

Article

Enhancing the Electric Field-Induced Response of Graphene with Metal Oxides: Experimental and DFT Study

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Abstract

The potential of graphene for electric field sensing is limited by its zero bandgap. This study employs a combined first-principles and experimental approach to enhance its response via heterojunctions with ZnO, SnO₂, and Al₂O₃. Calculations reveal spontaneous formation and interfacial charge transfer in all systems, with SnO₂/graphene exhibiting the most significant charge transfer (0.3636 e) and inducing a finite bandgap (0.017–0.064 eV). Experimentally, SnO₂-graphene/PDMS composites demonstrated the highest relative permittivity (3.19) and a 7.76% increase in normalized induced voltage over pure PDMS within 50 Hz–50 kHz. This work establishes a direct correlation between interfacial charge transfer, bandgap opening, and macroscopic dielectric enhancement, identifying SnO₂/graphene as the optimal heterojunction. The integrated multi-scale methodology provides a clear design principle for high-performance, graphene-based field-sensitive materials.

Keywords: graphene; metal oxides; heterojunction; electric field sensing; first-principles; dielectric properties



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1. Introduction

Since 2004, graphene has emerged as a prototypical two-dimensional material, garnering significant research interest across diverse disciplines owing to its distinctive electronic structure and superior electrical characteristics. This atomically thin carbon allotrope, featuring a hexagonal lattice of sp²-hybridized carbon atoms, exhibits remarkable physical properties including high charge carrier mobility (up to $2.5 \times 10^5 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ at room temperature), an exceptionally high theoretical specific surface area ($\sim 2630 \text{ m}^2 \cdot \text{g}^{-1}$), and outstanding mechanical strength. These attributes render it a promising candidate for developing next-generation high-performance sensing devices [1–3]. Particularly in the realm of electric field sensing, graphene's theoretically predicted capacity for rapid and sensitive response to external electric field variations presents substantial potential for applications in power system monitoring and environmental electric field detection. Nevertheless, the intrinsic zero-bandgap nature of graphene results in the degeneracy of its valence and conduction bands at the Dirac point, a structural characteristic that significantly hinders its performance in electric field sensing applications. Specifically, graphene-based field-effect devices exhibit undesirably low on/off ratios, presenting challenges in achieving sufficient sensitivity and signal-to-noise ratio for DC or low-frequency AC electric field measurements [4,5]. This fundamental limitation has motivated substantial research efforts

dedicated to developing effective modification strategies to engineer its electronic structure and enhance its macroscopic electric field response capabilities.

Among various modification strategies, heterostructure engineering with metal oxides has emerged as a particularly promising technical route. Metal oxides such as zinc oxide (ZnO), tin oxide (SnO₂), and aluminum oxide (Al₂O₃) typically possess distinctive characteristics including wide bandgaps, high relative permittivity, and excellent chemical stability [6–8]. These properties enable complementary advantages when combined with graphene: the introduction of metal oxides can effectively modulate graphene's Fermi level through interfacial charge transfer and doping effects, while their inherent polarization characteristics enhance the overall dielectric response of the composite system. This synergistic interaction provides a novel pathway for improving the electric field sensitivity of graphene-based materials [9].

Recent first-principles studies have shown that graphene–oxide heterojunctions exhibit pronounced interfacial electronic interactions, including charge transfer, Fermi-level modulation, and interface dipole formation, which significantly influence band alignment and polarization at the interface. These microscopic mechanisms play an important role in determining the dielectric and electric-field response of graphene-based composites and provide theoretical support for correlating electronic structure with macroscopic sensing behavior [9–11]. Li et al. [12] demonstrated through first-principles calculations that fluorine and chlorine functionalized Janus-structured ZnO forms van der Waals heterostructures with graphene, enabling the transition from Schottky to ohmic contact by controlling the stacking configuration. This approach effectively enhances interlayer charge transfer, showing considerable potential for developing high-performance field-effect transistors and nano-optoelectronic devices. Zheng and colleagues [13] designed a graphene-bridged SnO₂-rGO/SnS₂ hierarchical heterostructure that establishes an efficient charge transfer “highway” at the interface, substantially improving both the detection sensitivity and response performance toward nitrogen dioxide (NO₂) gas. Furthermore, Zhu et al. [14] synthesized rGO-SnO₂-Fe₂O₃ nanocomposites via an in situ hydrothermal method, revealing that graphene incorporation promotes uniform distribution of transition metal oxide particles. This not only increases the specific surface area and initial discharge capacity of the material but also effectively suppresses volume expansion during charge–discharge cycles, thereby significantly enhancing the rate capability and cycling stability of the electrode material. Canto B et al [15]. employed plasma-enhanced atomic layer deposition to fabricate Al₂O₃ encapsulation layers of varying thicknesses on graphene field-effect transistors. Their research demonstrated that the encapsulated devices maintained stable transfer characteristics and photo response under ambient conditions and at elevated temperatures up to 107 °C. Notably, these devices achieved high responsivity in the near-ultraviolet spectrum, suggesting their potential for developing photodetectors capable of operating in harsh environments. Furthermore, Snure M et al. [16] discovered that inserting a few-layer BN buffer layer, grown via metalorganic chemical vapor deposition, between graphene and Al₂O₃ effectively protected graphene from oxidation during the plasma-enhanced atomic layer deposition process. This interfacial engineering approach significantly reduced interface charge trapping, resulting in top-gated field-effect transistors with minimized Dirac point voltage and hysteresis, thereby substantially improving device performance.

These research findings collectively demonstrate the crucial regulatory role of microscopic interface engineering on the macroscopic electrical properties of graphene. However, several critical challenges remain incompletely understood in current research: First, the quantitative structure–property relationships between microstructural parameters (such as interaction energy, charge transfer amount, and induced bandgap size) and macroscopic electric field-sensitive characteristics (including relative permittivity and induced voltage

output) in different metal oxide/graphene heterojunction systems remain unclear [17]. The distinct crystal structures, electron affinities, and work functions of different metal oxides may lead to significant variations in their regulatory mechanisms and effects on graphene's electronic structure, necessitating systematic comparative investigations [18]. Second, how the interfacial morphological characteristics of heterojunctions—including filler dispersion, interfacial bonding strength, and elemental interdiffusion behavior—affect the ultimate dielectric properties and electric field sensing capabilities of composite materials requires in-depth correlative analysis integrating both experimental characterization and theoretical calculations [19].

