

## Article

# The Electronic Properties of g–ZnO Modulated by Organic Molecules Adsorption

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**Abstract:** Molecular doping is an excellent instrument to modify the electronic properties of two-dimensional materials. In our work, the structure and electronic properties of the adsorption systems of g–ZnO adsorbed by organic molecules (including Tetracyanoethylene (TCNE), Tetracyanoquinodimethane (TCNQ), and Tetrahydrofulvalene (TTF)) were investigated computationally using Density Functional Theory (DFT). The results showed that the TCNE and TCNQ, as electron receptors, doped the LUMO energy level above the valence band maximum (VBM) of the g–ZnO band structure, demonstrating effective p–type doping. The n–type doping of g–ZnO was obtained that the TTF molecules, as electron donors, doped the HOMO energy level below the conduction band minimum (CBM) of the band structure for g–ZnO. In addition, the TCNE, TCNQ, and TTF breathed additional holes or electrons into the monolayer g–ZnO, creating surface dipole moments between the g–ZnO and organic molecules, which caused work function to be adjustable, ranging from 3.871 eV to 5.260 eV. Our results prove that organic molecular doping was instrumental in improving the performance of g–ZnO–based nano–electronic devices, providing theoretical support for the fabrication of p–doping or n–doping nano–semiconductor components. The tunable range of field emission capability of g–ZnO–based electronic devices was also extended.

**Keywords:** g–ZnO; organic molecules; molecular doping; work function; density functional theory



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## 1. Introduction

Two-dimensional (2D) materials have transverse dimensions of tens to hundreds of nanometers and even longer [1,2]. However, the thickness is only one or a few atomic layers. 2D materials have unique electronic [3–5], optoelectronic [6–8], and catalytic [9–11] properties owing to the surface and quantum confinement effects, which have become a hot research topic in the recent years. Two-dimensional zinc oxide (2D ZnO) is one of the semiconductor materials with excellent properties.

ZnO is the II–VI direct bandgap semiconductor material with a fibrillated zincite structure in stable conditions [12]. Its non-centrosymmetric crystalline fibrous zincate phase demonstrates intense piezoelectric and thermoelectric properties [13]. Thus, it has essential applications in manufacturing piezoelectric sensors [14] and temperature detectors [15]. In addition, ZnO exhibits high electron mobility and exaction binding energy (60 meV) [16], which has critical applications in the preparation of gas detectors [17] and high-efficiency UV laser emitters [18].

Theoretical calculations [19] and experimental studies [20] have shown that the fibrillated zinc ore structure can be transformed into a graphene-like structure for ZnO when the thickness is reduced to a few atoms. The graphene-like zinc oxide (g–ZnO) structure is stable [21,22]. Since then, experimental methods for preparing g–ZnO have been published successively. For example, Sahoo et al. [23] reported a solution-based method

for synthesizing g-ZnO, and Ta et al. [24] reported a method for the in situ fabrication of freestanding monolayer and bilayer ZnO films in graphene pores.

Recently, there has been significant development of research on the modification of g-ZnO. Guo et al. [25] conducted a theoretical study on the monolayer g-ZnO doped with non-metal. They found that the non-metal doped g-ZnO has tunable magnetic and electronic properties. Ren et al. [26] conducted a first-principles study on transition metal-doped g-ZnO. They found that transition metals doping can alter the electronic and magnetic properties of g-ZnO. Rahimi et al. [27] used density generalized function theory calculations to investigate heptazine-g-C<sub>3</sub>N<sub>4</sub>/g-ZnO vdW heterostructure and found that this heterostructure is a potential solar-driven photocatalyst for the water-splitting reaction. Cui et al. [28] performed first-principles analyses on MoSSe/ZnO vdWs and found that the formation of heterostructures would change the light absorption properties of g-ZnO. Rahimi et al. [29] used first-principles calculations based on density functional theory, proposing the vdW g-ZnO/2H-TiS<sub>2</sub> heterostructure for potential optoelectronic devices adjustable by the electric field and strain. However, g-ZnO suffers from a production process that makes it challenging to achieve p-type doping [30]. The molecular doping approach holds promise to solve this issue.

