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# Structural, electronic and optical properties of hybrid triazine-based graphitic carbon nitride and graphene nanocomposite

Jie Cui<sup>1</sup>, Shuhua Liang<sup>1,\*</sup>, Xianhui Wang<sup>1</sup>, Jian-Min Zhang<sup>2</sup>

<sup>1</sup>*Shaanxi Province Key Laboratory for Electrical Materials and Infiltration Technology, Xi'an University of Technology, Xi'an 710048, P.R. China*

<sup>2</sup>*College of Physics and Information Technology, Shaanxi Normal University, Xi'an 710062, Shaanxi, P.R. China*

The interfacial effect on the structural, electronic and optical properties of hybrid triazine-based graphitic carbon nitride and graphene nanocomposite is calculated by first-principles method. It reveals the favorable stacking pattern utilizing the *Ab initio* thermodynamics approach. The electronic band structure presents that the high carrier mobility is maintained in hybrid g-CN/G nanocomposite, and a moderate band gap is opened by the interactions between g-C<sub>3</sub>N<sub>4</sub> and graphene. Moreover, the opened band gap can be tuned regularly with the interfacial distance. Based on the analysis of the imaginary part of dielectric function of graphene, g-C<sub>3</sub>N<sub>4</sub> monolayer and the hybrid g-CN/G nanocomposite, it is found that hybrid g-CN/G nanocomposite displays enhanced and extended optical absorption compared to simplex graphene and g-C<sub>3</sub>N<sub>4</sub> monolayer.

## I. Introduction

As a stable metal-free photocatalyst, the graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) has been recently considered as a promising photocatalyst for hydrogen production through photoelectrochemical water splitting. Wang et al.<sup>1</sup> reported on a cross-linked g-C<sub>3</sub>N<sub>4</sub> polymeric semiconductor, which can produce hydrogen from water under visible-light irradiation in the presence of a sacrificial donor. Nevertheless, pure g-C<sub>3</sub>N<sub>4</sub> suffers from shortcomings such as rapid recombination of electron-hole pairs, a small specific surface area and a low visible light utilization efficiency.<sup>2-7</sup> In recent years, considerable efforts have been devoted to improve the photocatalytic performance of g-C<sub>3</sub>N<sub>4</sub> and various strategies have been developed to address this issue, including nanostructure engineering,<sup>8,9</sup> metal/non-metal doping,<sup>10-13</sup> and surface coupling hybridization.<sup>14-17</sup>

Due to the outstanding mechanical, thermal, and electrical properties, graphene has been widely used in nanoelectronics, capacitors, and catalysis domains.<sup>18,19</sup> However, the

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\* Author to whom correspondence should be addressed. E-mail address:

liangsh@xaut.edu.cn

the zero-band-gap feature of graphene implies that the current cannot be turned off completely, which is a formidable hurdle to the use in electronic nanodevices. Therefore, it is highly desirable that an opening gap should be introduced in graphene. Recently, several 2D graphene based nanocomposites have garnered particular attention, such as graphene/graphitic carbon nitride,<sup>20-22</sup> graphene/MoS<sub>2</sub> nanosheet,<sup>23-25</sup> graphene/MoSe<sub>2</sub> nanosheet,<sup>26,27</sup> graphene/graphitic ZnO<sup>28</sup> and graphene/graphitic carbon nitride.<sup>16,29</sup> In addition, a universal reversible semiconductor-to-metal transition is observed in some semiconducting bilayer sheets at a critical pressure.<sup>30-32</sup>

