes decrease accordingly. When the flakes with thickness are less than 5 nm, the A^1_{1g} and the E^1_{2g} modes even disappear. At the same time, as shown in the Figure 2b, we find that the peak position of A^2_{1g} mode shows red-shift while its full wave at half maximum (FWHM) increases with decreasing the flake thickness, suggesting that the interaction between neighbouring layers becomes weak for the thin flake.[18, 21]Moreover, a new mode located at about 252 cm^{-1} appears for the 3 nm thick flake. Because both STEM image and SAED pattern (Supporting information, Figure S4) show that the thin GaSe flake with less than 4 layers possesses of a good crystal structure, while the thin GaSe flake is obtained by the mechanical exfoliation from the crystal with good stoichiometry, we consider that the mode at 250 cm^{-1} could not be due to defects or metallic Se in GaSe. Although the

ascription of this mode is unclear at present and required further investigation, we contribute it temporarily to arise from the interplay between the flake and the substrate.[18, 21]
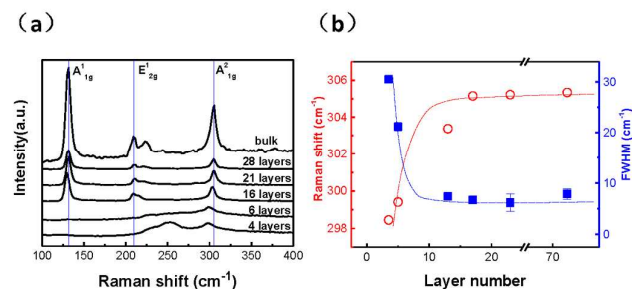

Figure 2. (a) Raman spectra of the GaSe bulk and the flakes with different thickness. The spectra are vertically shifted for clarity. (b) The variation of the peak position (red) and the FWHM (blue) of A^2_{1g} mode with the layer number of GaSe flake. The lines are guides for eye.

We use copper phthalocyanine (CuPc) molecule as a Raman probe in our investigation because of its large Raman scattering cross section and the negligible PL background.[13, 22] The molecules were deposited uniformly on the substrate by the thermal evaporation instead of solution soaking. This can keep the same amounts of molecules on each substrate and allow a reasonable comparison between the different substrates. Figure 3a shows the typical Raman spectra of CuPc with 1nm thickness on the SiO_2/Si (black line) and the monolayer GaSe (red line) under 514 nm excitation, respectively. Clearly, a series of Raman vibration modes of CuPc located at 679, 1141, 1341, 1451 and 1527 cm^{-1} can be observed on both substrates.[23] However, the Raman signals of CuPc on the GaSe substrate are much stronger than those on the SiO_2/Si substrate, suggesting that the monolayer GaSe has obvious Raman enhancement effect. The enhancement can be further visualized directly from the mapping images. Figure 3b and Figure 3c are an optical image of the GaSe flake on the SiO_2/Si substrate and the corresponding Raman mapping image for the 1527 cm^{-1} mode of CuPc, obtained by integrated the intensity of the mode from 1510 cm^{-1} to 1540 cm^{-1}. As seen from Figure 3b, the regions with different thickness of the flake (monolayer, few-layer and multilayer) demonstrate the different optical contrasts clearly. By comparing Figure 3c with Figure 3b, we can find that the thinner the flake, the stronger the Raman intensity. Therefore, we conclude that thin GaSe flake can enhance the Raman signal of probe molecule.

In order to investigate the thickness dependence of GaSe flake for the enhancement effect, a series of flakes with different layers were prepared and 1nm thick of CuPc was deposited on the each flake. The flakes' size is much larger than the spot of the laser to ensure the same excitation condition. Figure 4a shows the high frequency region of Raman spectra of CuPc on the monolayer, few-layer, and multilayer GaSe, while the low frequency region results are shown in Figure S5 (Supporting information). As seen, although the features of the Raman

spectra of CuPc (peak position and FWHM) are nearly the same for all samples, the intensity decreases clearly with increasing the flake thickness. As for the multilayer GaSe, the Raman signal of CuPc is even weaker than that on the SiO_2/Si substrate, which can also be observed from the bottom part of Figure 3c.
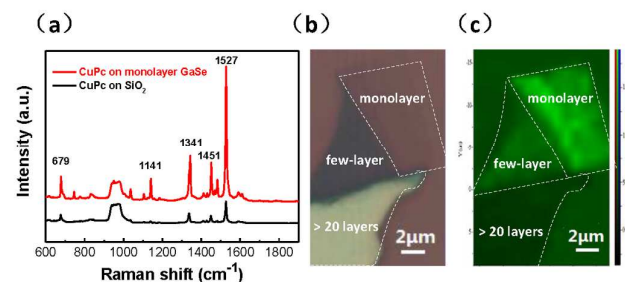

