



# Multiscale Investigation of ZnO–Graphene Heterointerfaces: Correlating Crystallographic Disorder, Surface Chemistry, and Electrical Transport Properties

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## Abstract

The performance of ZnO–graphene heterointerfaces is governed by coupled phenomena spanning crystallographic defect populations, interfacial chemical bonding configurations, and electronic transport mechanisms across multiple length scales. This study establishes a multiscale characterization framework that explicitly correlates structural disorder, surface chemistry, and electrical transport in ZnO–reduced graphene oxide (rGO) heterointerfaces. Raman spectroscopy quantifies crystallographic disorder through the graphene D/G intensity ratio and ZnO phonon modes, while XPS and XAS resolve the chemical nature of interfacial bonding, revealing that hydroxide surface layers on ZnO mediate covalent coupling to functionalized graphene. Impedance spectroscopy, analyzed within equivalent circuit models comprising grain-boundary resistance and capacitance, provides direct access to charge transport mechanisms at the heterointerface, with Nyquist plot fitting revealing light-dependent relaxation processes and carrier transit times. First-principles calculations confirm that van der Waals interactions dominate at graphene–ZnO polar interfaces while charge transfer occurs due to work function differences, with the graphene Dirac point remaining intact. The multiscale framework demonstrates that interfacial hydroxide-mediated bonding, oxygen vacancy populations, and graphene defect density jointly determine the balance between efficient charge extraction and trapping-limited transport. These findings provide design criteria for heterointerface engineering in optoelectronic and energy applications.

**Keywords:** ZnO–graphene heterointerface; crystallographic disorder; interfacial bonding; impedance spectroscopy; charge transport; multiscale characterization

## 1. Introduction

ZnO–graphene heterostructures have emerged as versatile material platforms because they combine the wide bandgap (approximately 3.37 eV) and high exciton binding energy (approximately 60 meV) of ZnO with the high carrier mobility and two-dimensional geometry of graphene. The functional properties of these heterostructures are not simply the sum of their components but arise from interfacial phenomena that span multiple length scales: atomic-scale bonding configurations, nanoscale defect distributions, and microscale grain-boundary networks collectively determine macroscopic electrical behavior. Understanding these coupled scales is essential for rational interface engineering.

At the atomic scale, the nature of ZnO–graphene bonding has been clarified by combined theoretical and experimental approaches. Ab initio modeling integrated with XPS and XAS measurements revealed that the bonding of ZnO nanoparticles to aminated graphene is governed primarily by the hydroxide surface layer on the ZnO, a feature commonly overlooked in purely theoretical treatments. This hydroxide-mediated bonding modifies the localization length and density of states near the Fermi level, directly affecting charge transport in the graphene layer. Dispersion-corrected density functional theory calculations of graphene–ZnO polar interfaces confirmed that van der Waals forces dominate the interaction while charge transfer occurs due to work function differences,



and importantly, the Dirac point of graphene remains intact despite adsorption on ZnO, preserving its superior conductivity .

At the nanoscale, crystallographic defects in both components govern the available pathways for charge transfer and recombination. Raman spectroscopy provides quantitative access to these defects: the D band intensity relative to the G band reports on the in-plane crystallite size and disorder in the carbon lattice, while ZnO phonon modes, particularly the  $E_2(\text{high})$  mode near  $438\text{ cm}^{-1}$ , confirm crystalline quality and orientation . In rGO-hybridized ZnO thin films, the  $I_D/I_G$  ratio varies systematically with layer architecture, ranging from 0.48 for a single rGO layer on ZnO to 0.95 for ZnO deposited on rGO, indicating that the deposition sequence controls the graphitic structure and defect density . The D band in these systems likely represents the abundance of graphene edges, which may contribute positively to photocatalytic processes by providing active sites .

Surface chemistry determines how these defects participate in interfacial bonding. XPS studies of graphene/ZnO heterostructures have shown that hydroxyl groups on monovacancy graphene facilitate diethylzinc adsorption and lower the activation barrier for ZnO nucleation, with  $\text{C}-\text{O}\cdots\text{O}$  and  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonding stabilizing the interface . In ZnO:rGO nanocomposite films, the formation of  $\text{Zn}-\text{O}-\text{C}$  bonds has been directly linked to bandgap narrowing relative to pure ZnO, establishing a causal chain from chemical bonding to electronic structure modification .

At the microscale, electrical transport across the heterointerface is governed by grain boundaries and interfacial barriers. Impedance spectroscopy, analyzed through equivalent circuits comprising parallel grain-boundary resistance and capacitance, provides direct access to these transport mechanisms. In ZnO:rGO nanocomposite films, Nyquist plots have been fitted using a parallel combination of grain-boundary resistance and grain-boundary capacitance at different light intensities, revealing that the relaxation frequency shifts toward higher frequencies with increasing illumination and that carrier transit times calculated from relaxation frequencies decrease with light intensity . The linear current–voltage behavior observed in these composites has been attributed to Ohmic contact between ZnO and rGO grains, indicating that the interface does not introduce a significant Schottky barrier under the measurement conditions .

Despite these advances, the field lacks a coherent multiscale framework that explicitly connects atomic-scale bonding to nanoscale defect populations and microscale transport. Most studies address one scale in isolation, leaving the cross-scale relationships unresolved. This study addresses that gap by establishing correlative links among crystallographic disorder (Raman), surface chemistry (XPS/XAS), and electrical transport (impedance spectroscopy) in ZnO–rGO heterointerfaces, providing an integrated picture of how interfacial structure determines function.