As the first metal-free candidate, graphene is preferentially used to construct layered g-C<sub>3</sub>N<sub>4</sub>/graphene nanocomposites in experiments. The heptazine-based g-C<sub>3</sub>N<sub>4</sub>/graphene (g-CN<sup>h</sup>/G) nanocomposite was successfully prepared by Xiang et al.<sup>16</sup>, which can be utilized in visible-light photocatalytic H<sub>2</sub>-production containing Pt as a co-catalyst. The microscopic mechanism underlying the interfacial effects on the properties of interest of g-CN<sup>h</sup>/G nanocomposite has been also recognized from the viewpoint of density functional theory (DFT).<sup>29,33</sup> However, only heptazine-based g-C<sub>3</sub>N<sub>4</sub> was considered in this 2D nanocomposites. In fact, a different allotrope of layered g-C<sub>3</sub>N<sub>4</sub> can also exist.<sup>34-36</sup> The basic building block of this material is a triazine unit (C<sub>3</sub>N<sub>3</sub>) instead of a heptazine unit (C<sub>6</sub>N<sub>7</sub>). Considering the lattice mismatch and the effect of anion- $\pi$  repulsive interaction between g-C<sub>3</sub>N<sub>4</sub> and graphene, the relatively small triazine unit may present some different properties from heptazine unit when composited with graphene, especially for the equilibrium interlayer spacing and the charge transfer between the two layers. Moreover, the different electronic structure behaviors between the two allotropes will display unique optical absorption. Therefore, it would be quite interesting to investigate if the triazine-based g-C<sub>3</sub>N<sub>4</sub> can be used in hybrid with graphene. If it can be used, subsequently, it is of significance to understand the interfacial effect on the structural, electronic and optical properties of triazine-based g-C<sub>3</sub>N<sub>4</sub>/graphene nanocomposite (g-CN/G).

In the present work, the structural, electronic and optical properties of hybrid g-CN/G with different stacking patterns are systematically explored by means of van der Waals (vdW) corrected DFT. It reveals that compared with the heptazine-based g-C<sub>3</sub>N<sub>4</sub>, triazine-based g-C<sub>3</sub>N<sub>4</sub> shows a relatively strong anion- $\pi$  repulsive interaction with graphene, and thus a

larger equilibrium interlayer spacing is presented between the two layers. It is further pointed out that the weaker interfacial interactions associated with the larger equilibrium interlayer spacing resulted in a much smaller band gap opening in graphene. What's more, the hybrid g-CN/G nanocomposite displays enhanced and extended optical absorption compared to simplex graphene and g-C<sub>3</sub>N<sub>4</sub> monolayer.

## II. Calculation methods

Our first-principles calculations were based on DFT implemented in the Vienna ab initio simulation package (VASP) code.<sup>37</sup> The projected augmented wave (PAW) method<sup>38</sup> within the generalized gradient approximation of Perdew, Burke, and Ernzerhof (PBE)<sup>39</sup> was used. Herein, the vdW interaction proposed by Grimme (DFT-D2)<sup>40</sup> was chosen to investigate the physical properties of g-CN/G, due to its good description of long-range. To separate the interactions between neighboring slabs, the periodic boundary conditions with a relatively large vacuum space of about 17 Å were applied. The energy cutoff and convergence criteria for energy and force was set to be 500 eV, 10<sup>-4</sup> eV, and 0.01 eV/Å, respectively. During the optimization, 9×9×1 K-point<sup>41</sup> was adopted, while 15×15×1 was used for total energy calculations. Considering that the PBE functional underestimates the band gaps of semiconductors, the state-of-the-art hybrid functional (HSE06) was used to calculate the electronic structures and optical properties. In the default HSE06 functional, the full PBE correlation energy was added, and 1/4 of the PBE exchange was replaced by the Hartree–Fock exact exchange.

To address the interaction between the g-C<sub>3</sub>N<sub>4</sub> monolayer and graphene, the interface binding energy was calculated using the equation

$$E_b = E_{\text{graphene}} + E_{\text{g-C}_3\text{N}_4} - E_{\text{g-C}_3\text{N}_4/\text{graphene}} \quad (1)$$

where  $E_{\text{graphene}}$ ,  $E_{\text{g-C}_3\text{N}_4}$  and  $E_{\text{g-C}_3\text{N}_4/\text{graphene}}$  are the total energies of the fully relaxed graphene, g-C<sub>3</sub>N<sub>4</sub> monolayer and g-CN/G bilayer, respectively. The positive  $E_b$  denotes that the interface structure of graphene and g-C<sub>3</sub>N<sub>4</sub> layers is stable.