Furthermore, at the application level, developing high-performance graphene-based composite materials that simultaneously possess high relative permittivity, appropriate dielectric loss, good frequency stability, and ease of processability, while identifying their optimal operational modes, represents a key challenge for advancing their practical implementation [20]. Particularly in specific application scenarios such as power line electric field measurement, the material's response characteristics at power frequency conditions are of paramount importance. This necessitates a more comprehensive understanding of the dielectric behavior of composite materials within the 50 Hz–50 kHz frequency range. Building upon the research background and existing challenges outlined above, this study centers on the core theme of “investigating the influence mechanisms of graphene microstructure on macroscopic electric field-sensitive characteristics and developing modification methodologies.” Three representative metal oxides (ZnO, SnO₂, Al₂O₃) were selected as modifying agents for graphene. Through a multi-scale, integrated research strategy, we systematically examine the intrinsic relationships between graphene microstructure modulation and macroscopic performance enhancement [21].

The research methodology employs a comprehensive, multi-scale approach: Initially, first-principles calculations were performed using the Dmol³ module in Materials Studio software to construct heterojunction models of graphene with the three metal oxides (ZnO, SnO₂ and Al₂O₃). Geometric optimization and electronic structure calculations yielded key parameters including interaction energy, charge transfer, band structure, and density of states, thereby revealing the physical nature of interfacial interactions at the atomic scale [22]. Subsequently, corresponding heterojunction powder materials were synthesized via hydrothermal method [23,24]. Systematic characterization using FE-SEM and EDS provided detailed information on micromorphology, elemental distribution, and interfacial bonding states, establishing structural basis for interpreting macroscopic properties. Furthermore, the heterojunction materials were incorporated as functional fillers into PDMS (Polydimethylsiloxane) matrix to fabricate flexible composite films. The dielectric properties across the 50 Hz–50 kHz frequency range and induced voltage outputs under uniform alternating electric fields were comprehensively evaluated using an LCR digital bridge and a custom-built parallel-plate electric field test system. Finally, by integrating theoretical calculations with experimental characterization results, we establish correlations between microscopic electronic structures and macroscopic electrical properties, elucidating the regulatory mechanisms of graphene heterojunction modifications on macroscopic electric field-sensitive characteristics.

Through this systematic investigation, we anticipate not only achieving fundamental understanding of interfacial interaction mechanisms in graphene/metal oxide heterojunctions but also providing crucial theoretical foundations and practical guidance for developing next-generation high-performance electric field-sensitive materials. This research is expected to advance practical applications of graphene materials in domains such as power monitoring and environmental sensing.

2. Experimental and Computational Methods

2.1. Materials Synthesis

All raw materials and reagents used in the experiments were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China) and could be directly applied for material synthesis. According to the provided material specifications, the ZnO, SnO₂, and Al₂O₃ powders correspond to the wurtzite, rutile, and α -Al₂O₃ (corundum) phases, respectively. These are thermodynamically stable structures typically obtained through hydrothermal or high-temperature oxide synthesis. Composite materials consisting of three metal oxides and graphene were prepared via the hydrothermal method. As illustrated in Figure 1, 0.5 g of zinc oxide was first weighed and added into 30 mL of deionized water. The mixture was stirred at room temperature using a magnetic stirrer for 30 min to obtain a turbid solution. Then, 0.5 g of graphene was weighed, making the mass ratio of zinc oxide to graphene 1:1, and gradually added into the above zinc oxide solution under continuous magnetic stirring. The stirring was maintained for 1 h to form a homogeneous mixture. Subsequently, a 0.1 mol/L dilute hydrochloric acid solution was added to adjust the pH of the mixture to 5.0 ± 0.1 . The pH-adjusted mixture was then transferred entirely into a 200 mL hydrothermal synthesis autoclave. After sealing, the autoclave was placed in a constant-temperature blast drying oven and heated at 200 °C for 12 h. Upon completion of the heating process, the resulting mixture was washed and centrifuged, followed by a drying treatment to obtain the zinc oxide/graphene composite material. The preparation procedures for the other two metal oxide/graphene composites were consistent with that described above for the zinc oxide and graphene composite, and the mass ratio of metal oxide to graphene is maintained at 1:1.

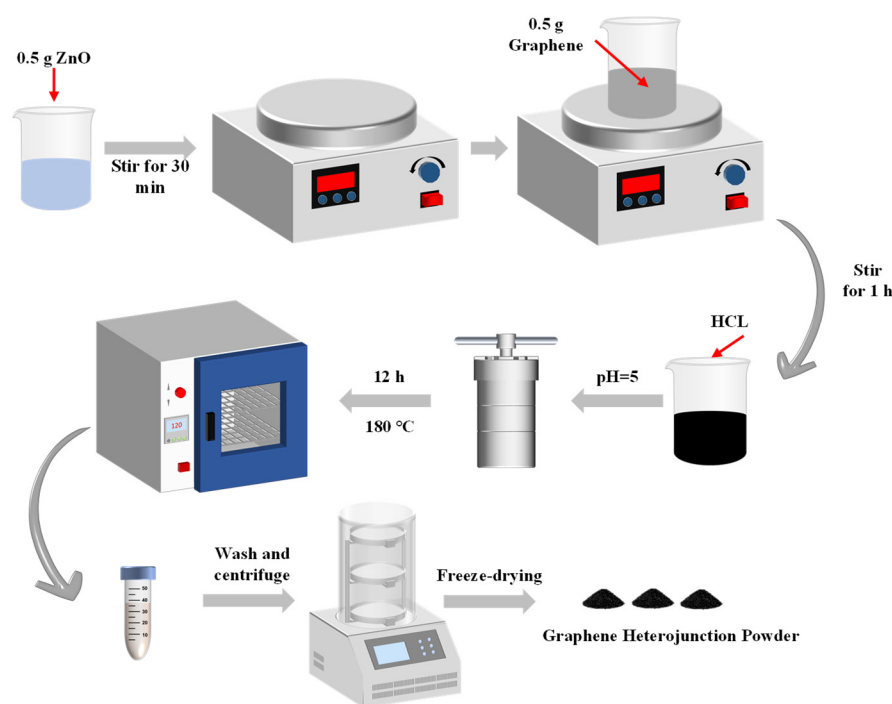


Figure 1. Preparation of Graphene-Based Heterojunctions.

As shown in Figure 2, the prepared heterojunction powder and PDMS prepolymer (base material) were mechanically mixed to form a composite material. Subsequently, an appropriate amount of defoamer and crosslinking agent (Sylgard 184 Part A) was added to the mixture, with the amount of defoamer and crosslinking agent being one-tenth of the

amount used in the previous composite material. Finally, planetary stirring was performed under vacuum conditions to completely remove air bubbles and achieve final curing.