Figure 3. (a) Raman spectra of CuPc deposited on the monolayer GaSe (red line) and the SiO_2/Si substrate (black line) under 514 nm excitation. (b) Optical image of the GaSe flake on the SiO_2/Si. The regions with different thickness (monolayer, few-layer and multilayer) show the different contrasts. (c) Corresponding Raman mapping for the vibration mode of CuPc at 1527 cm^{-1}, in which the strongest intensity is found from the monolayer GaSe region. The lines are guides for eye.

For a more quantitative understanding of the Raman enhancement effect, we calculate the relative enhancement factor (REF), which is defined by the Raman intensity ratio of CuPc on the GaSe flake to that on the SiO_2/Si substrate. The results of REF for several typical Raman peaks of CuPc on the GaSe flake with different thickness are given in Figure 4b. As seen, the tendency of the REF demonstrates two features. First, the value changes with the different Raman vibration modes of CuPc. Taking the monolayer GaSe as an example, the REF varies over a wide range from ~ 3.6 for the 679 cm^{-1} mode to ~14 for the 1141 cm^{-1} mode. This behaviour of the selective Raman enhancement for the specific vibration mode of the detected molecule is frequently observed from other 2D substrates such as the graphene, BN and graphene oxide,[8, 11, 13] but the underlying reason remains unclear at the moment. For the CuPc molecule, it has been reported that the low frequency modes (such as 681, 1141 cm^{-1}) are usually related with the macrocycle breathing vibrations, while the high frequency modes (such as 1341, 1451, 1527 cm^{-1}) are mostly assigned to the stretching or the bending vibrations of the isoindole ring.[24, 25] Considering that the GaSe flake has distinctly different enhancement for 679 cm^{-1} and 1141 cm^{-1} modes of CuPc, we suspect that the enhancement is probably dependent on both the configuration of CuPc on the flake and the special interaction in between for the different vibration modes.[26, 27] Second, being consistent with the observation in Figure 3c, Figure 4b shows a clear character that the REF decreases monotonically with respect to the flake thickness. Taking the 1141 cm^{-1} mode as an example, the REF can reach up to ~14 for the monolayer GaSe but decreases to ~2.8 for the GaSe flake with 12 layer thickness and even becomes less than one when the thickness of GaSe exceeds 20 layers. This behaviour is probably related with that the electronic structure

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of the GaSe flake changes with the thickness,[28] resulting in the variation of chemical enhancement for Raman scattering.
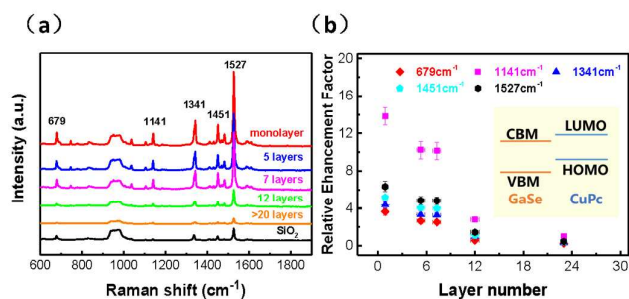

Figure 4. (a) Raman spectra of CuPc deposited on the SiO$_2$/Si substrate and the GaSe flakes with different thickness. The spectra are vertically shifted for clarity. (b) The relative enhancement factors as a function of layer number of GaSe flakes for several typical vibration modes of CuPc. Inset shows the schematic of the charge transfer between CuPc and GaSe.

