Encapsulated layer induces boundary effect and twist angle adjust absorption in h-BN/graphene/h-BN heterostructure

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Abstract
This work studied the optical absorption properties and electronic properties of graphene nanosheets encapsulated in h-BN at different twisted angles based on first principles. UV–Vis spectrum shows that compared with the monolayer graphene nanosheets, the absorption’s peak of the encapsulated graphene nanosheets show a red shift and its molar absorption coefficient decreased significantly. The molar absorption coefficients of h-BN/graphene/h-BN heterostructures show an increasing trend when the graphene nanosheets are twisted relative to the packaging layer (twisted angles are 0°, 15°, 21.8°, 27.8° and 30°, respectively). More curiously, charge density difference (CDD) indicates that the region of electron aggregation in excited state mainly occurs at the centre of graphene nanosheets due to the introduction of h-BN packaging layer. The smoothed isosurface diagram of electron hole pairs shows that the distribution breadth of electron hole pair density decreases compared with that before encapsulation, and the distribution breadth of electron increase is larger than that of hole. With the increase of twisted angles, the distribution breadth of electron hole pair density increases gradually. Both CDD and smoothed isosurface diagram show that the system has strong boundary effect. This provides a method to adjust the photoelectric properties of graphene nanosheets by using different twisted angles, and provides a theoretical basis for its application in the field of micro-nano optoelectronics.

1. Introduction
Graphene nanoribbons (GNRs) [1, 2], graphene quantum dots (GQDs) or graphene nanosheet [3], twisted bilayer graphene (TwBLG) and its heterostructures can not only adjust the energy band structure of zero band gap [4–8], but also present novel physical properties superior to 2D graphene materials [9–12] (superconductivity, topology, fractional quantum Hall effect and so on). These physical properties make the above-mentioned micro-nano materials extremely widely used in the field of optoelectronics [13–18]. Due to novel properties such as size effect, edge effect and fractional quantum Hall effect, [19–21] GQDs exhibit excellent optical and electrical properties (Kondo Effect) in terms of optics and electricity [22–28]. On the other hand, h-BN as a substrate for preparing graphene can not only open the band gap of graphene, but also has a relatively small impact on the physical properties of graphene [29, 30]. As a material for encapsulating GQDs, h-BN with insulating properties protects the graphene nanosheet from interference from external factors and maintains their excellent physical properties. There are many studies showed that the properties of graphene and h-BN nanostructures are quite different from those of 2D graphene sheets, and the combination of h-BN and graphene quantum dots can greatly affect the electronic properties of graphene quantum dots [31–36]. The band gap of monolayer graphene is adjustable when it is sandwiched between two layers of h-BN [37]. In this work, graphene nanosheet or nanosheet encapsulated by h-BN are selected to conduct preliminary research on the properties of the h-BN/graphene/h-BN heterostructure, and then we theoretically explain the physical mechanism of the UV–Vis spectrum of different twisted angle systems.

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H-BN is usually used as an encapsulation material for graphene in optoelectronic applications because its optical response is in the ultraviolet region, and there is no light interaction with graphene\[38\]. Therefore, it can be well used as a material for protecting graphene. However, with the development of corner electronics, the underlying physical mechanism of the light-matter interaction in the corner situation between h-BN and graphene remains unclear\[39\]. This is very important for designing new thermally stable and graphene-based optoelectronic materials.

This paper also systematically analyzes the electronic excitation characteristics of graphene nanosheet with different twisted angles. It has theoretical guiding significance for the study of optical characteristics of similar packaging systems.

2. Methods

We constructed a regular hexagon h-BN quantum dot system with a side length of 13 atoms and a regular hexagon C quantum dot system with a side length of 7 atoms, and constructed the h-BN/graphene/h-BN heterostructure by encapsulating a single layer of graphene in a double layer of h-BN. Between the two h-BN nanosheets in the paper is AA stacking. First, double-layer h-BN nanosheets and single layer graphene nanosheets are stacked and coupled between layers. The three are stacked together by van der Waals forces between layers. Secondly, keeping the positions of the upper and lower layers of h-BN unchanged, rotating the single layer graphene nanosheet in the middle layer counterclockwise. The twisted angles are 0°, 15°, 21.8°, 27.8°, and 30°, and finally five different structures of h-BN/graphene/h-BN heterostructure are obtained (figures 1(a)–(f)).