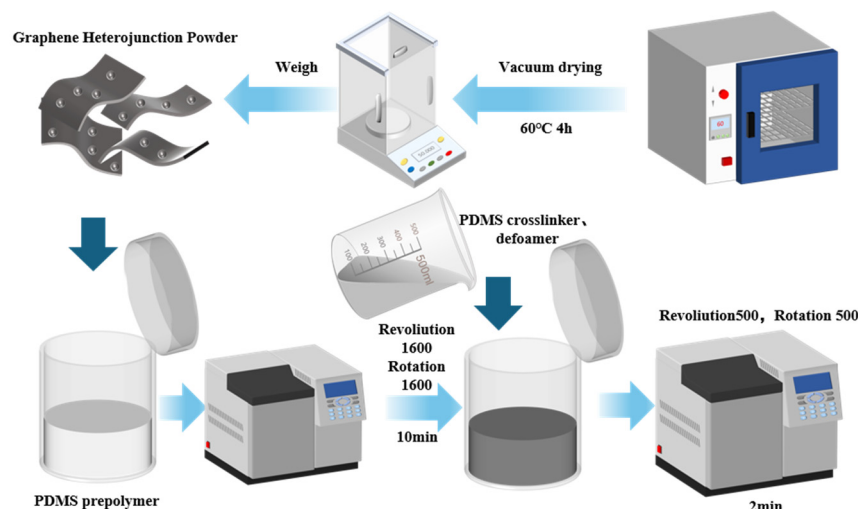


Figure 2. Fabrication of Graphene Heterojunction/PDMS Prepolymer Composites.

2.2. Materials Characterization Methods

To systematically investigate the microstructure, interfacial bonding state, and elemental distribution of the graphene heterojunction materials—thereby verifying their suitability as functional fillers and the effectiveness of the composite structure—this study conducted comprehensive characterization using a ZEISS Gemini SEM 300 field emission scanning electron microscope (FE-SEM, Carl Zeiss AG, Oberkochen, Germany) equipped with an Oxford Instruments Xplore 30 energy dispersive X-ray spectroscopy (EDS, Oxford Instruments plc, Abingdon, UK) system. The as-synthesized heterojunction powder was uniformly dispersed in anhydrous ethanol and subjected to ultrasonication for 15 min. An appropriate amount of the suspension was then drop-cast onto a sample stage and allowed to dry at room temperature. A thin layer of gold–palladium (Au/Pd) alloy film, approximately 5 nm thick, was deposited on the sample surface using a Leica EM ACE600 ion sputter coater. (Leica Microsystems GmbH, Wetzlar, Germany).

2.3. Dielectric Spectroscopy and Electric-Field Sensing Tests

Dielectric spectroscopy measurements were carried out using the lumped circuit method, with a Tonghui TH2830 LCR (Tonghui Electronic Co., Ltd., Changzhou, China) meter as the core measurement device, assisted by a dedicated tweezer-type fixture. To minimize capacitive errors caused by air gaps, double-sided conductive copper foil with a diameter of 30 mm was selected as the flexible contact electrode. The preparation of test samples proceeded as follows: First, a PDMS 184 release agent was sprayed onto a glass substrate, and a uniform film with a thickness of $100 \pm 10 \mu\text{m}$ was prepared using a wire rod coater (BEVS Industrial Co., Ltd., Guangzhou, China). The film was then dried at 80°C under vacuum for 2 h to achieve complete curing. After curing, the film was heated in a water bath to 80°C , peeled from the substrate with the aid of the release agent, and cut into $40 \text{ mm} \times 40 \text{ mm}$ square pieces. Subsequently, circular double-sided conductive copper foil electrodes (30 mm in diameter) were attached to the geometric center of both sides of each sample, ensuring tight adhesion without air bubbles, to construct a parallel-plate capacitor structure.

To evaluate the modification effects of the three metal oxides, five types of samples were prepared: pure PDMS, graphene/PDMS, ZnO-G/PDMS, SnO_2 -G/PDMS, and Al_2O_3 -G/PDMS. The test conditions were set as follows: frequency range of 50 Hz–50 kHz,

logarithmic sweep mode, with 5 characteristic frequency points collected per decade, and an AC test signal of 1.0Vrms. The sample thickness was determined via a high-precision micro-thickness gauge (model TDGC2-5 kVA, Tianjin Tianshi Power Supply Co., Ltd., Tianjin, China), performing three-point measurements and taking the average value, denoted as d^{etest} . Each sample was tested three times to ensure data reliability, and all measurements were performed and recorded in automatic frequency sweep mode.

During data processing, the capacitance value C^{etest} and loss factor d^{etest} were directly read from the LCR meter, while the phase angle θ^{etest} was recorded at each frequency point. The measured relative permittivity can be expressed as:

$$\epsilon^{\text{etest}} = \frac{C^{\text{etest}} d^{\text{etest}}}{\epsilon_0 A^{\text{etest}}} \quad (1)$$

where A^{etest} is the electrode area, and the dielectric loss factor $\tan\delta$ can be directly obtained from the measured values.

To accurately evaluate the sensing response characteristics of the materials under electric field conditions, this study designed and constructed a parallel-plate electrode system for electric field generation and testing (shown in Figure 3). This system is capable of producing a uniform and controllable standard electric field over a wide range of field strengths, enabling direct measurement of the sensor voltage output from functional thin-film materials under electric field exposure. This provides an experimental basis for their application in power line electric field measurement.

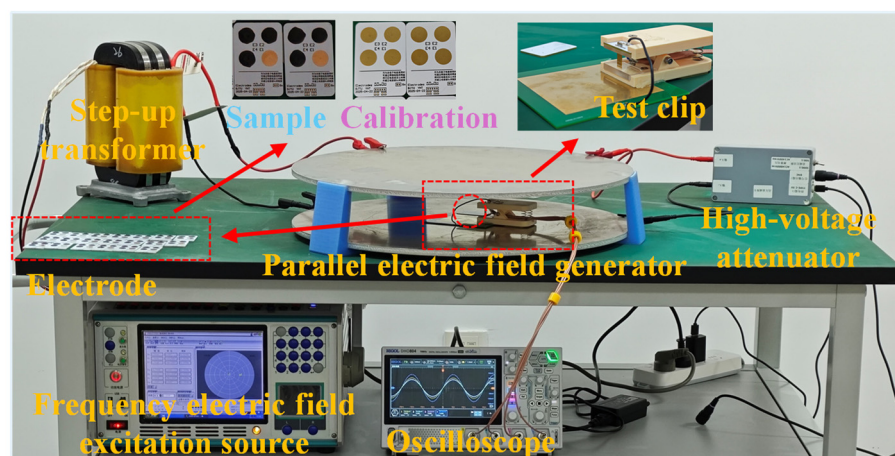


Figure 3. Schematic of the Electric Field Sensing Measurement.