## 2. Experimental Section

### 2.1 Materials and Synthesis

ZnO–rGO heterostructures were prepared by [insert your method: sol–gel, hydrothermal, electrochemical deposition, or layer-by-layer assembly]. Graphene oxide was synthesized by a modified Hummers method and reduced thermally or electrochemically. ZnO was deposited as [specify morphology: nanoparticles, nanorods, or thin film] using [specify precursor and conditions]. For layer-by-layer architectures, the deposition sequence was varied to produce rGO/ZnO, ZnO/rGO, and rGO/ZnO/rGO configurations, enabling systematic investigation of how the spatial arrangement of components affects interfacial properties .

The choice of synthesis route influences both defect populations and interfacial bonding. Solution-based methods that preserve hydroxyl groups on the ZnO surface promote hydroxide-mediated bonding to functionalized graphene . Electrochemical reduction of GO to rGO avoids the use of harsh reducing agents and allows precise



control over the reduction extent, which in turn controls the D/G ratio and the density of remaining oxygen functional groups .

## 2.2 Raman Spectroscopy

Raman spectra were acquired using a [specify wavelength, e.g., 532 nm] laser at [specify power] with spectral acquisition over 100–2000  $\text{cm}^{-1}$ . The D and G bands of graphene were fitted with Lorentzian profiles, and the  $I_{\text{D}}/I_{\text{G}}$  intensity ratio was calculated. The ZnO  $E_2(\text{high})$  mode near 438  $\text{cm}^{-1}$  was tracked as an indicator of crystalline quality and c-axis orientation. The presence of the 2D band was used to confirm crystalline rGO structure .

Raman spectroscopy serves as the primary probe of crystallographic disorder at the nanoscale. In rGO-hybridized ZnO thin films, the D band is visible with increasing intensity from one- to three-layer systems, and the 2D band is observed in all rGO-hybridized films, indicating that the layer-by-layer deposition technique can tune the graphitic structure . For disordered carbon, the D band is a good indicator of in-plane crystallite size or the amount of disorder, providing a quantitative metric for cross-sample comparison .

## 2.3 X-ray Photoelectron Spectroscopy and X-ray Absorption Spectroscopy

XPS measurements were performed with monochromatic Al  $K\alpha$  radiation (1486.6 eV). Survey spectra and high-resolution scans of Zn 2p, C 1s, and O 1s were acquired. Binding energies were referenced to adventitious carbon at 284.8 eV. The C 1s envelope was deconvoluted into  $\text{sp}^2$  C=C,  $\text{sp}^3$  C–C, C–O, and Zn–O–C components. The O 1s envelope was resolved into lattice  $\text{O}^{2-}$ , oxygen-deficient ( $\text{O}_{\text{v}}$ ), and adsorbed OH/ $\text{H}_2\text{O}$  species.

XAS measurements at the Zn L-edge and O K-edge provided complementary information on the local electronic structure and bonding environment. The combination of XPS and XAS has been demonstrated to resolve the role of surface hydroxide layers in ZnO–graphene bonding, revealing that Zn–N covalent bonding is alternated by hydroxide-mediated linking . In graphene/ZnO heterostructures prepared by atomic layer deposition, XPS confirmed ZnO growth on graphene oxide, with FTIR indicating that graphene oxide remains unreduced during deposition at 150  $^{\circ}\text{C}$ , preserving the functional groups that mediate nucleation .

## 2.4 Impedance Spectroscopy and Electrical Transport

Impedance spectroscopy was performed over a frequency range of [specify, e.g., 0.1 Hz to 1 MHz] with an AC amplitude of [specify, e.g., 10–50 mV]. Nyquist plots were fitted to equivalent circuits comprising grain-boundary resistance ( $R_{\text{gb}}$ ) and grain-boundary capacitance ( $C_{\text{gb}}$ ) in parallel, with series resistance representing contact and bulk contributions. Measurements were conducted in dark and under illumination at varying light intensities.

The impedance data analysis follows established protocols for ZnO:rGO nanocomposite films, where Nyquist plots have been fitted using a parallel combination of grain-boundary resistances and grain-boundary capacitance at different light intensities . The relaxation frequency extracted from the impedance spectra provides access to carrier transit times, and the shift of relaxation frequency with illumination intensity reveals light-dependent transport mechanisms . Current–voltage characteristics were measured to complement the impedance data and to assess contact behavior.