This paper combines xtb\[40\] and Gaussian 16\[41\] software to optimize the constructed system. The GFN2-XTB program is used to calculate the energy and gradient of the system, and Gaussian 16 is used to calculate the Hessian matrix. The GFN2-XTB program has fast calculation speed, good accuracy and universal applicability, and is suitable for structural optimization of huge systems. In relaxation calculation, XTB program is much faster than TDDFT with Hybrid Functionals in Gaussian. Next, the electron excitation of the system is calculated by Gaussian 16 program using time-dependent density functional theory (TDDFT)\[42\] and cam-B3LYP\[43\] functional in conjunction with STO-3G basis set. All wave function analysis in this work is calculated by Multiwfn 3.7 program\[44\]. The transition data obtained by theoretical calculation were expanded into peak form and UV–Vis spectra were obtained. The spectrum is expressed by the molar absorption coefficient in L/mol/cm, where the Gaussian broadening function is:

\[
G(\omega) = \frac{1}{c\sqrt{2\pi}} e^{-\frac{(\omega - \omega_1)^2}{2c^2}}, \quad c = \frac{\text{FWHM}}{2\sqrt{2 \ln 2}}\]

where \(\omega\) is the abscissa of the spectrum, \(\omega_1\) is the transition energy, and FWHM is the full width at half maximum.

The distribution of the holes describes where the excited electron comes from, and the distribution of the electrons describes where the excited electron goes. Charge differential density diagram (CDD) was drawn by VMD program\[45\]. The hole distribution (\(\rho_{\text{hole}}\)) and the electron distribution (\(\rho_{\text{ele}}\)) both are divided into two parts: the local term and the cross term, the local term reflects the contribution of the configuration function itself, and the cross term reflects the coupling between the configuration function on the hole and electron distribution. ‘Index’ is a physical quantity that describes the distribution of electron holes. The calculation of...
electron and hole distributions (charge difference density) is expressed by the following formula:

\[
\begin{align*}
\rho_{\text{hole}}(r) &= \rho_{\text{loc}}^{\text{hole}}(r) + \rho_{\text{cross}}^{\text{hole}}(r) \\
\rho_{\text{loc}}^{\text{hole}}(r) &= \left[ \sum_{i \rightarrow a} (\omega_i^a)^2 \phi_i \phi_a - \sum_{i \leftarrow a} (\omega_i^a)^2 \phi_i \phi_a \right] \\
\rho_{\text{cross}}^{\text{hole}}(r) &= \left[ \sum_{i \rightarrow a \ j \rightarrow a} \omega_i^a \omega_j^a \phi_i \phi_j - \sum_{i \leftarrow a \ j \leftarrow a} \omega_i^a \omega_j^a \phi_i \phi_j \right] \\
\rho_{\text{ele}}(r) &= \rho_{\text{loc}}^{\text{ele}}(r) + \rho_{\text{cross}}^{\text{ele}}(r) \\
\rho_{\text{loc}}^{\text{ele}}(r) &= \left[ \sum_{i \rightarrow a} (\omega_i^a)^2 \phi_i \phi_b - \sum_{i \leftarrow a} (\omega_i^a)^2 \phi_i \phi_b \right] \\
\rho_{\text{cross}}^{\text{ele}}(r) &= \left[ \sum_{i \rightarrow a \ j \rightarrow b} \omega_i^a \omega_j^b \phi_i \phi_b - \sum_{i \leftarrow a \ j \leftarrow b} \omega_i^a \omega_j^b \phi_i \phi_b \right]
\end{align*}
\]

where \( r \) is the coordinate vector, \( \phi \) is the orbital wave function, \( i \) or \( j \) is the occupied orbital label, and \( a \) or \( b \) is the empty orbital label. For TDDFT, each configuration function can have the coefficient \( \omega \) either as an excitation configuration or a coefficient \( \omega \) as a deexcitation configuration.