To explore the optical properties of g-CN/G nanocomposite, the frequency-dependent dielectric matrix was calculated. The imaginary part of dielectric matrix was determined by a summation over states according to the following relation<sup>28,29</sup>

$$\varepsilon''_{\alpha\beta} = \frac{4\pi^2 e^2}{\Omega} \lim_{q \rightarrow 0} \frac{1}{q^2} \sum_{c,v,k} 2w_k \delta(\varepsilon_{ck} - \varepsilon_{vk} - \omega) \times \langle \mu_{ck+e_{\alpha}q} | \mu_{vk} \rangle \langle \mu_{ck+e_{\beta}q} | \mu_{vk} \rangle^* \quad (2)$$

where  $\Omega$  is the volume of the primitive cell,  $w_k$  is the  $k$  point weight,  $c$  and  $v$  are the conduction and valence band states, respectively. In the present work, a large number of empty conduction band states (two times more than the number of valence band) and frequency grid points (2000) are adopted.

### III. Results and discussions

The calculated lattice parameters of graphene and g-C<sub>3</sub>N<sub>4</sub> monolayer are 2.47 and 4.78 Å, respectively, which fully agree with previous experimental measurements and theoretical studies.<sup>28,43-45</sup> In order to simulate the g-CN/G nanocomposite, a  $1 \times 1$  unit cell of g-C<sub>3</sub>N<sub>4</sub> (3 carbon and 4 nitrogen atoms) is used to match a  $2 \times 2$  supercell of graphene (8 carbon atoms) with the small lattice mismatch of 3%. Three optimized stacking patterns of the g-CN/G nanocomposite are shown in Fig. 1. To evaluate the structural stability of the three stacking patterns, the interface binding energies are calculated and the results are listed in table 1. The positive binding energy denotes that the interface structure of g-C<sub>3</sub>N<sub>4</sub> and graphene layers is stable. Thus, it can be concluded that pattern I (part of C atoms of g-C<sub>3</sub>N<sub>4</sub> are located above C atoms of graphene, whereas N atoms placed on graphene hollow) is more favorable in energy than other stacking patterns. This is related to the anion- $\pi$  repulsive interaction between graphene and g-C<sub>3</sub>N<sub>4</sub> monolayer. The N anions prefer to be located right above the center of carbon hexagon. In the following sections only the most favorable structure of g-CN/G nanocomposite (pattern I) is considered. Furthermore, as the same as the recent theoretical calculations<sup>22,24,27,29</sup>, a typical vdW equilibrium spacing between g-C<sub>3</sub>N<sub>4</sub> monolayer and graphene of about 3.38 Å is obtained. The hybrid g-C<sub>3</sub>N<sub>4</sub> monolayer and graphene have barely noticeable geometric distortion as a result of the weak vdW interactions between them. It is noted that the equilibrium spacing between triazine-based g-C<sub>3</sub>N<sub>4</sub> and graphene layers is larger than that between heptazine-based g-C<sub>3</sub>N<sub>4</sub> and graphene layers calculated by Du et. al.<sup>29</sup> and Li et. al.<sup>33</sup> This may be responsible for the smaller binding energy (149 meV per unit cell) obtained here. Moreover, the large equilibrium interlayer spacing and the small binding energy imply that g-C<sub>3</sub>N<sub>4</sub> and graphene can be used as ideal

substrates for each other with their intrinsic electronic structures merely undisturbed.

Table 1 Calculated total and binding energies (eV per unit cell) of three different stacking patterns.

|                | graphene | g-C <sub>3</sub> N <sub>4</sub> | g-CN/G   |          |          |
|----------------|----------|---------------------------------|----------|----------|----------|
|                |          |                                 | I        | II       | III      |
| Total energy   | -74.206  | -58.824                         | -133.178 | -133.125 | -133.145 |
| Binding energy |          |                                 | 0.149    | 0.095    | 0.115    |