Organic molecule doping is difficult to achieve in the production process, so an alternative approach, using organic molecule adsorption to achieve practical doping effects, is widely used. Cai et al. [31] performed first-principles calculations on organic molecule-doped MoS<sub>2</sub> and defective MoS<sub>2</sub>. They found that organic molecules can adjust the carrier concentration and work function of MoS<sub>2</sub>. Wang et al. [32] showed that n-type and p-type doped graphene sheets are realized by adsorbing organic molecules. Sun et al. [33] calculated the molecular doping of by first-principles calculations. They found that efficient p-type and n-type doping is achieved by the adsorption of organic molecules. Cui et al. [34] used first-principles estimates for the adsorption of MoSi<sub>2</sub>N<sub>4</sub> by organic molecules. They reported that efficient p-doping was achieved by organic molecules. While the studies mentioned above demonstrate the feasibility of this approach, more in-depth studies are needed for the molecular doping of g-ZnO.

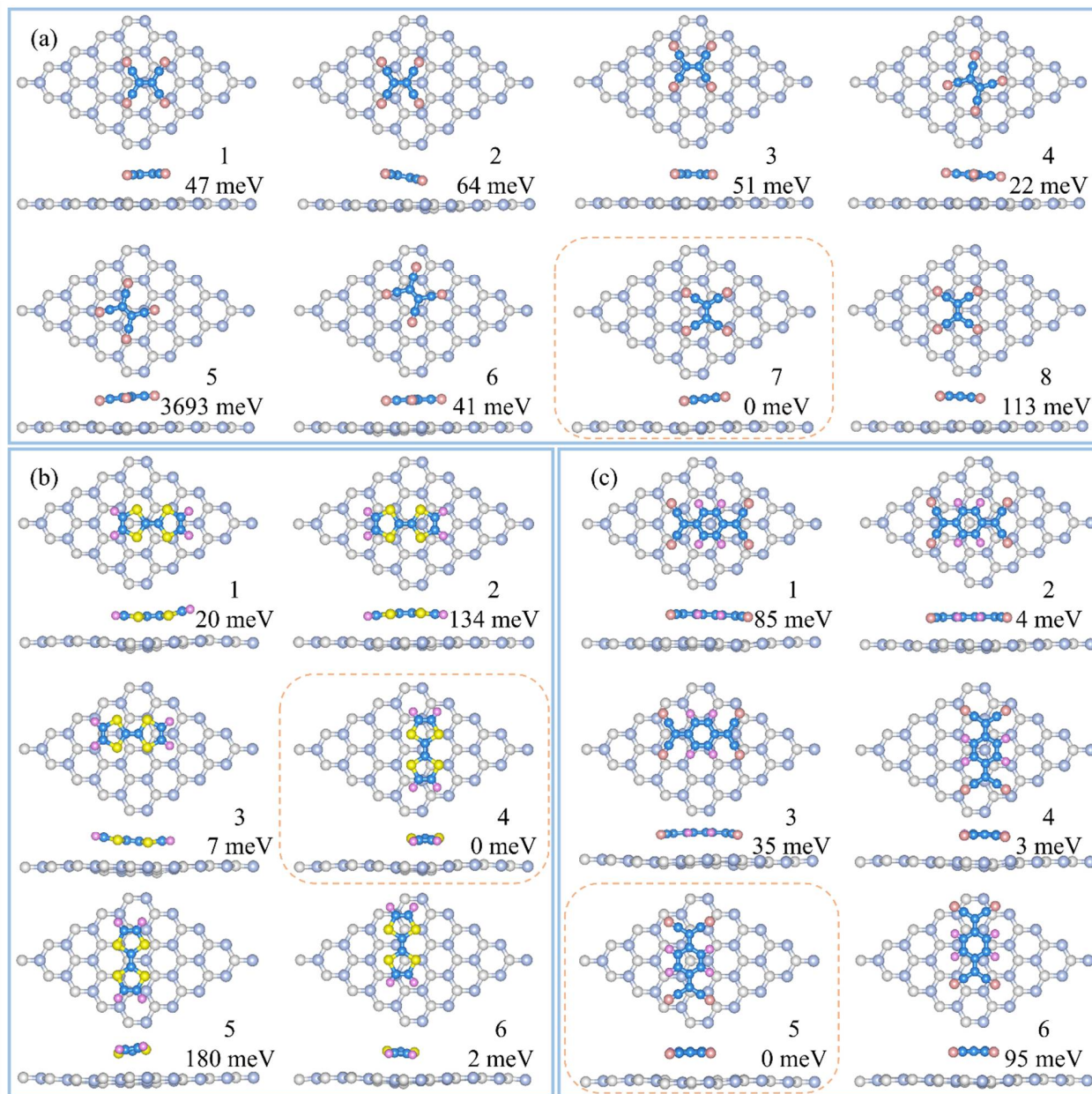
Therefore, we calculate the structural and electronic properties of g-ZnO adsorbed by tetracyanoethylene (TCNE), tetracyanoquinodimethane (TCNQ), and tetrahydrofullvalene (TTF) using a first nature principle based on density generalization theory. We have analyzed the structure, differential charge density, Bader charge, work function, and band structure of the TCNE/g-ZnO, TTF/g-ZnO, and TCNQ/g-ZnO systems. It is concluded that molecular doping in organic molecular adsorption can induce effective p-doping of g-ZnO. It is also shown that molecularly doped g-ZnO has better field emission properties. A theoretical basis is provided for preparing p-doped g-ZnO semiconductors as well. The application scope of the field emission properties of g-ZnO is broadened.