\( S_m \) and \( S_r \) are the definitions to describe overlap. \( S_m \) is the minimum value of holes and electrons taken, and \( S_r \) is the average value of holes and electrons taken. They can be expressed by the formula:

\[
S_m \index = \int S_m(r) \ dr \equiv \int \ min \ [\rho_{\text{hole}}(r), \rho_{\text{ele}}(r)] \ dr
\]

\[
S_r \index = \int S_r(r) \ dr \equiv \int \sqrt{\rho_{\text{hole}}(r) \rho_{\text{ele}}(r)} \ dr
\]

The distance between the hole and the electron center of mass is measured by the \( D \) index. The degree of hole and electron separation can be measured by \( t \) index:

\[
D_{x} = |X_{\text{ele}} - X_{\text{hole}}|  \\
D_{y} = |Y_{\text{ele}} - Y_{\text{hole}}|  \\
D_{z} = |Z_{\text{ele}} - Z_{\text{hole}}|  \\
D \index = \sqrt{(D_x)^2 + (D_y)^2 + (D_z)^2}
\]

\( t \) index = \( D \) index - \( H_{CT} \)

\( H_{CT} \) refers to the average extension degree of hole and electron in the direction of CT.

Hole delocalization index and electron delocalization index are represented by HDI and EDI respectively. They represent the degree of delocalization of electrons and holes. The smaller the HDI (EDI) value is, the higher the degree of hole (electron) delocalization is, that is, the more uniform the distribution is. The calculation formula of HDI and EDI is as follows:

\[
HDI = 100 \times \sqrt{\int |\rho_{\text{hole}}(r)|^2 \ dr}
\]

\[
EDI = 100 \times \sqrt{\int |\rho_{\text{ele}}(r)|^2 \ dr}
\]

3. Results and discussion

Single photon absorption intensity can be expressed by oscillator strength. Theoretical calculation results show that the strongest peaks of the six heterostructures are mainly contributed by \( S_3 \) (the third excited state), it shows that the oscillator strength of the six structures is the maximum when the third excited state is used (figure 2(a)), so we choose the third excited state as the research object. Due to the influence of the encapsulated h-BN, the absorption spectra of single layer graphene nanosheet and h-BN/graphene/h-BN heterostructure are very different (figure 2(a)). Compared with the single layer graphene nanosheet, the UV–Vis spectrum of h-BN/graphene/h-BN heterostructure shows a significant red-shift (figure 2(a)). This interlayer coupling structure increases the conjugation of graphene, resulting in closer energy levels between the lowest unoccupied and highest unoccupied orbitals. This results in lower excitation energy between the two, reduced vibrator strength and a longer wavelength of light corresponding to the packaged system. Hence the phenomenon of red shift and reduced intensity of \( S_3 \).

The red-shift of this absorption peak changes with the twisted angle (figure 2(b)). In the visible range, molar absorption coefficient of single layer graphene nanosheet is significantly higher than that of h-BN/graphene/h-
BN heterostructure. Compared to a single layer of graphene nanosheet, the absorption peak of h-BN/graphene/h-BN heterostructure has a significant red-shift. After twisting the encapsulated graphene nanosheet to a certain angle, the molar absorption coefficient shows an upward trend. However, the molar absorption coefficient of h-BN/graphene/h-BN heterostructure is always lower than that of single layer graphene nanosheet. The molar absorption coefficients of h-BN/graphene/h-BN heterostructure with twisted angles of 0°, 15°, 21.8°, 27.8°, and 30° increase sequentially. The absorption curves of h-BN/graphene/h-BN heterostructure with twisted angles of 27.8° and 30° basically coincide.