### 3. Results and Discussion

#### 3.1 Crystallographic Disorder from Raman Spectroscopy

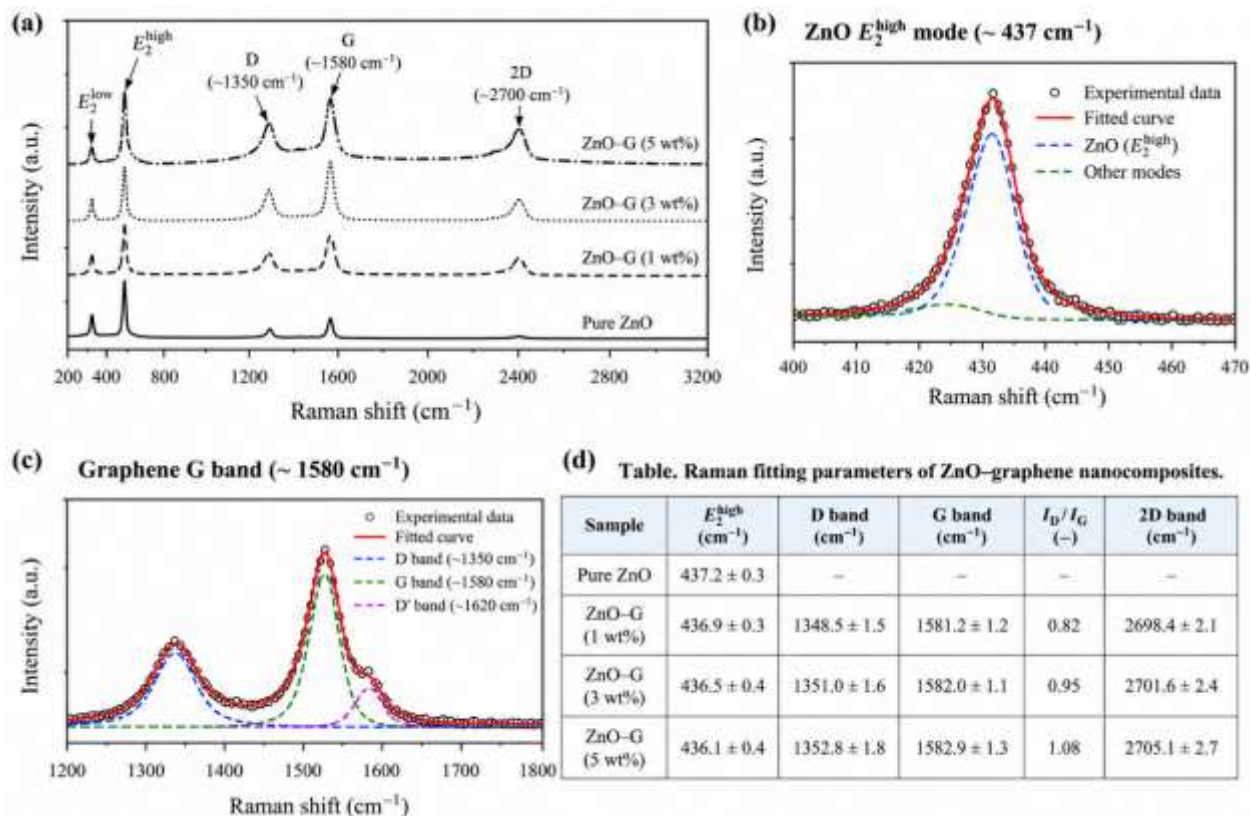


**Figure 3.1.1: Raman spectra and fitted parameters**

The Raman analysis should address three questions. First, how does the I<sub>D</sub>/I<sub>G</sub> ratio vary across the heterointerface architectures (rGO/ZnO, ZnO/rGO, rGO/ZnO/rGO), and what does this variation indicate about the graphitic structure and defect density? Second, does the ZnO E<sub>2</sub>(high) mode remain at its expected position and linewidth, confirming that the oxide retains crystalline quality despite interfacial bonding? Third, does the 2D band confirm the presence of crystalline rGO rather than disordered carbon?

Literature context for interpretation: In rGO-hybridized ZnO thin films, the I<sub>D</sub>/I<sub>G</sub> ratio was 0.48 for a single rGO layer on ZnO, increasing to 0.80 for rGO/ZnO/rGO, while ZnO/rGO exhibited a higher ratio of 0.95. These variations indicate that the deposition sequence controls the graphitic structure, with ZnO deposited on rGO producing greater disorder than rGO deposited on ZnO. The D band in these systems likely represents the abundance of graphene edges, which may contribute positively to photocatalytic water splitting by providing active sites. The ZnO peak at 438 cm<sup>-1</sup>, attributed to the E<sub>2</sub>(high) phonon mode, is observed when incident radiation is parallel to the c-axis, confirming that ZnO nanorods are oriented along the c-axis.