The test system consists of three parts: a parallel-plate electric field generation device, a sensing unit, and a signal acquisition unit. The parallel-plate electric field generation device uses a pair of circular aluminum electrodes, each 500 mm in diameter. The upper electrode is connected to an adjustable high-voltage AC source, composed of a programmable frequency-conversion AC power supply and a step-up transformer, while the lower electrode is grounded through a protective resistor. The two electrodes are strictly maintained parallel with a fixed separation distance, forming a uniform spatial electric field between the plates with controllable amplitude and frequency. The sensing unit is a customized triple-electrode assembly, which includes a calibration electrode and supports rapid loading/unloading and simultaneous testing of multiple samples. The signal acquisition section employs a multi-channel digital oscilloscope. One channel monitors the high-voltage excitation signal between the parallel plates via a high-voltage differential probe, while the other three channels use high-impedance single-ended probes connected to the three test electrodes of the sensing unit, respectively. This setup enables synchronous in situ measure-

ment and recording of multi-channel response signals. All data are uploaded to a computer via an interface for processing and analysis.

During testing, the programmable frequency-conversion AC power supply is first activated. It generates a high-voltage AC signal with preset parameters via the step-up transformer, which is applied to the upper electrode plate. This establishes a spatially uniform alternating electric field under the condition that the lower electrode plate is grounded. The generated electric field can be calculated as:

$$E^{\text{etest}} = \frac{V^{\text{etest}}}{d^{\text{etest}}} \quad (2)$$

where V^{etest} is the voltage between the electrode plates (monitored via the high-voltage differential probe), and d^{etest} is the fixed inter-electrode distance. Prior to each test cycle, a zero-field calibration was performed: the baseline readings of the three probe channels were recorded under a no-sample condition to eliminate the influence of system parasitic capacitance and ambient electromagnetic noise. The sensing unit was secured using a mechanical fixture to ensure consistent installation position and orientation for each test. The prepared graphene/PDMS composite film (with a controlled thickness of $100 \pm 10 \mu\text{m}$) was accurately aligned and placed within the electrode-sensitive area. Vacuum adsorption was employed to eliminate air bubbles. The material underwent an 80°C , 2 h vacuum curing process to ensure stable interfacial contact with the electrodes. During the formal testing, the three high-impedance single-ended probes synchronously collected the induced charge signals from the composite material. Each set of experiments was repeated five times, and the average value was taken as the final result.

2.4. Calculation Details

Geometry optimization and energy calculations were performed using first-principles theory within the Dmol3 module of the Materials Studio 2019 (MS) software. The electron exchange–correlation interaction was described with the Perdew–Burke–Ernzerhof (PBE) functional under the generalized gradient approximation (GGA) [25,26]. Nucleus–electron interactions and electron pseudopotentials were treated using DFT semi-core pseudopotentials (DSPP) along with a double numerical basis set plus polarization functions (DNP). Dispersion corrections, including van der Waals forces and other long-range interactions, were incorporated via the DFT scheme [27]. For both geometric optimization and electronic structure calculations, a $7 \times 7 \times 1$ k-point mesh was applied for sampling the Brillouin zone. The convergence criteria were set as follows: energy tolerance of 10^{-5} Ha, maximum force of 2×10^{-3} Ha/Å, and maximum displacement of 5×10^{-3} Å. In the self-consistent field (SCF) electronic structure calculations, the global orbital cutoff radius was set to 5 Å, the SCF energy convergence threshold to 10^{-6} Ha, and an orbital smearing value of 0.005 Ha was applied [28]. To ensure consistency with the purchased metal oxide powders, wurtzite ZnO, rutile SnO₂, and corundum α -Al₂O₃ crystal structures relevant to the experiment were used. In terms of heterojunction model construction, a $4 \times 4 \times 1$ graphene supercell was employed, resulting in an in-plane lattice constant of $a = b = 9.84$ Å. Correspondingly, $3 \times 3 \times 1$ ZnO, $3 \times 3 \times 1$ SnO₂, and $2 \times 2 \times 1$ Al₂O₃ surface supercells were constructed, with in-plane lattice constants of 9.358 Å (ZnO), 9.692 Å (SnO₂), and 9.518 Å (Al₂O₃), respectively. By selecting commensurate supercells, the in-plane lattice mismatch between graphene and each oxide surface was minimized and kept within a few percent. All heterojunction structures were fully relaxed during geometry optimization, and no external mechanical strain was explicitly imposed. The formulas for calculating the

lattice mismatch rate are listed in Equation (3), where a_1 and a_2 are the lattice constants of two different structures.

$$\Delta = \frac{2|a_1 - a_2|}{a_1 + a_2} \quad (3)$$

To quantitatively evaluate the interaction strength between graphene and the three materials, the concept of interaction energy was introduced. The interaction energy is defined by the following equation [29]:

$$E_b = E_H - E_O - E_G \quad (4)$$

where E_b is the interaction energy, E_H represents the total energy of the heterojunction composed of graphene and the material, E_O denotes the energy of the material in the heterojunction excluding graphene, and E_G is the energy of the graphene within the heterojunction. During the formation of heterojunctions between graphene and the three materials, charge transfer occurs. The amount of charge transfer is obtained using the Mulliken layout analysis method, and the calculation formula is as follows [29]:

$$Q_T = Q_a - Q_b \quad (5)$$

where Q_T represents the total charge transfer of the system, Q_a is the total charge of the system after the interaction, and Q_b is the total charge of the system before the interaction. A negative value of Q_T indicates that the other materials gain electrons from graphene.

3. Results and Discussions

3.1. Characterization of Material Properties

High-resolution scanning electron microscopy (SEM) images clearly reveal the microscopic morphology and interfacial structure characteristics of the three metal oxide–graphene heterojunctions (ZnO-G, SnO₂-G, and Al₂O₃-G). As shown in Figure 4, in all three types of heterojunctions, the metal oxide fillers are uniformly distributed in the form of nanoscale particles across the graphene sheet surfaces, with no significant agglomeration or interfacial gaps observed, indicating good dispersibility and interfacial compatibility. These structural features reflect that the synthesis process adopted enables uniform loading of the fillers on the graphene substrate, laying a structural foundation for the construction of high-performance composite sensitive materials. Such a uniformly distributed and closely contacted interfacial structure facilitates enhanced charge transfer efficiency and reduced interfacial resistance, thereby optimizing the electrical performance of the composite system.