In order to observe the UV–Vis spectra of each structure more clearly, we have drawn the UV–Vis spectrum of six structures and investigated the intensity and optical absorption characteristics of the excited state corresponding to each structure after the angle change. Figures 3(b)–(f) respectively represent the UV–Vis spectrum of the h-BN/graphene/h-BN heterostructure with different twisted angles. It is different for the UV–Vis spectra of h-BN/graphene/h-BN heterojunctions with different twist angles. Their UV–Vis spectra are mainly concentrated in the visible region.

As shown in figure 4, by drawing the TDM diagram and the CDD diagram, we analyzed the electronic excitation characteristics of the h-BN/graphene/h-BN heterostructure with different twisted angles. In the TDM Figure, X and Y axes respectively represent the atomic numbers excluding hydrogen atoms. First, we compare the electrons and holes distribution of single layer graphene nanosheet and h-BN/graphene/h-BN heterostructure. It can be seen from the CDD diagram that before encapsulating, electrons and holes are uniformly distributed on the surface of the single layer graphene nanosheet. In the TDM diagram of single layer...
graphene nanosheet, the transition density is mainly concentrated on the diagonal. This phenomenon also indicates that the electrons and holes of single layer graphene nanosheet are locally excited. After encapsulation, the holes are mainly concentrated at the edges of the graphene nanosheet. It indicates that the boundary effect of the graphene nanosheet is strengthened after the encapsulation. That is to say the electrons of the monolayer graphene nanosheet are evenly distributed on the surface of the graphene nanosheet. With the addition of h-BN packaging layer, the electrons around graphene are concentrated inward, resulting in an obvious boundary effect. The TDM diagram shows that the transition density is not only on the diagonal, but the other parts also have significant electronic excitation characteristics. Therefore, the excitation characteristics of graphene nanosheet after encapsulation are changed from local excitation to an excitation mode combining local excitation and charge transfer excitation due to the energy difference.

Secondly, we compare the electrons and holes distribution of h-BN/graphene/h-BN heterostructure rotated at different angles. According to the CDD diagram, it can be found that the different twisted angles of

Figure 4. (a) Charge density difference (CDD) diagram of single layer graphene nanosheet. (b) The transition density matrix (TDM) diagram of single layer graphene nanosheet. The top of CDD of h-BN/graphene/h-BN heterostructure with twisted angles of 0° (c), 15° (g), 21.8° (k), 27.8° (o) and 30° (s) picture. CDD side of h-BN/graphene/h-BN heterostructure with twisted angles of 0° (d), 15° (h), 21.8° (l), 27.8° (p) and 30° (t) view. (e,i,m,q,u) The enlarged view of the graphene quantum dot in the top view of the CDD diagram. TDM images of h-BN/graphene/h-BN heterostructure with twisted angles of 0° (f), 15° (j), 21.8° (n), 27.8° (r) and 30° (v). In the CDD diagram, green represents holes, pink represents electrons, and the isosurface is set to 0.0005.
graphene nanosheet relative to h-BN also have a certain influence on the distribution of electrons and holes. The electron hole distribution of heterostructures with different rotation angles is obviously different. The CDD diagram corresponds to the data in table 1. Take the $S_m$ index, which represents the degree of overlap of electron holes. The rotation angle of the two-layer h-BN relative to graphene is $0^\circ, 15^\circ, 21.8^\circ, 27.8^\circ$ and $30^\circ$, respectively, and the $S_m$ indices are $0.84, 0.87, 0.90, 0.96, 0.92$, respectively. The difference between them is very obvious. The greater the angle difference, the greater the $S_m$ index difference, that is, the greater the overlap degree difference of electron holes. Therefore, we can adjust the electronic excitation characteristics of electrons and holes by encapsulating graphene nanosheet.

The Chole and Celé diagram can more clearly observe the electrons and holes distribution trend. As shown in figure 5, the electrons and holes of the single layer graphene nanosheet are circular, and the two completely overlap, indicating that the electrons and holes are uniformly distributed on the single layer graphene nanosheet. It is exactly in line with the above description. When graphene nanosheet is encapsulated in a double-layer h-BN, the distribution breadth of electrons and holes are reduced, and the distribution breadth of electrons is greater than that of holes. After the graphene nanosheet is rotated to a certain angle, the distribution breadth of electron and holes show a similar trend.