We now turn to discuss the possible underlying mechanism for the Raman enhancement effect on the GaSe flake. We first consider the change in interference enhancement due to the different thicknesses of GaSe layers used in the experiments. To this end, we calculate the electromagnetic enhancement *via* the multiple-interference from the GaSe and SiO$_2$ layers, and the result is shown in Figure S6 (Supporting information). After compared the calculated result with the experiment data, we can safely conclude that the interference has little influence on the Raman enhancement, which is consistent with previous reports.[8] Secondly, we consider the possible plasmonic EM contribution to the Raman enhancement. GaSe is known as a p-type semiconductor with an indirect bandgap of 2.11 eV.[17, 29] For unintended doped GaSe, the carrier density is less than 10^{17}cm^{-3},[17] and the corresponding frequency of plasmonic resonance is in the infrared region, which is remarkably beyond the investigation range of Raman spectroscopy here. These exclude the EM as the cause for the Raman enhancement on the GaSe flake. On the other hand, since the resonance excitation can also enhance the Raman signal, there is sometimes confusion between the resonant Raman scattering and the chemical enhancement. To rule out the possible cause of the resonance Raman scattering, we further preformed the Raman spectrum of CuPc on the GaSe flake using the excitation light with wavelength of 633 nm, and the result is shown in the Figure S7 (Supporting Information). It is found that, similar to that excited with the wavelength of 514 nm, the Raman enhancement can also be observed on the thin flake of GaSe. Therefore we can safely attribute the cause of the Raman enhancement on the GaSe flake to the chemical mechanism.[8, 13]

As pointed in the aforementioned paragraphs, the chemical mechanism for the Raman enhancement from 2D materials is mainly contributed to either the charge transfer or the dipole-dipole interaction or both. Unlike the h-BN sheet with large intrinsic in-plane polarity and the 2H-MoS$_2$ with weak polarity, GaSe hardly has the polarity due to its unique D$_{3h}$ symmetry

and Se-Ga-Ga-Se four-layer structure.[29] Moreover, it has been predicted that the Raman enhancement based on the dipole–dipole interaction is independent of the thickness of 2D materials,[13] which is in stark contrast to our experimental finding shown in Figure 4b. Consequently, we speculate that the charge transfer between GaSe and CuPc is the most probable chemical mechanism for the Raman enhancement. The presumption can be further understood by considering the electronic structures and energy levels of GaSe and CuPc. It has been known that the positions of the LUMO (lowest-unoccupied molecular orbital) and the HOMO (highest-occupied molecular orbital) of CuPc are at about -3.1eV and -5.1 eV (related to the vacuum energy level), respectively, while the conductive band minimum（CBM）and the valence band maximum（VBM）of GaSe are located at about -5.6 eV and -3.4 eV, respectively.[30, 31] Therefore, as the CuPc molecules contact with the GaSe, the charge transfer can occur between CuPc and GaSe as schematically shown in the inset of Figure 4b, resulting in the chemical Raman enhancement. In order to back up this claim, we measured the photoluminescence (PL) emission of GaSe. As shown in Figure S8 (Supporting Information), under 514 nm laser excitation, we find the significant quenching effect of GaSe after CuPc coating, and the degree of quenching decreases with increasing the thickness of GaSe. The result provides a conceivable evidence for the charge transfer. It is worthy of mentioning that the vibration mode of molecule can frequently be modified by the charge transfer process, leading to the possibly observable spectral shift for the Raman mode consequently.[32] However, as compared to that on the SiO$_2$/Si substrate, we do not find such Raman shift of CuPc mode on the GaSe flake within the uncertainty of the measurement. Note that the spectral shift is obviously dependent on the amounts of the transferred charge, it is therefore not the prerequisite to identify the charge transfer mechanism. In fact, it has been reported that no Raman spectral shift occurs even the chemical mechanism is ascribed to the charge transfer[13].

The proposed charge transfer mechanism can be further validated by the investigation of "first-layer effect".[10] This is because that the charge transfer is a short-range effect and the chemical enhancement follows exponential decay with the distance between the probe molecule and the substrate.[33] To this end, we investigate the Raman enhancement of CuPc with different thicknesses on the GaSe flake. Figure 5a shows the Raman spectra of CuPc with 0.8, 1.0 and 1.6 nm thickness on the thin GaSe flake (6 layers of thickness). It is found that the peak positions of typical Raman signals of 679, 1141, 1341, 1451 and 1527 cm^{-1} of CuPc are the same as those shown in Figure 4a, while the absolute intensities increase with the thickness of CuPc. After normalized the intensity to the thickness of CuPc, we plot the normalized enhancement factor in Figure 5b. As seen, the normalized enhancement factor decreases clearly with increasing the thickness of CuPc. This is also a strong evidence to support the claim of the charge transfer, i.e., the charge transfer occurs dominantly between