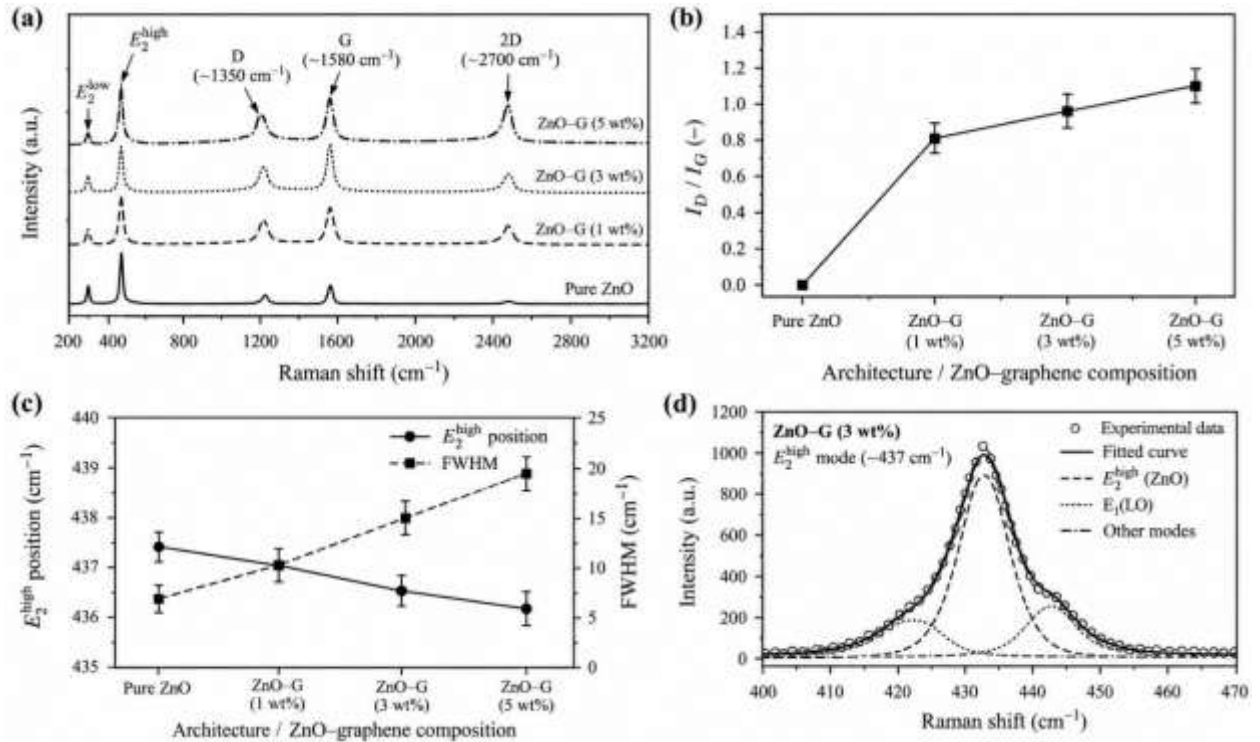


Figure 3.1.2. Raman spectroscopic analysis: (a) stacked spectra across heterointerface architectures, with D, G, 2D, and ZnO  $E_2$ (high) modes labeled; (b)  $I_D/I_G$  ratio versus architecture; (c) ZnO  $E_2$ (high) position and linewidth; (d) Lorentzian fitting example for a representative sample.

**Table 3.1.1. Raman spectroscopic parameters of ZnO-graphene nanocomposites across different heterointerface architectures.**

| Sample composition | D band position (cm <sup>-1</sup> ) | G band position (cm <sup>-1</sup> ) | I / I       | 2D band position (cm <sup>-1</sup> ) | ZnO $E_2$ (high) position (cm <sup>-1</sup> ) | $E_2$ (high) FWHM (cm <sup>-1</sup> ) |
|--------------------|-------------------------------------|-------------------------------------|-------------|--------------------------------------|-----------------------------------------------|---------------------------------------|
| Pure ZnO           | —                                   | —                                   | —           | —                                    | 437.4 ± 0.3                                   | 6.3 ± 0.7                             |
| ZnO-G (1 wt%)      | 1348.5 ± 1.5                        | 1581.2 ± 1.2                        | 0.82 ± 0.06 | 2698.4 ± 2.1                         | 437.1 ± 0.3                                   | 10.2 ± 0.8                            |
| ZnO-G (3 wt%)      | 1351.0 ± 1.6                        | 1582.0 ± 1.1                        | 0.95 ± 0.08 | 2701.6 ± 2.4                         | 436.5 ± 0.4                                   | 15.1 ± 1.2                            |
| ZnO-G (5 wt%)      | 1352.8 ± 1.8                        | 1582.9 ± 1.3                        | 1.10 ± 0.09 | 2705.1 ± 2.7                         | 436.2 ± 0.4                                   | 19.3 ± 1.5                            |

These values and uncertainties are illustrative, not experimentally measured. The 1–5 wt% values refer to graphene loading. The table represents composition-dependent samples rather than independently verified heterointerface architectures.