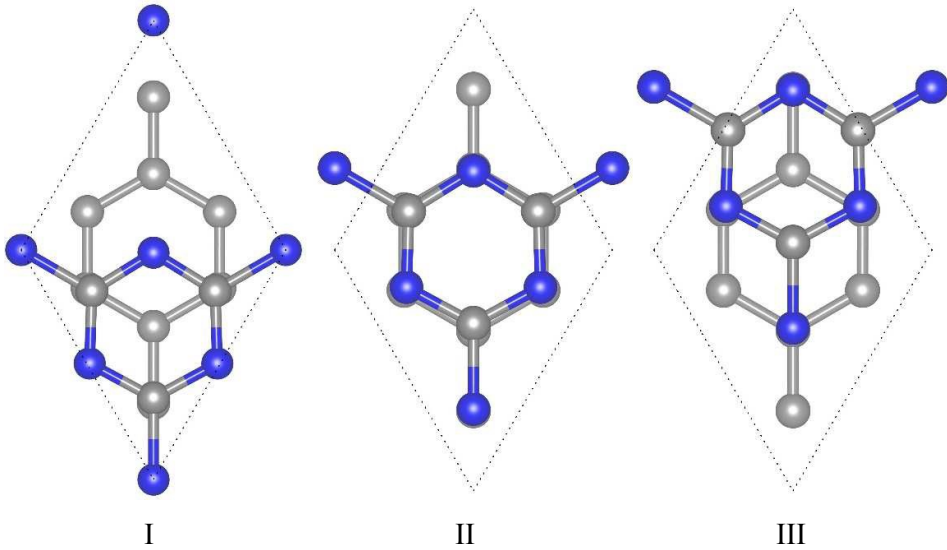


FIG. 1. Three optimized stacking patterns of g-C<sub>3</sub>N<sub>4</sub>/graphene nanocomposite. The gray and blue spheres represent the C and N atoms, respectively. I: C belonged to g-C<sub>3</sub>N<sub>4</sub> layer on top of C belonged to graphene and N on top graphene hollow; II: C and N belonged to g-C<sub>3</sub>N<sub>4</sub> layer on top of C belonged to graphene; III: N on top of C belonged to graphene and C belonged to g-C<sub>3</sub>N<sub>4</sub> layer on top graphene hollow.

Electronic properties of graphene, g-C<sub>3</sub>N<sub>4</sub> monolayer and g-CN/G nanocomposite are calculated utilizing the HSE06 formula and the band structures are plotted in Fig. 2. The Fermi level is marked by the dashed line. From Fig. 2(a), the Dirac cone is located at the K point (1/3, 1/3, 0), showing a linear dispersion relation around the Fermi levels. According to the  $\pi$ -electron tight-binding approximation, the dispersion relation near the Fermi level is approximated as  $E(k) = \pm \sqrt{\Delta^2 + (\hbar v_F k)^2}$ <sup>46</sup>. Here,  $v_F$  is the Fermi velocity, and  $\Delta$  is the onsite energy difference between the two sublattices. For the perfect graphene monolayer, the onset energies of the two sublattices are identical, and thus the energy difference is zero ( $\Delta = 0$ ). The calculated Fermi velocity  $v_F$  is equal to  $0.89 \times 10^6$  m/s at the Dirac cone, which is close to the experimental value ( $10^6$  m/s<sup>47</sup>).

Fig. 2(b) shows that the g-C<sub>3</sub>N<sub>4</sub> monolayer is a kind of direct band gap semiconductor. The

valence band maximum (VBM) and the conductive band minimum (CBM) are both located at the  $\Gamma$  point (0, 0, 0) of the Brillouin zone with a band gap of 3.18 eV. Considering the effect of the quantum confinement effect, the monolayer g-C<sub>3</sub>N<sub>4</sub> should have a slightly larger band gap than the bulk g-C<sub>3</sub>N<sub>4</sub><sup>11</sup>. Previous experimental research shows that the band gap for the bulk g-C<sub>3</sub>N<sub>4</sub> is 3.1 eV<sup>34</sup>, which indicates the HSE06 functional used here can give us an accurate band gap.