## 2. Computational Models and Methods

The Vienna Ab Initio Simulation Package (VASP) package was used to carry out the first principles [35] based on density functional theory (DFT). The weak dispersion force was corrected by using DFT-3 of the Grimme. Intermolecular interaction generalizations were approximated with the generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) [36] parameterization. The GGA-PBE method correctly reflects the trend of the energy band structure, although it underestimates the band gap value. The convergence cut-off energy was 500 eV, and the first Brillouin zone was summarized in a  $3 \times 3 \times 1$  K-point applying a  $\Gamma$ -center scheme. All atoms were relaxed completely until the Hellmann-Feynman force on each atom was less than  $10^{-2}$  eV Å<sup>-1</sup>, and the total energy changes were below  $10^{-5}$  eV. Additionally, the VASPKIT code [37] was used for data export and processing.

The g-ZnO model of organic molecule adsorption adopted an organic molecule adsorbed onto a  $5 \times 5 \times 1$  g-ZnO supercell. All organic molecules were placed parallel to g-ZnO with a vacuum layer of 20 Å along the Z-direction to isolate the interaction

of the periodic adjacent layers. We regarded eight different TCNE adsorption sites and six different TTF and TCNQ adsorption sites to confirm the most stable conformation, as shown in Figure 1.



**Figure 1.** The adsorption configurations of (a) TCNE, (b) TTF, or (c) TCNQ molecules on g-ZnO. The pale purple, grey, pale red, dark blue, yellow, and pink balls represent Zn, O, N, C, S, and H atoms, respectively. The lowest energy configuration is in the orange dashed box, and its energy difference is zero.

The most stable configuration of the g-ZnO system adsorbed by three organic molecules was identified from the adsorption energy data, and the adsorption energy of the system was calculated as follows:

$$E_{\text{ad}} = E_{\text{Total}} - E_{\text{g-ZnO}} - E_{\text{molecule}} \quad (1)$$

where the  $E_{\text{ad}}$  represents the adsorption energy,  $E_{\text{Total}}$ ,  $E_{\text{g-ZnO}}$ , and  $E_{\text{molecule}}$  are the energy of the adsorption system, monolayer g-ZnO, and organic molecule, respectively. The

charge density difference (CDD) was used to reflect the charge transfer between the organic molecular layer and the monolayer g-ZnO in the organic molecules adsorbed g-ZnO system. The CDD of the system was calculated as follows:

$$\Delta\rho = \rho_{\text{Total}} - \rho_{\text{g-ZnO}} - \rho_{\text{molecule}} \quad (2)$$

where  $\rho_{\text{Total}}$ ,  $\rho_{\text{g-ZnO}}$ , and  $\rho_{\text{molecule}}$  denote the charge density of the adsorbed g-ZnO system, g-ZnO monolayer, and organic molecule, respectively. The work function was derived from the difference between the vacuum energy level and the Fermi energy level, expressed as:

$$w = E_{\text{Vac}} - E_{\text{F}} \quad (3)$$

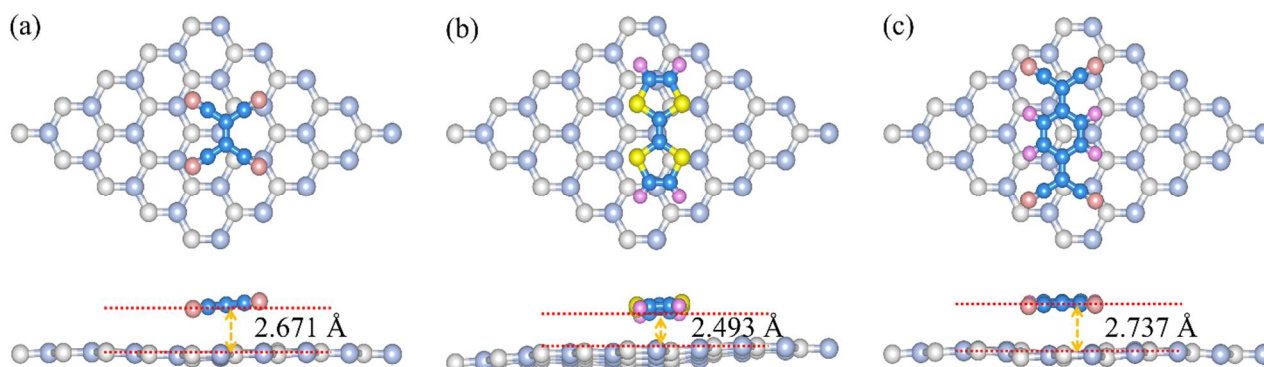
where  $E_{\text{Vac}}$  and  $E_{\text{F}}$  are the vacuum level and Fermi level, respectively.

### 3. Results and Discussion

The relaxed lattice parameters of monolayer g-ZnO were calculated as  $a = b = 3.289 \text{ \AA}$ , and the band structure shows that the monolayer intrinsic g-ZnO is a direct bandgap with 1.651 eV. The valence band maximum (VBM) and conduction band bottom minimum (CBM) were located at the  $\Gamma$  point. Previously, Xiang et al. [38] used the GGA-PBE method to calculate the monolayer g-ZnO lattice parameter of 3.290  $\text{\AA}$  with a direct bandgap value of 1.600 eV at the  $\Gamma$  point. Hu et al. [39] reported that the monolayer g-ZnO lattice parameter was 3.290  $\text{\AA}$  and the immediate bandgap value at the  $\Gamma$  point was 1.670 eV for g-ZnO. Guo et al. [25] obtained an immediate bandgap value of 1.660 eV for monolayer g-ZnO at the  $\Gamma$  point. The consistency of our results with these previous reports demonstrates the reliability of our work.

The lowest total energy indicates the most stable structure. The structures of all the adsorption configurations of g-ZnO adsorbed by the organic molecules are shown in Figure 1, and the numerical value represents energy differences along with the minimum energy adsorption system (orange dashed frame). Slight differences in energy were observed between individual adsorption configurations. Hereafter, subsequent research was based on the lowest energy stable structure.

The TCNE/g-ZnO, TTF/g-ZnO, and TCNQ/g-ZnO systems with the lowest energy stable structure were screened out and shown in Figure 2a–c, respectively. Their relevant parameters are listed in Table 1. For the most stable configurations, the organic molecules were inclined to be arranged vertically, and the adsorption energy was  $-0.855 \text{ eV}$  (TCNE/ZnO),  $-1.263 \text{ eV}$  (TTF/ZnO), and  $-1.260 \text{ eV}$  (TCNQ/ZnO), respectively. For the TCNE/g-ZnO and TTF/g-ZnO systems, the optimal adsorption site was the C–C bond in the center of TCNE and TTF adsorbed on the Zn atom, and the adsorption heights decreased to 2.671  $\text{\AA}$  and 2.493  $\text{\AA}$ , respectively. Among them, the TCNE was tilted relative to the monolayer g-ZnO plane, yet all cyano groups remained horizontal to the plane of the TCNE molecule. For the TTF, it was curled against the g-ZnO plane. This phenomenon was similar to the previous reports on the adsorption of g-GaN [40] or MoSSe [41] by TCNE or TTF. However, for the TCNQ–ZnO system, the optimal adsorption site was the central carbon ring center of TCNQ adsorbed on the O atom, which enhanced the interaction between the delocalized  $\pi$  electrons and the lone pair electrons of the O atom. The optimal adsorption height became 2.737  $\text{\AA}$ . The TCNQ molecule remained horizontal for the g-ZnO plane without deformation. The small adsorption energy values and high adsorption heights of the three organic molecular adsorption systems indicated the physical adsorption properties of g-ZnO. In addition, the layered structure of g-ZnO had no large distortion, which proved that organic molecules had less influence on the band structure of g-ZnO.