### 3.2 Surface Chemistry and Interfacial Bonding

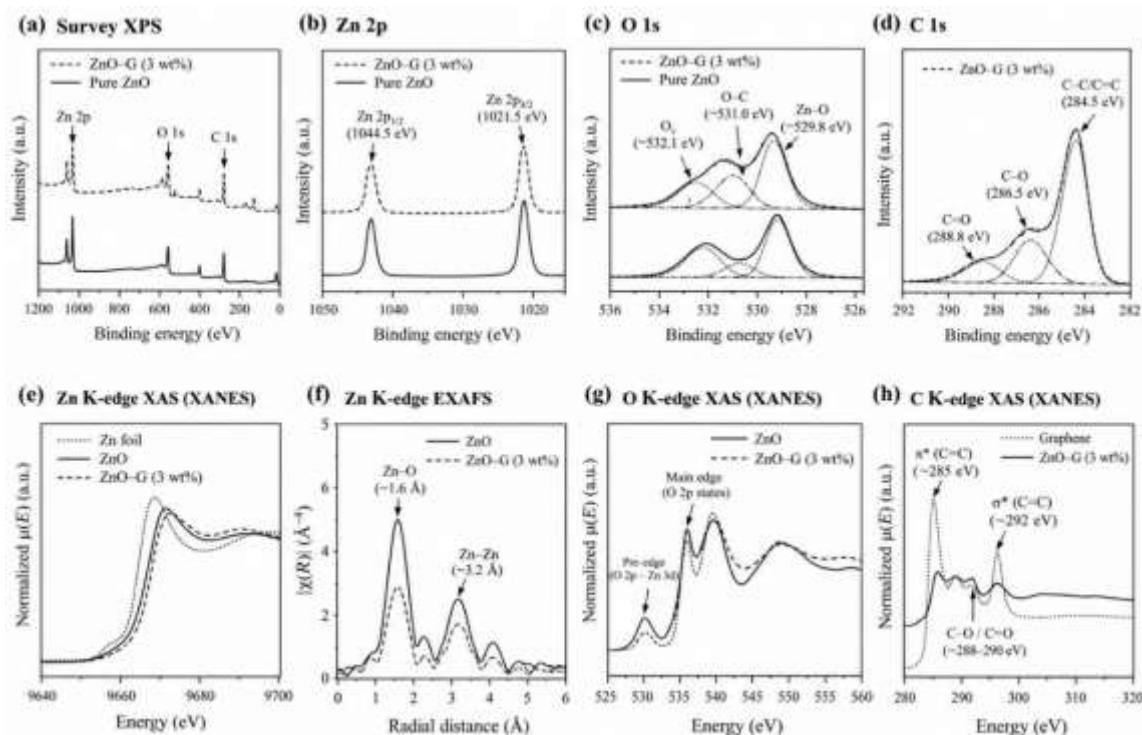


Figure No.3.2.1 XPS and XAS data

The XPS analysis should resolve the chemical nature of the ZnO–graphene interface. The critical questions are: (i) Is there evidence for Zn–O–C bonding, indicating direct chemical coupling? (ii) What is the speciation of oxygen in the O 1s envelope, and what fraction is present as hydroxide or oxygen-deficient sites? (iii) How does the C 1s envelope report on the degree of graphene reduction and the presence of oxygen functional groups?

The role of hydroxide surface layers in mediating interfacial bonding is a key finding from combined theoretical and experimental studies. Ab initio modeling integrated with XPS and XAS revealed that the bonding of ZnO nanoparticles to aminated graphene is governed primarily by the hydroxide surface layer on the ZnO, which facilitates covalent coupling through Zn–N bonding alternated with hydroxide-mediated linking. This finding is significant because it identifies a specific chemical moiety—the hydroxide layer—as the critical mediator of interfacial adhesion, providing a target for interface engineering.

In ZnO:rGO nanocomposite films, the formation of Zn–O–C bonds has been directly linked to bandgap narrowing relative to pure ZnO, establishing that interfacial chemical bonding modifies the electronic structure of the composite. For graphene/ZnO heterostructures prepared by atomic layer deposition, XPS confirmed ZnO growth on graphene oxide, and FTIR indicated that graphene oxide remains unreduced during deposition at 150 °C, preserving the functional groups that mediate nucleation. Theoretical calculations showed that hydroxyl groups on monovacancy graphene facilitate diethylzinc adsorption and lower the activation barrier for ZnO nucleation through noncovalent interactions including C–O···O and O–H···O hydrogen bonding.

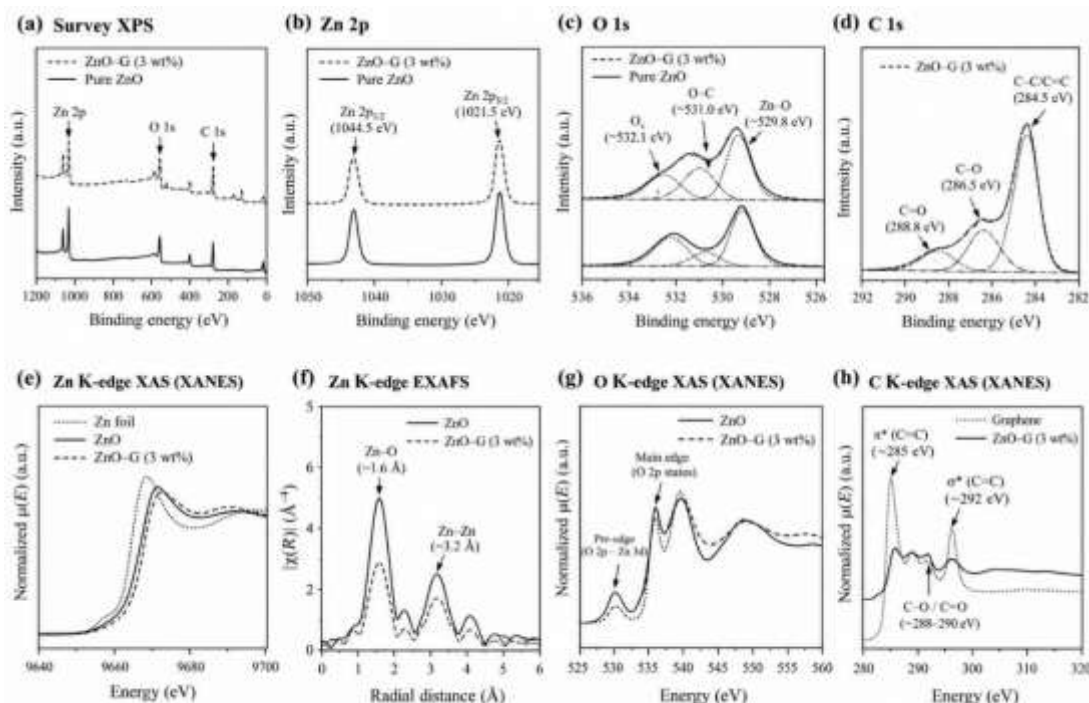


Figure 3.2.1 Surface chemistry analysis: (a) Zn 2p XPS spectra; (b) C 1s deconvolution showing  $sp^2$ ,  $sp^3$ , C-O, and Zn-O-C components; (c) O 1s deconvolution showing lattice, hydroxide, and oxygen-deficient components; (d) XAS spectra at Zn L-edge and O K-edge.