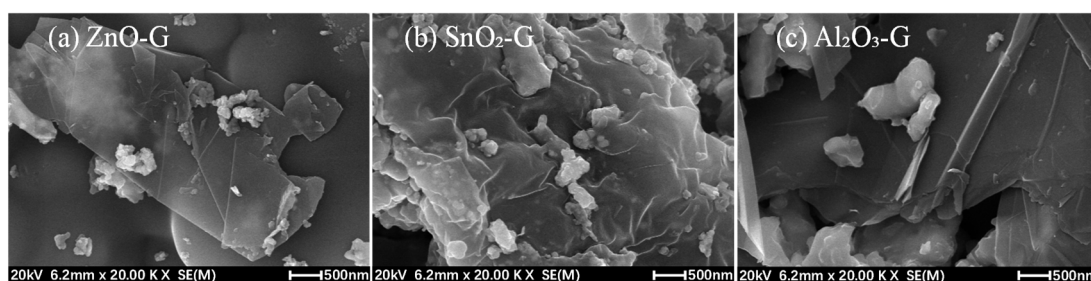


Figure 4. SEM characterization results of graphene/PDMS composites.

Further elemental distribution analysis via energy-dispersive X-ray spectroscopy (EDS) was conducted, with results presented in Figure 5. In all three heterojunction systems, the signals of the metallic elements (Zn, Sn, Al) and oxygen (O) exhibit high

spatial correspondence with the carbon (C) signal from graphene, confirming the successful loading of metal oxides onto the graphene substrate. Simultaneously, a certain degree of interfacial elemental interdiffusion was observed in each system, which contributes to enhancing the interfacial bonding strength between the filler and the substrate.

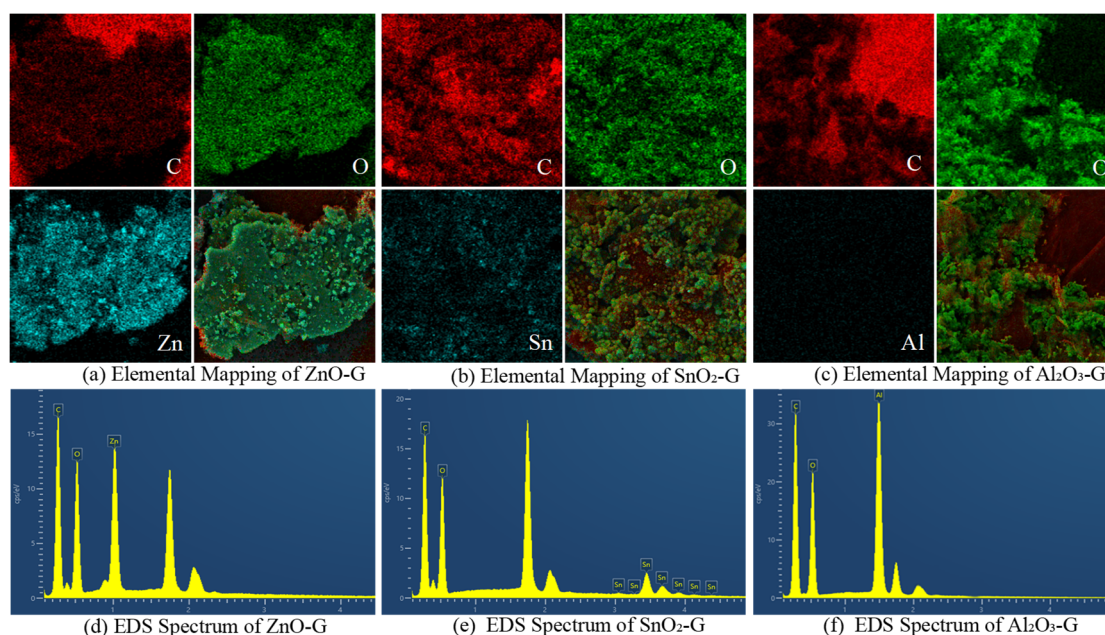


Figure 5. EDS results of ZnO-G, SnO₂-G and Al₂O₃-G heterojunctions.

Specifically, in the ZnO-G system, the distribution regions of Zn and O show significant overlap with that of C, forming a relatively broad transition zone. This indicates noticeable diffusion of Zn/O into the graphene layers, facilitating the formation of a stable chemically bonded interface and thereby improving both the thermal stability and electron transport efficiency of the composite. In the SnO₂-G system, the Sn and O signals display a gradient distribution at the interface, with Sn showing a tendency to penetrate into the graphene layers. Although this may lead to localized elemental enrichment, it also enhances the interfacial catalytic activity. In the Al₂O₃-G system, the distribution boundaries of Al and O are relatively distinct, with limited diffusion confined mainly to atomic layers near the interface. All three types of heterojunctions exhibit an enhanced interfacial structure characterized by moderate elemental interdiffusion. This structure helps strengthen the bonding between the filler and the graphene matrix, providing a favorable microscopic foundation for the functional design of composite materials.

3.2. Dielectric and Electric-Field Performance Test Results

The dielectric spectroscopy results are shown in the figure, presenting the relative permittivity spectra of the five composite materials within the frequency range of 50 Hz to 50 kHz. Overall, the relative permittivity of the graphene-doped PDMS composites is significantly enhanced compared to the pure PDMS system. Furthermore, the relative permittivity of all heterojunction-modified composites exceed that of the PDMS composite with graphene alone, indicating that the introduction of functional graphene heterojunction fillers effectively enhances the polarization capability of the matrix, resulting in a composite system with superior dielectric properties.

The composites with different components exhibit distinct gradient differences in dielectric performance. Among them, the tin dioxide-graphene (SnO₂-G) heterojunction-modified sample demonstrates the highest relative permittivity across the entire tested

frequency range, reaching a value of 3.19. Figure 6b further illustrates the variation in the loss tangent ($\tan\delta$) with frequency for the corresponding composites. It can be observed that the $\tan\delta$ values of all materials gradually decrease with increasing frequency. Meanwhile, the graphene heterojunction-modified samples exhibit relatively higher $\tan\delta$ values, indicating that significant dielectric loss is introduced alongside the achievement of strong polarization. This characteristic can, under certain conditions, contribute to an improved signal-to-noise ratio in sensors.