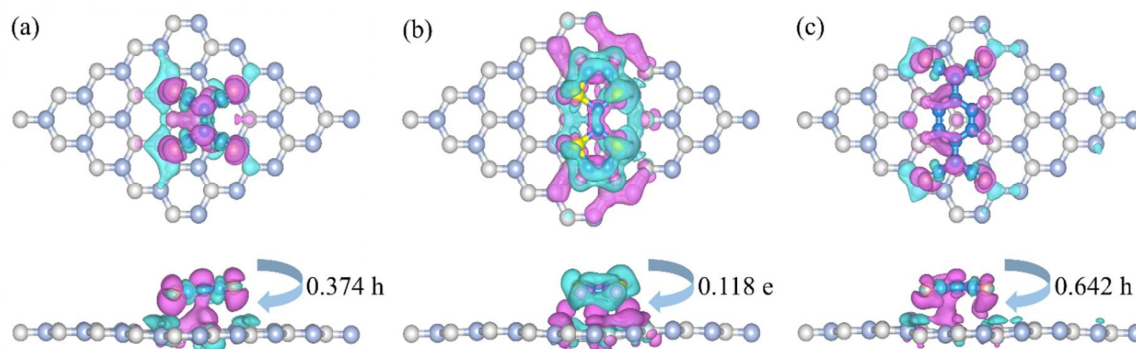


**Figure 2.** The optimized ground state atomic structures of the most stable configurations of the (a) TCNE, (b) TTF, or (c) TCNQ molecules adsorbed g-ZnO systems. The upper is the top view, and the bottom is the side.

**Table 1.** Adsorption energy ( $E_{ad}$ ), doping bandgap ( $E_g$ ), adsorption height ( $h$ ), charge transfer ( $\Delta Q$ ), and injected carrier concentration ( $n$ ) for the most stable configurations of TCNQ, TTF, or TCNQ molecules adsorbed on g-ZnO.

| Configuration | $E_{ad}$ (eV) | $E_g$ (eV) | $h$ (Å) | $\Delta Q$ ( $ e $ ) | $n$ ( $10^{13} \text{ cm}^{-2}$ ) |
|---------------|---------------|------------|---------|----------------------|-----------------------------------|
| TCNE          | −0.855        | 0.085      | 2.671   | 0.374                | 1.600 h                           |
| TTF           | −1.263        | 0.954      | 2.493   | 0.118                | 0.510 e                           |
| TCNQ          | −1.260        | 0.089      | 2.737   | 0.642                | 2.740 h                           |

The adsorption of organic molecules effectively induced a charge transfer between TCNE, TTF, or TCNQ and g-ZnO, which contributed a vital role in modifying the properties of g-ZnO. The CDD graphs of TCNE, TTF, or TCNQ adsorbed on g-ZnO are shown in Figure 3a–c, respectively. Purple and blue represent electron aggregation and electron dissipation, respectively. The fact that the TCNE and TCNQ molecules contain cyano gives them a high adiabatic electron affinity (2.884 eV for TCNE [42] and 2.80 eV for TCNQ [43]) and means they are more capable of gaining electrons. Therefore, from Figure 3a,c, it can be observed that the electrons provided by the monolayer g-ZnO were obtained by cyano and located in the interlayer region between the TCNE or TCNQ molecules and g-ZnO sheet. From Figure 3b, because the TTF molecule has low ionization potential [44], it acts as an electron donor. The transferred electrons are mainly gained by the g-ZnO layer. The more accurate results of the Bader charge calculations are presented in Table 1. For the TCNE/g-ZnO and TCNQ/g-ZnO systems, 0.374 and 0.642 electrons are transferred from the g-ZnO layer to TCNE or TCNQ molecules. For the TTF/g-ZnO system, 0.118 electrons are transferred from the TTF molecule to the g-ZnO layer.



**Figure 3.** Charge difference density of organic molecules (a) TCNE, (b) TTF, and (c) TCNQ adsorbed on the g-ZnO. The iso-surface value is set to  $0.0004 \text{ e } \text{\AA}^{-3}$ . The purple and blue represent electron aggregation and electron dissipation, respectively.