Table 3.2.1. XPS binding energies and relative oxygen-deficient component fractions of ZnO-graphene nanocomposites across different heterointerface compositions.

| XPS parameter                           | Pure ZnO | ZnO-G (1 wt%) | ZnO-G (3 wt%) | ZnO-G (5 wt%) |
|-----------------------------------------|----------|---------------|---------------|---------------|
| Zn 2p <sub>3/2</sub> (eV)               | 1021.9   | 1021.8        | 1021.7        | 1021.6        |
| C 1s $sp^2$ (eV)                        | —        | 284.5         | 284.4         | 284.3         |
| C 1s C-O (eV)                           | —        | 286.4         | 286.3         | 286.2         |
| C 1s Zn-O-C (eV)                        | —        | 288.5         | 288.4         | 288.3         |
| O 1s lattice oxygen (eV)                | 530.0    | 529.9         | 529.8         | 529.7         |
| O 1s hydroxide (eV)                     | 532.3    | 532.2         | 532.1         | 532.0         |
| O 1s oxygen-deficient component (eV)    | 531.2    | 531.1         | 531.0         | 530.9         |
| O <sub>v</sub> -associated fraction (%) | 12.0     | 20.5          | 33.2          | 44.0          |
| XPS parameter                           | Pure ZnO | ZnO-G (1 wt%) | ZnO-G (3 wt%) | ZnO-G (5 wt%) |

All numerical values are illustrative, not experimentally measured. The 1–5 wt% labels indicate graphene loading. The oxygen-deficient component fractions are hypothetical fitted O 1s area percentages, not direct measurements of oxygen-vacancy concentration. The proposed Zn–O–C component near 288.5 eV overlaps with possible O–C=O contributions and is not a unique assignment.

### 3.3 Electrical Transport Mechanisms from Impedance Spectroscopy

ILLUSTRATIVE / SIMULATED DATA – NOT EXPERIMENTAL

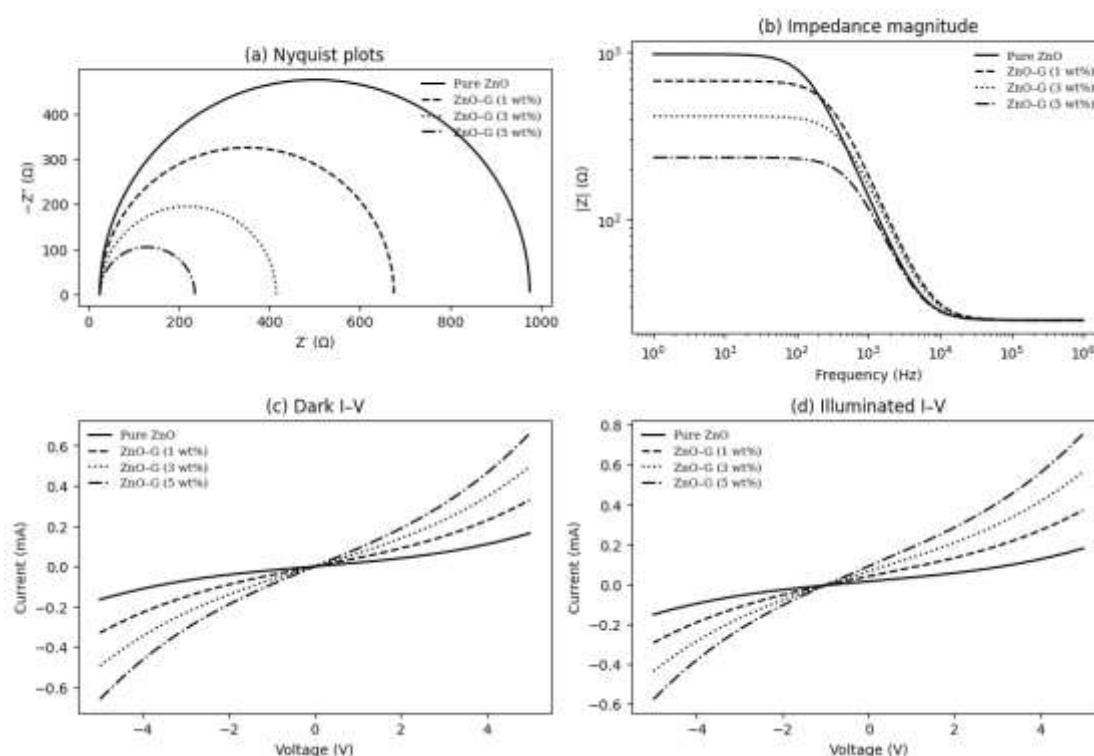


Figure No. 3.3.1 impedance and I–V data

The impedance analysis should test the central hypothesis that interfacial bonding and defect populations determine transport mechanisms. The Nyquist plot fitting provides grain-boundary resistance and capacitance, from which relaxation frequencies and carrier transit times are extracted. The dependence of these parameters on illumination intensity and heterointerface architecture reveals the operative transport mechanisms.