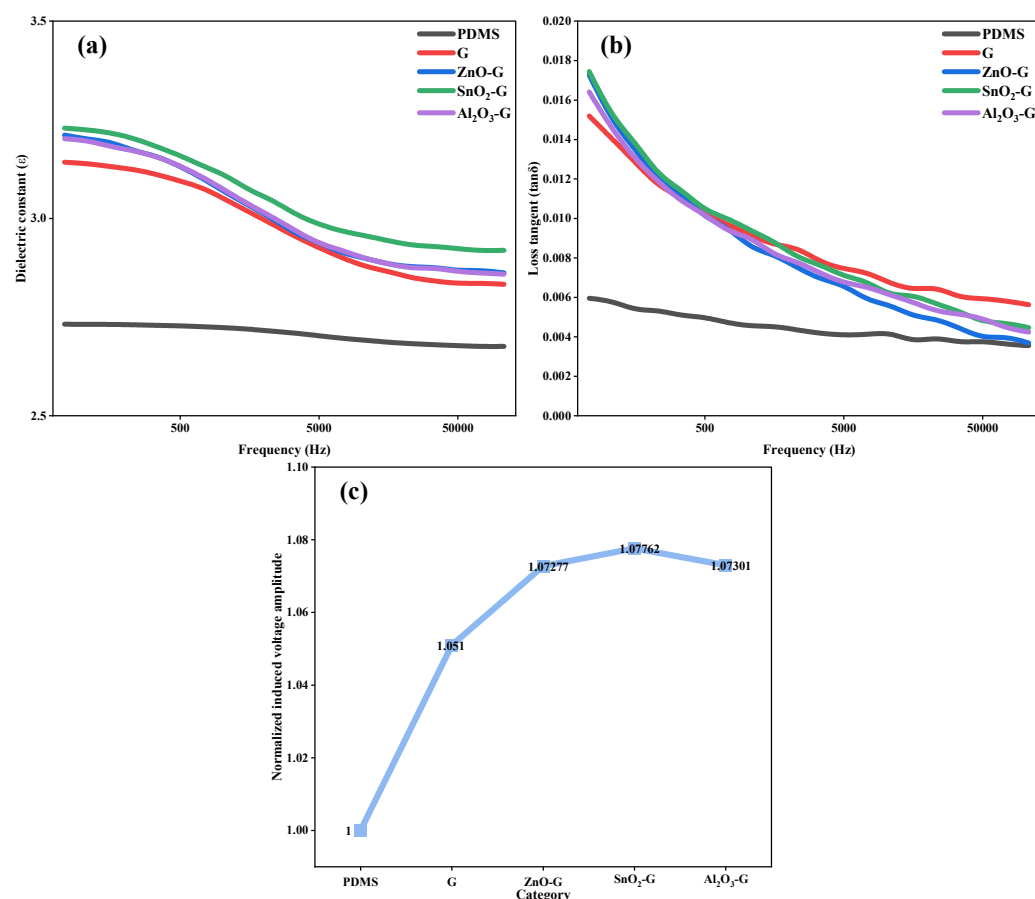


Figure 6. Results of Dielectric Spectroscopy and Electric Field Sensing Tests. (a) frequency dependence of relative permittivity; (b) frequency dependence of dielectric loss; (c) normalized induced voltage response under an alternating electric field.

From the perspective of frequency response characteristics, the tendency of the relative permittivity to decrease with increasing frequency can, to some extent, compensate for the inherent high-pass characteristics of capacitive sensors. The amplitude-frequency response of the sensor itself attenuates in the low-frequency region, while the decrease in the material's relative permittivity occurs primarily within the linear response frequency band. This creates a complementary relationship between the two effects, aiding in the expansion of the effective dynamic range of the sensing system and improving the overall linearity.

This study employed a two-layer calibration method to eliminate the influence of sensing unit individual variations and installation deviations on measurement results. First, the system gain coefficient for each channel was calibrated using the response of an uncovered reference sensing unit in a standard electric field to compensate for inherent errors. Second, before each test, a standard positioning calibration sheet with blank electrodes was used to obtain the position correction factor reflecting the installation posture. When measuring the graphene/PDMS composite samples, the raw output data were sequentially corrected using the system gain coefficient and the position correction factor to reconstruct

the true dielectric response of the material in an ideal uniform electric field. Finally, all test results were normalized relative to the pure PDMS material, yielding the normalized electric field sensing response curves shown in the figure. As shown in Figure 6c, the normalized induced voltage amplitudes of composite systems with different fillers (graphene, ZnO, SnO₂, and Al₂O₃) mainly fall within the range of 1.07–1.078, showing a significant improvement compared to pure PDMS. Among various heterojunction materials, the tin dioxide-graphene (SnO₂-G) heterojunction exhibits the most significant voltage response, improving by 7.76% compared to pure PDMS.

3.3. Analysis of the Calculated Results

Figure 7 shows the top view and differential charge density (including the side view) of the optimized structural models of heterojunctions formed between graphene and three metal oxides (labeled ZnO/G, SnO₂/G, and Al₂O₃/G, respectively). In the optimized ZnO/G structure, both ZnO and G components exhibit slight deformation, but no chemical bonds are formed, indicating a certain degree of interaction between them, namely, van der Waals forces. In contrast, the SnO₂/G and Al₂O₃/G heterojunctions in Figure 7b do not show significant structural deformation and still lack chemical bond formation, indicating that van der Waals forces play a major role in the interaction between graphene and the three metal oxides. The calculated interaction energies between graphene and zinc oxide, tin oxide, and aluminum oxide are −2.271 eV, −2.372 eV, and −2.693 eV, respectively. The negative values indicate that the formation of heterojunctions between graphene and these three materials is spontaneous and requires no external energy input. Among them, the interaction energy between aluminum oxide and graphene is the strongest, which may be attributed to its more complex crystal structure and larger number of atoms.

In terms of charge transfer, zinc oxide and tin oxide gain electrons from graphene during heterojunction formation, with transfer amounts of 0.0708 e and 0.3636 e, respectively, while aluminum oxide donates electrons to graphene. Among the three, the charge transfer in the tin oxide system is the most pronounced. To visualize the redistribution of interfacial charge more clearly, the charge density difference maps of the three heterojunction systems are also provided in Figure 7. From the charge density difference distributions, typical blue and yellow regions can be observed in the interfacial areas. The color differences intuitively reveal charge transfer at the heterojunction interface, indicating electron transfer from one side (the electron-deficient region, usually shown in blue) to the other (the electron-rich region, usually shown in yellow). To further investigate the deeper influence of these metal oxides on the electronic structure of graphene after heterojunction formation, their band structures were analyzed. Figure 8 presents the calculation results of the band gaps for the relevant materials.