the first layer of CuPc molecules and the GaSe flake, and decreases notably for the second or more molecular layers.
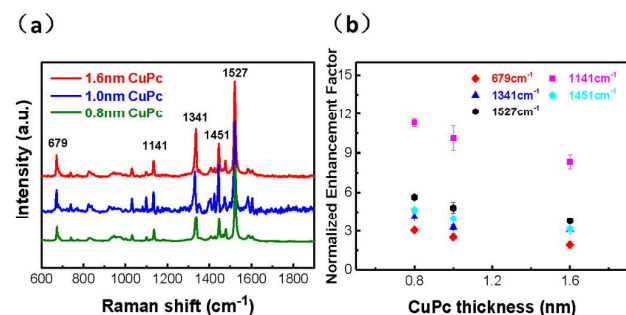

Figure 5. (a) Raman spectra of CuPc with different thickness deposited on 6 layers thick GaSe flake. The spectra are vertically shifted for clarity. (b) Normalized enhancement factors for several typical vibration modes of CuPc.

Experimental

The GaSe laminar precursor was prepared with high-purity Ga_2Se_3 (99.99%, Alfa Aesar Company) and Ga (>99.99%, Sigma Aldrich Company). Ga was mixed with Ga_2Se_3 at the molar ratio of 1:1 and sealed in an evacuated quartz tube under the pressure of $<5\times10^{-2}$ Pa. The mixture was heated to 950°C in 2h and kept for 1h. Then the system was cooled to 850°C in 2h followed by natural cooling. The obtained red-brown GaSe polycrystalline semiconductor has diverse morphologies, most of which are triangular or hexagonal layered structures with mica-like stacking form. The few-layer GaSe flakes were made from a bulk precursor by mechanical cleavage method. The GaSe flake was transferred onto the SiO_2/Si substrate which had been cleaned by acetone or ethanol and dried by flowing nitrogen gas. The thickness of GaSe flake was determined by using atomic force microscopy (AFM, Seiko Instruments, Inc.). The structure and composition of GaSe flake were characterized and analyzed by scanning electron microscopy (SEM, JSM-6301F), X-ray diffractometer (XRD, PHILIPS X'PERT PRO), and transmission electron microscopy (TEM, JEOL-2010F) attached with an energy dispersion X-ray spectroscopy (EDS，JSM-6301F). The CuPc molecules (95%, Alfa Aesar Company), used as the probe, were deposited on the GaSe flake and the SiO2/Si substrate by the thermal evaporation. The deposition thickness of CuPc molecules is controlled using a quartz crystal monitor. Photoluminescence (PL) was collected using a Fluorolog3-TAU. Raman spectra was obtained using a LABRAM-HR Raman spectrometer with the excitation wavelength of 514 nm from Ar+ laser or 633 nm from He−Ne laser. The laser power is about 1mW and attenuated to ~20 μw on the sample surface. The focused laser spot is about 2 μm.

Conclusions

In this study, we for the first time carried out systematic investigation of Raman enhancement effect on the GaSe flake by using CuPc as a probe. The GaSe flakes with different thickness were prepared through the mechanically exfoliated method while the CuPc molecules were deposited on the GaSe flake and the SiO_2/Si substrate by the thermal evaporation. The structural and morphology properties of GaSe have been characterized by XRD, HRTEM, AFM, PL and Raman spectroscopy. It is found that the Raman signal of CuPc on the monolayer GaSe shows much stronger intensity than that on the SiO_2/Si substrate, and the relative enhancement factor can reach up to ~14. Moreover, we find that the enhancement effect decreases with increasing the thickness of GaSe flake. Combined with the observation of "first layer effect" on the Raman enhancement for the CuPc molecules and the significant quenching effect of GaSe after CuPc coating, we attribute the Raman enhancement on the GaSe to the chemical mechanism arisen from the charge transfer between CuPc and GaSe. The results can deepen the understanding of the chemical mechanism for Raman enhancement and expand more practical applications of GaSe.

Acknowledgements

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