Electronic band structure of g-CN/G nanocomposite is shown in Fig. 2(c). The Dirac cone can still be seen at the K point, and dispersion relation near the Dirac cone is almost identical to that of graphene. This finding demonstrates that the high carrier mobility can be well maintained in hybrid g-CN/G nanocomposite. Furthermore, the interactions between g-C<sub>3</sub>N<sub>4</sub> and graphene break the symmetry of graphene layer, giving rise to a nonzero-band-gap. A band gap of 35.6 meV is opened as shown in the enlarged inset around the Dirac cone. The CBM and VBM mainly originate from the  $p_z$  orbitals of C atoms belonged to graphene as shown in Fig. S1. The band gap value opened here is moderately larger than thermal fluctuation (25~26 meV) at room temperature, with potential applications for graphene-based FETs. Compared to the recent calculations<sup>29,33</sup>, the band gap induced by triazine-based g-C<sub>3</sub>N<sub>4</sub> here is much small than that induced by the heptazine-based g-C<sub>3</sub>N<sub>4</sub>. The difference may come from the larger equilibrium interlayer spacing and the smaller interaction between triazine-based g-C<sub>3</sub>N<sub>4</sub> and graphene.

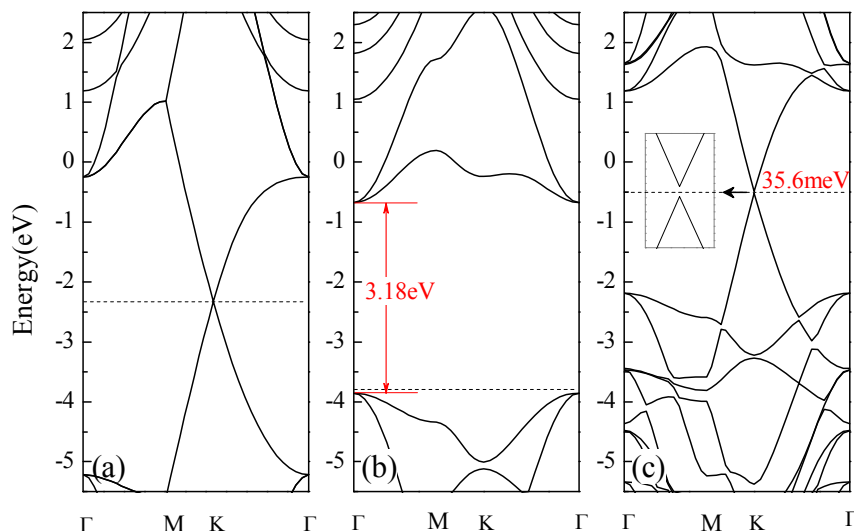


FIG. 2. The band structures of graphene (a), g-C<sub>3</sub>N<sub>4</sub> (b) and hybrid g-CN/G nanocomposite (c). The Fermi level is marked by the dashed line. The band gaps of g-C<sub>3</sub>N<sub>4</sub> and g-CN/G are shown in the inset.

In order to unravel more information about the mechanism of band gap opening for g-CN/G nanocomposite, the charge density difference is investigated by subtracting the electronic charge of a hybrid g-CN/G nanocomposite from that of the free graphene and g-C<sub>3</sub>N<sub>4</sub> monolayer, shown in Fig. 3. The yellow and wathet colors represent charge accumulation and depletion, respectively. It is clear that the electron density around graphene is no longer equivalent, and the charge redistribution is occurred between the two layers and also within the graphene layer. The redistribution drives the interlayer charge transfer from graphene to g-C<sub>3</sub>N<sub>4</sub>, meanwhile the inhomogeneous planar g-C<sub>3</sub>N<sub>4</sub> results in the formation of electron-rich and hole-rich regions within the graphene layer. This phenomenon is also found in some similar graphene based nanocomposite.<sup>29,33,48</sup> Moreover, a polarized field can be generated by the electron-hole puddle, which facilitates the separation of e<sup>-</sup>-h<sup>+</sup> pairs and promotes the photocatalytic activity.