Band structure calculations for the three metal-oxide/graphene heterojunctions (Figure 8) show that interfacial interactions induce slight perturbations in the electronic structure of graphene. Due to the weak symmetry breaking and low orbital hybridization at the interface, small band gaps of 0.017 eV (ZnO/G) and 0.064 eV (Al₂O₃/G) appear at the Dirac point, while SnO₂/G remains almost gapless. It is important to emphasize that these band gap values are within the numerical error range of the PBE-GGA calculations and should not be interpreted as band gaps with practical functional significance. They merely reflect minor interfacial perturbations caused by charge redistribution and weak hybridization between graphene and the oxide surface. The key electronic effects in these heterojunctions originate from interfacial charge transfer and density of states modulation, rather than the absolute value of the induced band gap.

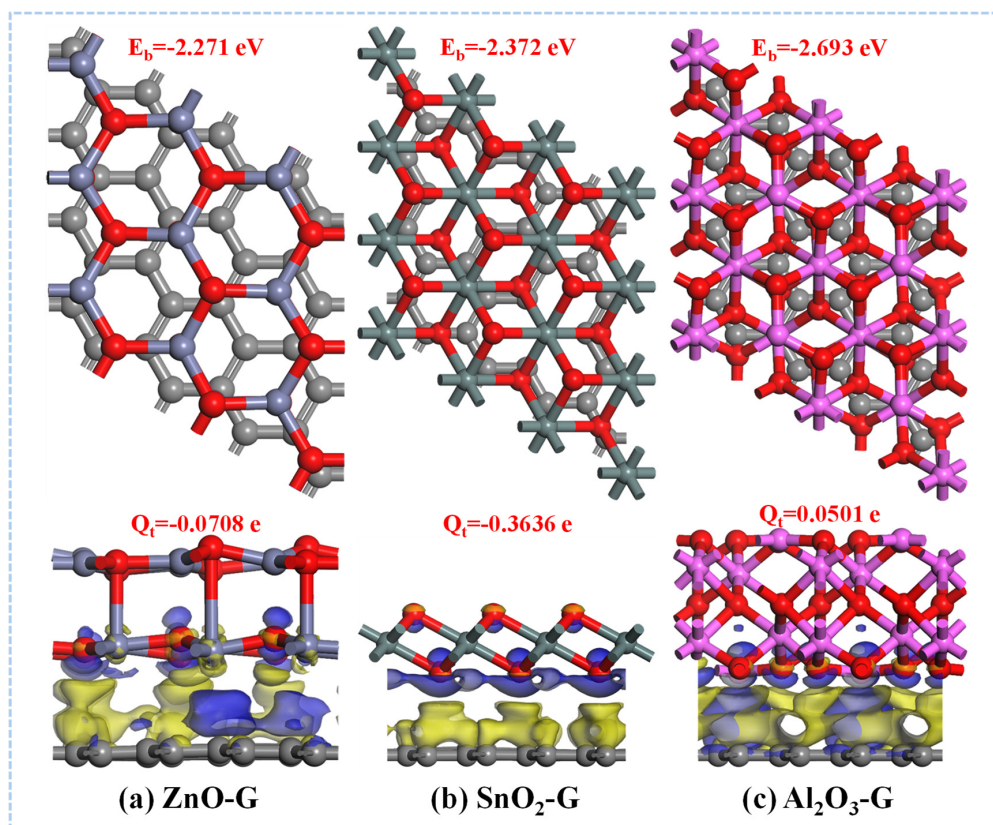


Figure 7. Optimized Structure and Charge Density Difference (Side View).

Figure 9 displays the density of states (DOS) distributions for the heterojunction systems composed of graphene and the three metal oxides. Taking the zinc oxide/graphene (ZnO/G) system as an example, its DOS includes both the total heterojunction DOS and the projected DOS of individual components. As shown in Figure 9a, the total heterojunction DOS dominates the overall distribution. To the right of the Fermi level (0 eV), each peak in the total heterojunction DOS is formed by the combined contributions from both ZnO and graphene component peaks, reflecting orbital hybridization at corresponding energy levels. Further examination of Figure 9a shows that the DOS of the ZnO/G heterojunction approaches zero at the Fermi level without any states crossing it, consistent with the finite bandgap observed for this system in Figure 8. In the DOS of the tin oxide/graphene (SnO₂/G) heterojunction shown in Figure 9b, similar characteristics to the ZnO/G system are observed: the total heterojunction DOS still dominates, with its peak positions similarly formed through hybridization of the DOS peaks from both components. This phenomenon is also present in the aluminum oxide/graphene (Al₂O₃/G) system. These consistent DOS hybridization behaviors indicate that significant charge transfer and electronic interactions occur at the interfaces during the formation of heterojunctions between graphene and the three metal oxides. The enhancement of the composite dielectric response originates from interfacial charge transfer, which induces localized interfacial dipoles and strengthens interfacial polarization under an external field. Although Al₂O₃-G shows the largest interaction energy, its intrinsically low permittivity and strong charge localization limit its macroscopic contribution. In contrast, SnO₂ possesses higher polarizability and forms more continuous charge-transport and polarization pathways with graphene, leading to the strongest macroscopic dielectric enhancement. Therefore, the differences among ZnO-G, SnO₂-G, and Al₂O₃-G arise from the combined effects of interfacial charge transfer, oxide permittivity, and the continuity of local polarization channels.