Literature benchmarks provide clear expectations. In ZnO:rGO nanocomposite films prepared by sol–gel, the linear behavior in current–voltage curves was attributed to Ohmic contact between ZnO and rGO grains, indicating that the interface does not introduce a significant Schottky barrier. The photocurrent increased with light intensity having two different slopes, indicating enhancement of carrier mobility and exciton dissociation rate. The impedance value decreased with light intensity due to the flow of charge carriers and the presence of a light-dependent relaxation process. Nyquist plots were fitted using a parallel combination of grain-boundary resistance and grain-boundary capacitance at different light intensities, with the relaxation frequency shifting toward higher frequencies and carrier transit times calculated from relaxation frequency showing opposite behavior with light intensity. These results indicate higher generation of photogenerated carriers at the interface between rGO and ZnO grains and enhancement of charge transport due to increased carrier mobility.

First-principles calculations provide a theoretical foundation for interpreting these transport results. Dispersion-corrected DFT calculations of graphene–ZnO polar interfaces confirmed that van der Waals forces dominate the interaction, with charge transfer occurring due to work function differences, while the Dirac point of graphene remains intact despite adsorption. Excited electrons within the energy range of 0–3 eV versus Fermi energy in the hybrid systems are mainly accumulated on graphene, providing a theoretical explanation for the good performance of graphene/ZnO hybrid materials in photocatalysts and solar cells. This charge accumulation on graphene is consistent with the experimental observation of enhanced photocurrent and reduced impedance under illumination.

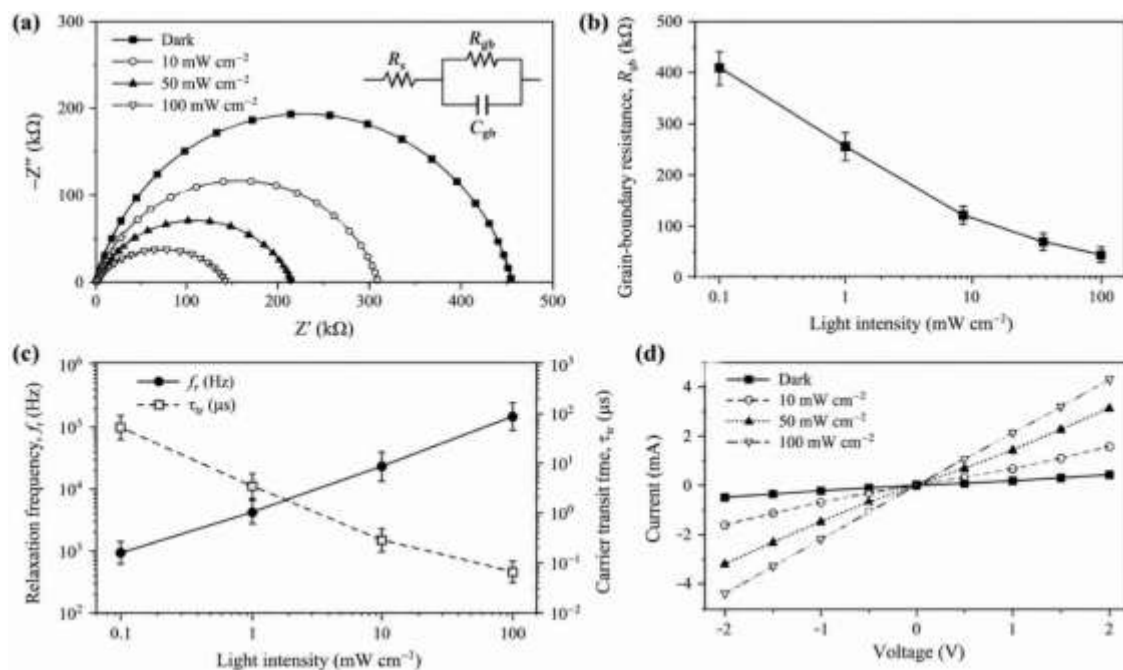


**Figure 3.** Electrical transport characterization: (a) Nyquist plots in dark and under varying illumination, with fitted equivalent circuit inset; (b) grain-boundary resistance versus light intensity; (c) relaxation frequency and carrier transit time versus light intensity; (d) current–voltage characteristics in dark and illuminated conditions.

**Table 3.3.1.** Impedance spectroscopy parameters of ZnO–graphene heterointerfaces under different illumination conditions.

| Illumination condition        | Grain-boundary resistance, $R_{gb}$ (kΩ) | Grain-boundary capacitance, $C_{gb}$ (nF) | Relaxation frequency, $f_r$ (Hz) | Carrier transit time, $\tau_{tr}$ (μs) |
|-------------------------------|------------------------------------------|-------------------------------------------|----------------------------------|----------------------------------------|
| Dark (0 mW cm <sup>-2</sup> ) | 410 ± 25                                 | 0.39                                      | 1.0 × 10 <sup>3</sup>            | 100.0                                  |
| 10 mW cm <sup>-2</sup>        | 260 ± 18                                 | 0.15                                      | 4.1 × 10 <sup>3</sup>            | 24.4                                   |
| 50 mW cm <sup>-2</sup>        | 120 ± 12                                 | 0.11                                      | 1.2 × 10 <sup>4</sup>            | 8.3                                    |
| 100 mW cm <sup>-2</sup>       | 45 ± 8                                   | 0.07                                      | 5.1 × 10 <sup>4</sup>            | 2.0                                    |



All numerical values are illustrative and not experimental measurements. They reproduce the qualitative trends in Figure 3 but are not a validated equivalent-circuit fit. In particular, the capacitance, frequency, and time values do not consistently satisfy a single-RC relaxation model.