Further, for the TCNE/g-ZnO system, it can be observed from Figure 3a that more charge was transferred to the TCNE below the left part of the TCNE compared to the right, which resulted in a more vital interaction between the TCNE and the monolayer g-ZnO on the left part than the right side. Therefore, the TCNE tilted left relative to the g-ZnO plane as described above. For the TTF-ZnO system, charge transfer also occurred, but the difference was that the charge was transferred from the TTF molecule to the Zn and O atoms adjacent to it, as can be observed in Figure 3b. The transferred charge was mainly distributed to the g-ZnO layer on the top and bottom side of the TTF, which led to more significant interaction between the TTF and g-ZnO on the top and bottom side than in the middle. This caused the TTF molecule to curl up and in line with the description above. For the TCNQ/g-ZnO system, from Figure 3c, the charge was transferred from the g-ZnO layer to the TCNE molecule. The difference was that the TCNQ/g-ZnO system showed symmetry in the interactions and charge transfer, which also verified that the TCNQ molecule remained horizontal, which did not undergo deformation as described earlier. Furthermore, it can be observed from Figure 3 that the charge transfer resulted in the injection of 0.374 hole carriers, 0.118 electron carriers, and 0.642 hole carriers into the monolayer g-ZnO for TCNE, TTF, and TCNQ, respectively. The concentrations were  $1.600 \times 10^{13} \text{ h cm}^{-2}$ ,  $0.510 \times 10^{13} \text{ e cm}^{-2}$ , and  $2.740 \times 10^{13} \text{ h cm}^{-2}$ , respectively.

The work function of g-ZnO can be modified as a result of charge transfer between the organic molecule TCNE, TTF, or TCNQ and the monolayer g-ZnO, inducing a surface dipole moment between the organic molecule and g-ZnO. The work function of organic molecules adsorbed on g-ZnO is shown in Figure 4. The work function of the intrinsic g-ZnO was 4.985 eV. For the TCNE/g-ZnO and TCNQ/g-ZnO systems, as mentioned above, TCNE and TCNQ inject hole carriers into the monolayer g-ZnO, which causes the Fermi energy level of g-ZnO to shift downwards, thus increasing the work function to 5.260 eV and 5.257 eV, respectively. However, for the TTF/g-ZnO system, the TTF injected electron carriers into the monolayer g-ZnO, which resulted in the Fermi energy level of g-ZnO shifting upwards, decreasing the work function to 3.871 eV. Thus, the adsorption of organic molecules allows the work function of g-ZnO to vary from 3.871 eV to 5.260 eV. The relatively large tuning range indicates the great potential of g-ZnO semiconductors adsorbed by organic molecules for applications in nano-electronic devices.