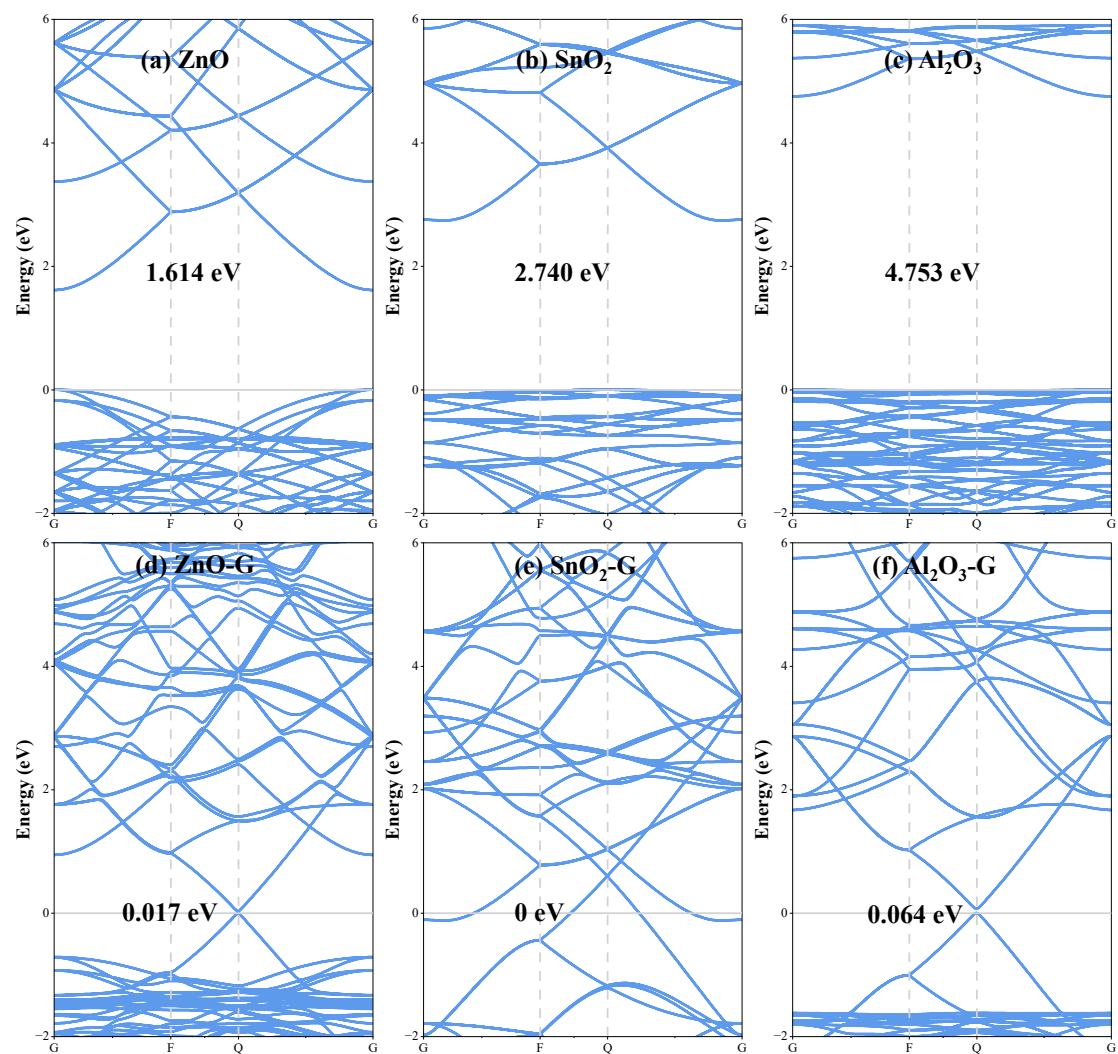


Figure 8. Band Structures of the Three Metal Oxides and Their Heterojunctions.

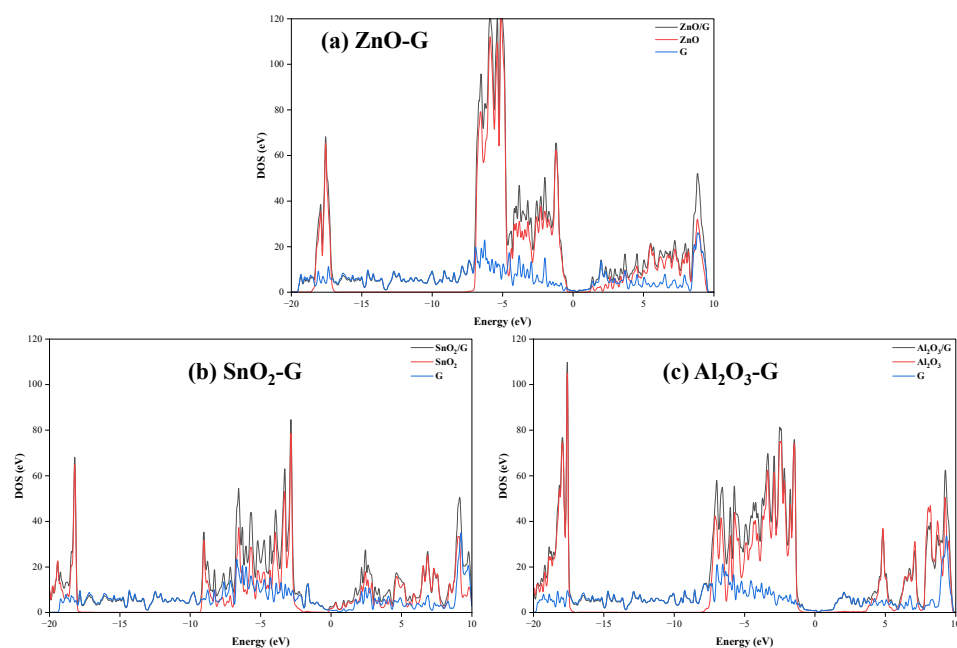


Figure 9. Density of States of the Three Metal Oxides and Heterojunctions.

4. Conclusions

This study combines first-principles calculations and experimental characterization to explore how graphene-oxide heterojunctions modulate the macroscopic electric field sensitivity of composite materials. Experimentally, scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) results confirmed that the three oxides are uniformly anchored on graphene nanosheets, forming stable nanoscale interfaces. Dielectric measurements showed that the relative permittivity of all heterojunction-modified composites was higher than that of pure PDMS and graphene/PDMS, with SnO₂-G/PDMS exhibiting the strongest dielectric enhancement and the highest electric field-induced voltage response. Density functional theory (DFT) calculations indicated that graphene forms thermodynamically favorable heterojunctions with ZnO, SnO₂, and Al₂O₃, as confirmed by their negative interaction energies. Interfacial charge transfer analysis showed that the SnO₂-G interface generated the largest electron redistribution, while density of states analysis confirmed weak orbital hybridization and interface-induced electronic reconstruction.

A microscopic-to-macroscopic mechanism was established, linking interfacial charge transfer to enhanced electric field sensitivity in graphene-based composites. Metal oxide modification provides an effective approach for modulating the interfacial electronic environment of graphene and improving its performance in electric line field measurement and flexible sensing devices. Future research will focus on optimizing the interfacial structure, exploring other oxide or doped systems, and advancing its practical applications in real-time electric field monitoring.

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