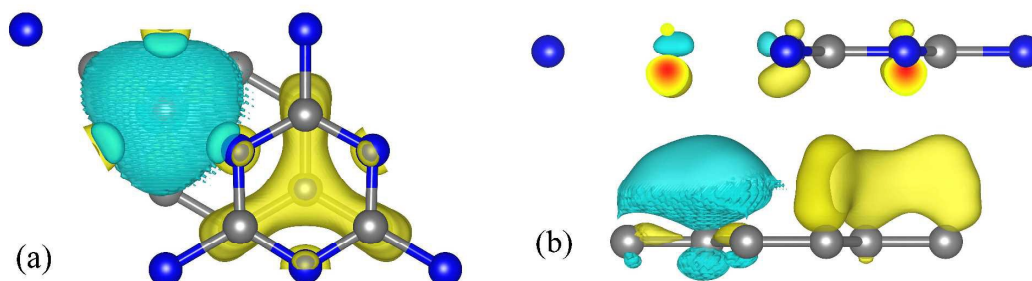


FIG. 3. Top (a) and side (b) views of charge density difference maps of g-C<sub>3</sub>N<sub>4</sub>/graphene nanocomposite for stacking pattern I. Grey and blue spheres represent the C and N atoms, respectively. The yellow isosurface represents positive charge density and the wathet isosurface negative charge density. Isosurface is taken at a value of 0.0001 e/Bohr<sup>3</sup>

It is noted that the induced band gap of dual-gated bilayer graphene are sensitive to external conditions, such as the interfacial distance<sup>20,22</sup> and external electric field<sup>49</sup>. The band gap of the hybrid g-CN/G nanocomposite in response to interfacial distance is plotted in Fig. 4. Generally, the band gaps increase obviously with the decrease in interfacial distance. Of physical reasons, the band gap has an exponential dependence on the interfacial distance, and the fitting form is  $y = a - b \times c^x$ . The values of constant a, b, and c are -1.02, 260515.35 and 0.07, respectively. Moreover, the band gap can also be tuned by the external electric field, as the diagram plotted in Fig. S2.

On the basis of the  $\pi$ -electron tight-binding model, the electron effective mass of hybrid g-CN/G nanocomposite at Dirac cone is proportional to the band gap, and is expressed as  $|m^*| \approx E_g / 2v_F^2$ . This is well confirmed by our calculation of the variation of the effective masses relative to the band gap, as shown in the inset of Fig. 4. A linear relationship between  $m^*/m_e$  and band gap is obtained.

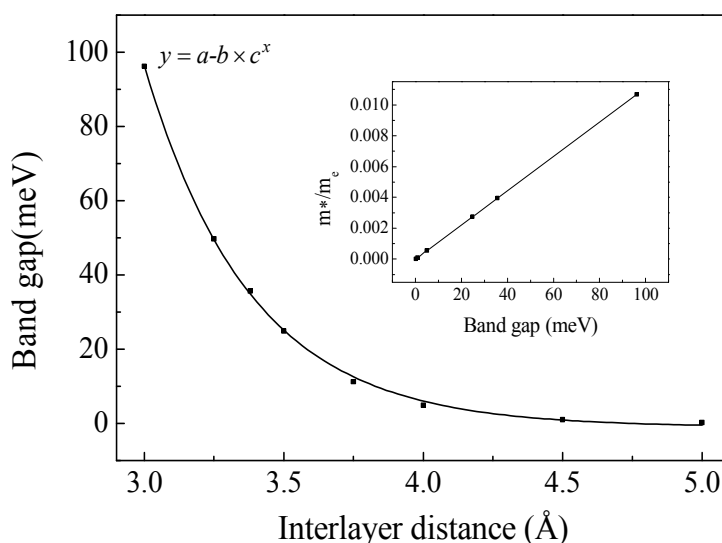


FIG. 4. Variation in the energy gap of hybrid g-CN/G nanocomposite as a function of the interfacial distance. The variation of the effective masses relative to the band gap is shown in the inset.

To explain the variation in band gap as a function of interfacial distance, the change in charge transfer between the layers as well as in graphene layer, with interfacial distance is investigated. The electrostatic potentials of g-CN/G nanocomposite at different interfacial distances are calculated and plotted in Fig. S3, where the graphene layer is fixed and only the g-C<sub>3</sub>N<sub>4</sub> layer is moved along Z direction. It is seen that with the interfacial distance decreased, the energy levels of g-C<sub>3</sub>N<sub>4</sub> and graphene shift up and down, respectively, indicating that there will be an overlap of electronic states between g-C<sub>3</sub>N<sub>4</sub> and graphene. Meanwhile, the tunneling energy barrier for electrons within the g-CN/G interface is reduced with the distance decreased. To investigate the change in charge transfer within the graphene layer, charge density differences within graphene at different interfacial distances are calculated and shown in Fig. S4. It is found that the charge transfer within graphene layer will be enhanced by the decreased interfacial distance. Given these findings, the asymmetry of electron density around graphene becomes more evident with the decrease in interfacial distance, which

resulted in the tunable band gap.