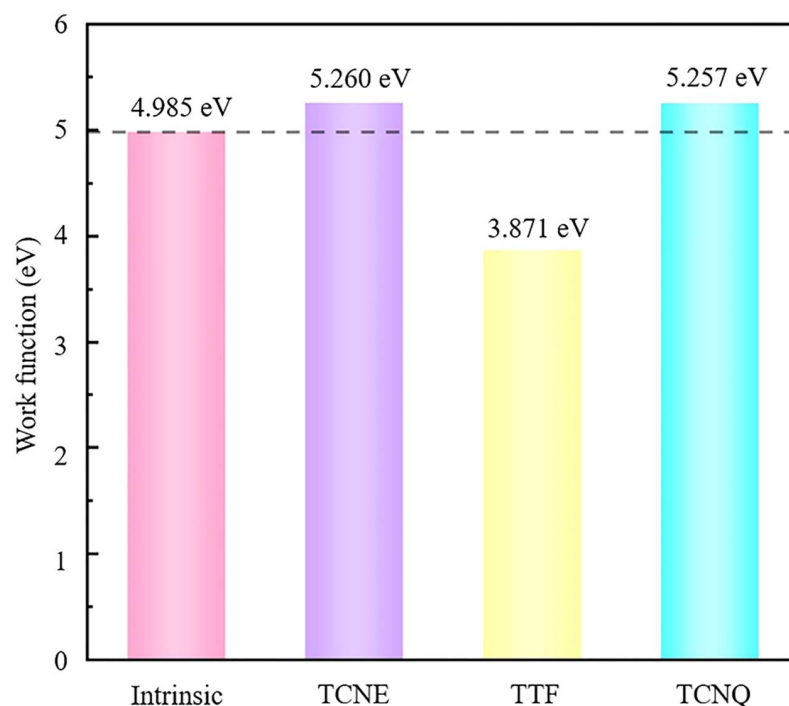
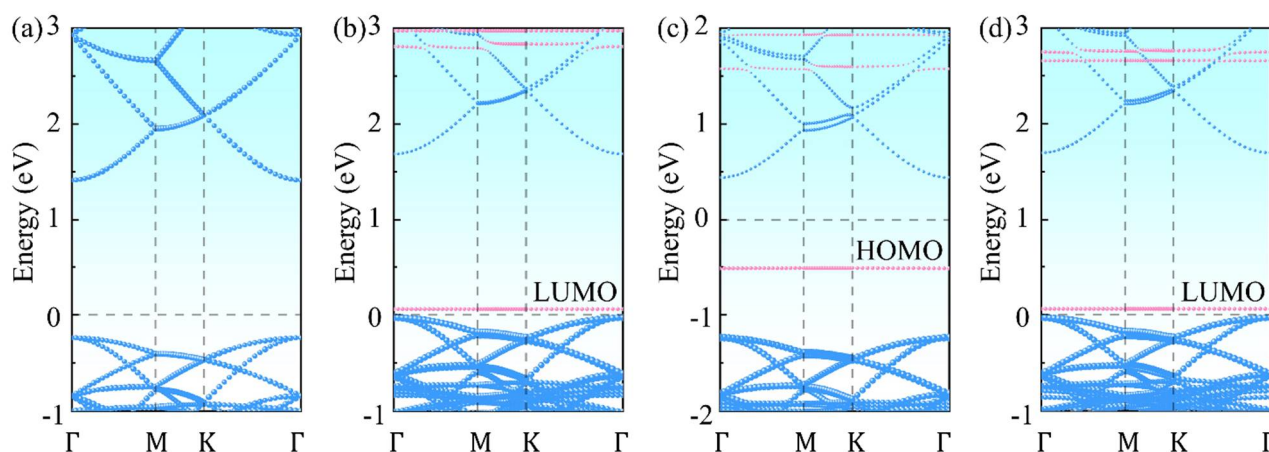
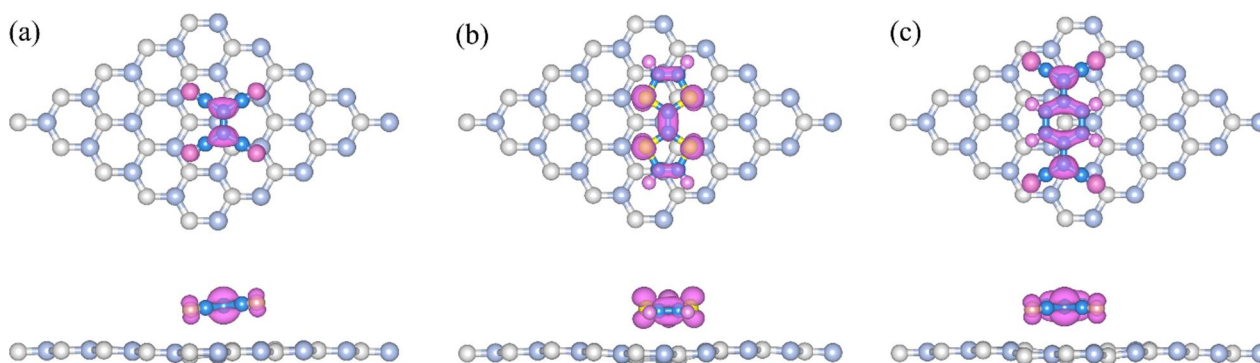


Figure 4. The work function of g-ZnO adsorption by organic molecules.

To more intensively interrogate the effect of organic molecular adsorption on the electronic properties of g-ZnO, the band structure of the adsorption system was investigated and shown in Figure 5b–d. For comparison, the band structure of the intrinsic g-ZnO, a  $5 \times 5 \times 1$  supercell, was placed in Figure 5a. As mentioned earlier, the organic molecules had less effect on the main band structure by physically adsorbing the monolayer g-ZnO. It can be observed in Figure 5b,d that the band structure of the TCNE/g-ZnO and TCNQ/g-ZnO systems was shifted upwards overall compared to the intrinsic g-ZnO, which was caused by the injection of hole carriers into the g-ZnO by the TCNE and TCNQ molecules. For the TTF/g-ZnO system, the band structure was displaced downwards owing to the TTF molecules inject electron carriers into the g-ZnO. At the same time, we can observe that for the TCNE/g-ZnO and TCNQ/g-ZnO systems, a new planar band appeared beyond the g-ZnO VBM, which was the lowest unoccupied molecular orbital (LUMO) of the organic molecule. For the TTF/g-ZnO system, a new flat band emerged below the CBM, which was the highest occupied molecular orbital (HOMO) of the organic molecule. From Figure 6, it can be observed that the impurity energy levels (LUMO and HOMO) are entirely contributed by organic molecules.



**Figure 5.** Band structures of (a) intrinsic g-ZnO, (b) TCNE/g-ZnO, (c) TTF/g-ZnO, and (d) TCNQ/g-ZnO. The Fermi level is moved to zero, represented by the black dash line.