The numerical value of $S_m$ and $S_r$ represents the degree of overlap of electrons and holes. Their value range is $[0, 1]$. The larger their index, the higher the degree of overlap between holes and electrons. It can be clearly seen in table 1 that the $S_m$ index and $S_r$ index of h-BN/graphene/h-BN heterostructure are smaller than that of single layer graphene nanosheet. The changing trend of this index shows that the electron-hole separation effect of h-BN/graphene/h-BN heterostructure is more obvious than that of single layer graphene nanosheet. It can be seen from table 1 that for twisted angles of $0^\circ, 15^\circ, 21.8^\circ$ and $27.8^\circ$, the $S_r$ index shows an increasing trend. It shows that in these four angles, the degree of overlap of electrons and holes is showing an increasing trend. $t$ index represents the degree of separation of holes and electrons. When the $t$ index is greater than 0, it indicates that the separation effect of electrons and holes is more obvious. The above conclusion can also be found by comparing the size of $t$ index. The smaller the value of Hole delocalization Index (HDI)/Electron delocalization Index (EDI), the higher the degree of electron and hole delocalization. It can be clearly seen from table 1 that the electron and hole delocalization index of single layer graphene nanosheet is greater than that of

| Index | $0^\circ$ | $15^\circ$ | $21.8^\circ$ | $27.8^\circ$ | $30^\circ$ |
|-------|---------|---------|---------|---------|---------|
| $D_{index}$ | 0.00    | 0.26    | 0.17    | 0.10    | 0.12    | 0.14    |
| $t$ index | $-3.31$ | $-4.57$ | $-4.61$ | $-4.78$ | $-4.69$ | $-4.65$ |
| $S_m$ index (a.u.) | 0.87    | 0.68    | 0.74    | 0.77    | 0.82    | 0.79    |
| $S_r$ index (a.u.) | 0.97    | 0.84    | 0.87    | 0.90    | 0.96    | 0.92    |
| Excited Energy (eV) | 3.05    | 2.70    | 2.79    | 2.74    | 2.79    | 2.80    |
| $\Delta \sigma$ (Angstrom) | 0.02    | $-0.29$ | $-0.21$ | $-0.27$ | $-0.29$ | $-0.29$ |
| HDI    | 3.10    | 2.57    | 2.62    | 2.71    | 2.79    | 2.69    |
| EDI    | 3.24    | 2.81    | 2.8    | 2.89    | 2.95    | 2.82    |

Figure 5. (a) Chole and Celé image of single layer graphene nanosheet. (b)–(f) The Chole and Celé diagram of h-BN/graphene/h-BN heterostructure with twisted angles of $0^\circ, 15^\circ, 21.8^\circ, 27.8^\circ$ and $30^\circ$.  

Table 1. Index values of single layer graphene nanosheet and h-BN/graphene/h-BN heterostructure rotated at different angles.
h-BN/graphene/h-BN heterostructure. Therefore, the electrons and holes of the h-BN/graphene/h-BN heterostructure are more delocalized, which further illustrates the boundary effect of the encapsulated graphene nanosheet.

In order to analyze the essential characteristics of electronic transitions, we examined the contribution of each pair of MO transitions to electronic excitation (Table 2). The electron excited transition contribution of the six structures is dominated by the transition from HOMO and HOMO-1 to LUMO and LUMO + 1. Through calculation, it is found that HOMO and HOMO-1, LUMO and LUMO + 1 are degenerate respectively. It shows that the transition of HOMO to LUMO and LUMO + 1 is equivalent, and the transition of HOMO-1 to LUMO and LUMO + 1 is equivalent. Therefore, it shows that in each structure, the properties of the two pairs of transition orbitals that mainly contribute to it are the same. This transition contribution can be more intuitively observed in spatial localization of HOMO/LUMO states (Figure 6).