To clarify the interfacial effect on the optical properties of hybrid g-CN/G nanocomposite, the dielectric functions of the graphene, g-C<sub>3</sub>N<sub>4</sub> monolayer and the hybrid g-CN/G nanocomposite are calculated at the HSE06 level, and the imaginary parts of dielectric function for the polarization vector perpendicular to the interface are shown in Fig. 5. Generally, the optical absorption of graphene is mainly from the electronic transitions from  $\pi$  to  $\pi^*$  and  $\sigma$  to  $\sigma^*$  states. As seen from Fig. 5(a), absorption lines in the UV spectrum, which is in good agreement with the results by Hu et al.<sup>28</sup>

It is believed that the optical absorption behavior of a semiconductor is strongly related to its electronic structure. Since the hybrid g-CN/G nanocomposite have interlayer coupling, new optical transitions may induced. As the same as other 2D nanocomposites, hybrid g-CN/G structure has the better optical absorption in the visible region, see Fig. 5(c). Compared with the g-C<sub>3</sub>N<sub>4</sub> monolayer (Fig. 5(b)), hybrid g-CN/G nanocomposite exhibits more effective UV absorption and enhanced visible light response. This can be understood by the fact that the interlayer coupling has modified the orbital, thus electrons can now be directly excited between graphene and g-C<sub>3</sub>N<sub>4</sub> monolayer.

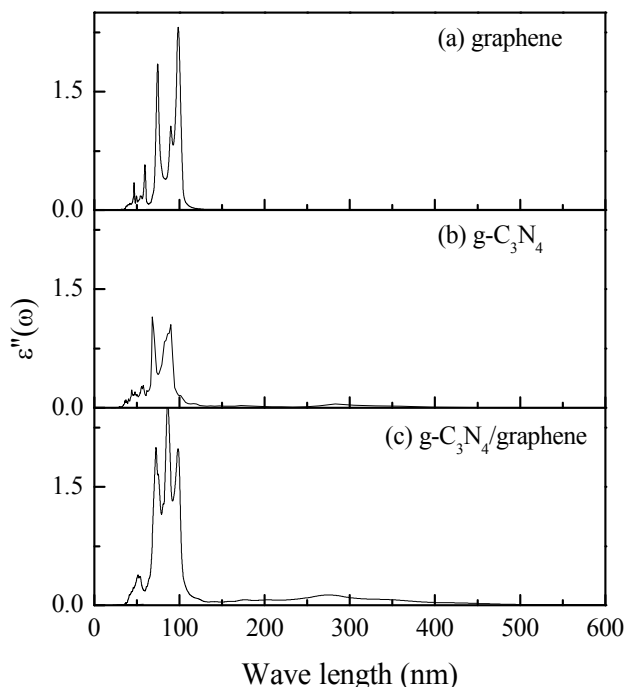


FIG. 5. Imaginary part of dielectric function of graphene (a), g-C<sub>3</sub>N<sub>4</sub> monolayer (b) and the hybrid g-CN/G nanocomposite (c) for the polarization vector perpendicular to the surface.

## IV. Conclusion

In the present work, the structural, electronic and optical properties of hybrid g-CN/G nanocomposite are studied at the HSE06 level. Three possible stacking patterns of g-CN/G nanocomposite are considered. The results show that the pattern I (part of C atoms of g-C<sub>3</sub>N<sub>4</sub> are located above C atoms of graphene, whereas N atoms placed on graphene hollow) is more favorable in energy than other stacking patterns. The high carrier mobility is maintained in hybrid g-CN/G nanocomposite, and a moderate band gap is opened in graphene. Moreover, the opened band gap can be tuned regularly with the interfacial distance. By analyzing the imaginary part of dielectric function of graphene, g-C<sub>3</sub>N<sub>4</sub> monolayer and the hybrid g-CN/G nanocomposite, it is found that the hybrid g-CN/G nanocomposite displays enhanced and extended optical absorption compared to simplex graphene and g-C<sub>3</sub>N<sub>4</sub> monolayer.

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