**Figure 6.** The partial charge densities of (a) TCNE/g-ZnO, (b) TTF/g-ZnO, and (c) TCNQ/g-ZnO systems (The purple area delegates the partial charge density corresponding to impurity bands).

The doping bandgap was defined as the gap between the LUMO of the p-dopants and the VBM of the host material, and the gap between the HOMO of the n-dopants and the CBM of the host material. A doping band gap value of 0.085 eV can be obtained for the TCNE/g-ZnO system. The smaller impurity band gap allowing the TCNE molecule, as the acceptor impurity, to have the hole carriers excited into the host material, creating an effective p-doping semiconductor. Similarly, the TCNQ/g-ZnO had a doping band

gap value of 0.089 eV. The TCNQ molecule, as the acceptor impurity, whose hole carrier was excited into the host material, also formed an effective p-doping semiconductor. However, for the TTF/g-ZnO system, the doping band gap value is larger at 0.954 eV. The HOMO energy level of the TTF molecule was located 0.514 eV below the Fermi energy level, providing a deeper impurity level. Although the TTF molecule, as the donor impurity, injected a relatively small number of electron carriers into g-ZnO, demonstrating n-doping behavior, it had a larger doping bandgap. Thus, the TTF was not enough to contribute to an effective n-doping semiconductor. These results were in agreement with the above CDD and Bader charge calculations.

In summary, effective doping can be achieved by adsorption of organic molecules, which was used to modulate the carrier type of g-ZnO. Furthermore, TCNE/g-ZnO and TCNQ/g-ZnO can be used as effective p-doping semiconductors.

#### 4. Conclusions

The structural and electronic properties of monolayers of g-ZnO adsorbed by organic molecules were investigated using DFT calculations. We conducted analysis of the structure, charge differential density, Bader charge, work function, and band structure of the intrinsic g-ZnO, TCNE/g-ZnO, TTF/g-ZnO, and TCNQ/g-ZnO systems. The results indicated that the g-ZnO structures adsorbed by TCNE, TTF, and TCNQ were stable and had physical adsorption characteristics. It suggested that the adsorption by organic has less effect on the host material (g-ZnO). The charge density difference revealed that the transferred charges were mainly distributed in the cyano groups and the g-ZnO layers below the upper and lower sides of the TTF. Bader charge analysis demonstrated the amount of charge transfer between the organic molecules and the monolayer g-ZnO with the charge transfer of TCNE/g-ZnO, TCNQ/g-ZnO, and TTF/g-ZnO was 0.374 |e|, 0.642 |e|, 0.118 |e|, respectively. Significantly, this phenomenon caused the power function to vary from 3.871 eV to 5.260 eV, widening the range of regulation of the g-ZnO field emission capability. Notably, the band structure revealed that TCNE and TCNQ molecules, as acceptor impurities, induced the LUMO energy levels at 0.085 eV and 0.089 eV (small doping band gap) above the VBM of g-ZnO with the formation of shallow acceptor states, respectively. This demonstrated an effective p-doping behavior. By contrast, the TTF molecule, as the donor impurity, exhibited n-doping behavior by entraining a HOMO energy level at 0.954 eV (a large doping band gap) below the CBM of g-ZnO, which formed a deep donor state. In addition, the TCNE, TCNQ, and TTF molecules contributed additional carriers to the g-ZnO layer at concentrations of  $1.600 \times 10^{13} \text{ h cm}^{-2}$ ,  $0.510 \times 10^{13} \text{ e cm}^{-2}$ , and  $2.740 \times 10^{13} \text{ h cm}^{-2}$ , respectively. Our study emphasized the critical role of the adsorption of organic molecules in modifying the electronic properties of g-ZnO. It is simultaneously demonstrated that the adsorption of monolayer g-ZnO by organic molecules can induce p- or n-doping, providing theoretical evidence for the fabrication of g-ZnO-based p or n-type semiconductor devices. In addition, the adsorption of organic molecules extended the tunable range of field emission capabilities of g-ZnO-based electronic devices.

**Author Contributions:** Conceptualization, Y.S., Z.C. and E.L.; data curation and formal analysis, Z.Y.; performed the statistical analysis, D.M.; writing—original draft preparation, Y.S. and Z.Y.; wrote sections of the manuscript, K.Y., Y.D., F.W. and P.Y. All authors have read and agreed to the published version of the manuscript.

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