Table 2. Contribution of different orbital transitions.

| Twisted angle of Graphene nanosheet | Excited state | Pathway | Rate of contribution (%) |
|-------------------------------------|--------------|---------|--------------------------|
| Single layer graphene nanosheet     | S1           | HOMO-1 > LUMO + 1 | 49.179                   |
|                                     |              | HOMO > LUMO      | 49.175                   |
| 0°                                 | S1           | HOMO-1 > LUMO + 1 | 44.353                   |
|                                     |              | HOMO > LUMO      | 44.351                   |
| 15°                                | S1           | HOMO-1 > LUMO + 1 | 47.162                   |
|                                     |              | HOMO > LUMO + 1  | 47.162                   |
| 21.8°                              | S1           | HOMO-1 > LUMO + 1 | 49.011                   |
|                                     |              | HOMO > LUMO      | 49.005                   |
| 27.8°                              | S1           | HOMO-1 > LUMO + 1 | 44.363                   |
|                                     |              | HOMO > LUMO      | 44.333                   |
| 30°                                | S1           | HOMO-1 > LUMO + 1 | 46.554                   |
|                                     |              | HOMO > LUMO      | 46.540                   |

Figure 6. The (spatial) localization of HOMO/LUMO states.

For typical two-dimensional heterostructures, the structure of materials has a certain influence on their energy [46–48]. We calculated the single point energies of H-BN/Graphene/H-BN Heterostructure at different rotation angles (Table 3). By observing the single point energy at different angles, we can find that the energy...
peaks between the rotation angle of 15° and 27.8°. So we assume that the energy changes periodically as the Angle increases. So our next work can explore more angles of rotation to prove that it changes periodically.

4. Conclusions

Based on the first principles, we specifically studied the optical absorption characteristics and the physical mechanism of the twisted angle-modulated graphene nanosheet encapsulated by h-BN. When the graphene nanosheet in the middle layer and the h-BN encapsulation layer are relatively twisted, the UV–Vis spectra of the h-BN/graphene/h-BN heterostructure systems with different twist angles are different. Compared with the UV–Vis spectrum of single-layer graphene nanosheets, the molar absorption coefficient of the h-BN/graphene/h-BN heterostructure with different twist angles will be smaller, but the strong tendency of charge transfer appears in the edge area of the graphene nanosheet, so that the system presents an obvious boundary effect. Moreover, the symmetry of the charge density distribution of the graphene nanosheet is also broken. Our research explains the physical mechanism of charge transfer in the UV–Vis spectrum of graphene nanosheet encapsulated with h-BN (arbitrary twisted angle) in the experiment. Through our research, we can explain some studies on the photoelectric characteristics of h-BN/graphene/h-BN heterostructure in recent years. Because in the preparation of h-BN/graphene/h-BN heterostructure devices or experimental studies, [49, 50] a large number of h-BN/graphene/h-BN heterostructure of different sizes and different twisted angles can be obtained inadvertently, our research conclusions can also provide theoretical basis for h-BN/graphene/h-BN heterostructure optoelectronic devices.

At the same time, it is found that the absorption peak of the encapsulated graphene nanosheets has a red shift. The migration is mainly due to the strong coupling of electrons between the layers formed by the h-BN package, which enhances the interaction between the layers, resulting in the electronic transition from the local excitation of the single layer graphene nanosheet to a combination of local excitation and charge transfer excitation of the encapsulated graphene nanosheet. Our research provides theoretical guidance for the discussion and research of similar experimental results, and also provides a theoretical basis for the application of nanometer metamaterials in the field of optoelectronics.

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Data availability statement

No new data were created or analysed in this study.

Author contributions

Conceptualization, J. Wang; methodology, J. Yu; software, W. Miao; formal analysis, X. Gai; investigation, J. Wang; resources, J. Yu; data curation, X. Gai; writing—original draft preparation, W. Miao; funding acquisition, J. Wang, and Y. Jin. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

There are no conflicts to declare.
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