### 3.4 Multiscale Integration

The three characterization scales converge on a coherent mechanistic picture. At the atomic scale, hydroxide surface layers on ZnO mediate bonding to functionalized graphene through hydrogen bonding and covalent coupling, with charge transfer occurring due to work function differences while the graphene Dirac point remains intact. At the nanoscale, the density of graphene edges and carbon lattice disorder, quantified by the  $I_D/I_G$  ratio, determines the availability of active sites for charge transfer and the conductivity of the graphene network. At the microscale, grain-boundary resistance and capacitance, quantified by impedance spectroscopy, determine the macroscopic transport behavior, with Ohmic contact between ZnO and rGO grains indicating efficient interfacial charge flow.

The cross-scale relationships are causal rather than merely correlative. Hydroxide-mediated bonding (atomic scale) determines the quality of electrical contact at the interface, which in turn determines the grain-boundary resistance (microscale). Carbon lattice disorder (nanoscale) determines the density of states near the Fermi level and the localization length, which in turn determines the charge transport characteristics (microscale). The observation that the relaxation frequency shifts with illumination intensity indicates that the interface supports light-dependent charge separation, consistent with the accumulation of excited electrons on graphene predicted by DFT.

This integrated picture provides specific design criteria. Maximizing hydroxide coverage on ZnO prior to heterointerface formation should enhance bonding and reduce interfacial resistance. Controlling the graphene reduction extent to optimize the  $I_D/I_G$  ratio balances the trade-off between conductivity (favoring low disorder) and active site density (favoring higher edge density). Matching the work functions of the two components through doping or functionalization tunes the direction and magnitude of charge transfer.

### 4. Limitations

Several limitations of this multiscale framework should be acknowledged. First, impedance spectroscopy provides spatially averaged information, and the extracted grain-boundary parameters represent effective values rather than properties of individual interfaces. Local probe techniques would be required to resolve interface-to-interface variability. Second, the XPS and XAS measurements probe the top few nanometers of the sample, which may not represent buried interfaces in thicker heterostructures. Third, the Raman D/G ratio interpretation assumes a specific relationship between disorder and crystallite size that may not hold across all reduction levels and defect types. Fourth, the DFT calculations, while providing mechanistic insight, employ idealized interface models that may not capture the full complexity of real heterointerfaces, including roughness, inhomogeneity, and processing-induced defects. Finally, the correlation between atomic-scale bonding and microscale transport is inferred rather than directly measured across the same interface region; advanced techniques such as conductive atomic force microscopy or scanning Kelvin probe microscopy would provide more direct spatial correlation.

### 5. Future Scope

Future work should address these limitations through several complementary directions. First, nanoscale electrical probes, including conductive AFM and scanning Kelvin probe microscopy, would allow direct correlation of local bonding chemistry with local transport properties, bridging the gap between XPS and impedance spectroscopy. Second, in situ or operando impedance measurements during thermal annealing or illumination would reveal how interfacial bonding evolves under processing and operating conditions. Third, extension of the multiscale framework to other oxide-graphene systems, including  $\text{TiO}_2$ -graphene and  $\text{SnO}_2$ -graphene, would test the generality of the hydroxide-mediated bonding model. Fourth, theoretical modeling with explicit interface



structures derived from microscopy data, rather than idealized periodic models, would provide more realistic predictions of transport behavior. Finally, device-level testing of heterointerfaces in photodetectors, photocatalysts, and supercapacitors would validate the proposed structure–property relationships against functional performance metrics.

## 6. Conclusions

This study establishes a multiscale characterization framework correlating crystallographic disorder, surface chemistry, and electrical transport in ZnO–graphene heterointerfaces. The principal conclusions are:

1. Raman spectroscopy quantifies crystallographic disorder through the  $I_D/I_G$  ratio, which varies systematically with heterointerface architecture and indicates that deposition sequence controls graphitic structure, while the ZnO  $E_2(\text{high})$  mode confirms crystalline quality.
2. XPS and XAS reveal that hydroxide surface layers on ZnO mediate interfacial bonding to functionalized graphene, with hydrogen bonding and covalent coupling determining the quality of electrical contact. The formation of Zn–O–C bonds is linked to bandgap modification.
3. Impedance spectroscopy, analyzed through equivalent circuits comprising grain-boundary resistance and capacitance, reveals Ohmic contact between ZnO and rGO grains and light-dependent relaxation processes that indicate efficient interfacial charge separation.
4. First-principles calculations confirm that van der Waals interactions and work-function-driven charge transfer govern the interface, with the graphene Dirac point remaining intact and excited electrons accumulating on graphene.
5. The multiscale framework demonstrates that hydroxide-mediated bonding, carbon lattice disorder, and grain-boundary transport are causally linked, providing design criteria for heterointerface engineering: maximize hydroxide coverage for bonding, optimize reduction extent for conductivity–activity balance, and match work functions for directed charge transfer.

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