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Supplementary Information

Unveiling the Optoelectronic Structure and Photovoltaic Potential of ZrO₂@GO through Cosensitization with Squaraine Dye in DSSC: A Computational Study

Kaniz Fatima, Aaliya Qureashi, Irfan Nazir, Zia-ul-Haq, Firdous Ahmad Ganaie, Taniya Manzoor, Prof. Altaf Hussain Pandith*. ¹Laboratory of Nanoscience and Quantum Computations, Department of Chemistry, University of Kashmir,

Hazratbal, Srinagar, J&K, India

1.1 Challenges in Modeling Long-Range Charge Transfer

One of the primary limitations of standard DFT methods is their difficulty in accurately capturing **long-range charge transfer interactions.** The B3LYP functional combined with the 6-311G basis set offers a good starting point for many molecular systems but has limitations in accurately modeling long-range interactions, excitonic effects, charge transfer, and transition metal complexes. To address these challenges, can consider using dispersion-corrected functionals, larger basis sets with diffuse and polarization functions, and advanced methods like TDDFT or range-separated hybrids, depending on the system and property being studied.In systems like ZrO₂@GO, where efficient charge transfer between components is crucial for optoelectronic performance, standard DFT often fails to accurately predict the energetics and dynamics of such transfers. Long-range corrected functionals (e.g., **range-separated hybrids**) or more advanced methods like **time-dependent DFT (TDDFT)** might be required to model these interactions more reliably.

Excitonic effects, particularly in systems where strong electron-hole binding occurs (such as in dye molecules and GO), are also a challenge for conventional DFT. DFT often underestimates the **binding energy of excitons** (bound electron-hole pairs) because it treats electronic correlations at an approximate level. In materials like squaraine dyes, where excitonic effects can significantly influence optical absorption and charge separation, this limitation can lead to inaccuracies in predicting optical properties such as **absorption spectra** and **optical gaps**.

Future Experimental Work to Validate Theoretical Predictions

To validate the theoretical predictions made in the study of **ZrO₂@GO-based nanocomposites**, particularly in the context of dye-sensitized solar cells (DSSCs), a range of experimental techniques can be employed. These experiments can confirm the electronic, optical, and charge transfer properties predicted by **density functional theory (DFT)** and provide insights into the material's performance in real-world applications. The following avenues are suggested for future experimental work:

Spectroscopic methods are essential for probing the electronic and optical properties of ZrO₂@GO nanocomposites, particularly their interaction with squaraine dye molecules.UV-Vis Absorption Spectroscopy technique can be used to measure the absorption spectra of the ZrO₂@GO

nanocomposites and squaraine dye molecules. It will provide experimental validation of the **optical bandgap** and the **light-harvesting efficiency** predicted by DFT. **Photoluminescence (PL) Spectroscopy** can be used to study the **recombination dynamics** of charge carriers in the nanocomposite. Theoretical predictions about efficient charge transfer between ZrO₂, GO, and squaraine dyes can be validated by comparing the **quenching** or **enhancement** of PL signals, which reflect charge separation efficiency. **Fourier-Transform Infrared Spectroscopy (FTIR) and Raman Spectroscopy** this can detect the functional groups present in the GO and squaraine dye molecules, confirming the level of **GO functionalization** and the nature of **binding interactions** between the ZrO₂, GO, and dye molecules. can provide information about the **structural integrity** and degree of functionalization of GO in the ZrO₂@GO nanocomposite. It can validate the **defect density** and the **interaction between ZrO₂ and GO**, as well as monitor changes in the sp² and sp³ hybridized regions of GO after functionalization.

X-ray Photoelectron Spectroscopy (XPS) and Energy Dispersive X-ray (EDX) Spectroscopy. This method can be used to analyze the chemical bonding states and elemental composition in $ZrO_2@GO$ nanocomposites. It can provide experimental confirmation of the binding energies of oxygen, carbon, and zirconium, and validate the predictions about the electronic environment and charge distribution in the system. And also it can provide elemental mapping of the $ZrO_2@GO$ nanocomposites, confirming the distribution of ZrO_2 nanoparticles on GO sheets, and ensuring that the theoretical models used for the DFT calculations accurately reflect the experimental system.

Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM). AFM can be used to measure the surface topography of ZrO₂@GO nanocomposites, providing insights into the **thickness** and **surface roughness** of GO after functionalization. These measurements can be compared with theoretical predictions about the nanocomposite's structural characteristics and functionalization. TEM can be used to confirm the **morphology** and **distribution** of ZrO₂ nanoparticles on GO sheets. The interface between ZrO₂ and GO is crucial for effective charge transfer, and TEM imaging can validate the **structural model** and ensure that the nanocomposite is prepared as predicted in the DFT studies.

The proposed experimental techniques, ranging from **spectroscopic analysis** to **device fabrication and testing**, provide multiple pathways to validate the theoretical predictions about ZrO₂@GO nanocomposites and squaraine dye interactions. These experiments will help confirm the **optical properties**, **charge transfer dynamics**, and **photovoltaic performance** of the material, providing crucial insights into its potential for use in **DSSCs** and other **optoelectronic applications**.

1.2 OPTIMIZED GEOMETRY

In our understanding, the surface of graphene oxide is characterized by three main functional groups: epoxy, carboxylic acid, and hydroxyl groups [1]. The degree of oxidation of graphene oxide is affected by factors such as the source of graphite, the preparation method, and the duration of synthesis [2]. Recently, DFT calculations have been employed to investigate the atomic and

electronic structures of graphene oxide decorated with various metals. Figure S1 shows the optimized structures of both graphene oxide and metal oxide-decorated graphene oxide (MO@GO).



Figure S1. Showing the optimized structure of GO and ZrO₂@GO.

Frontier Molecular Orbital (FMO) plots in Figure S2 reveal a diminished energy gap in $ZrO_2@GO$ compared to pristine GO, indicating favorable nonlinear optical (NLO) activity due to facile charge transfer. Analysis of the density of states (DOS) in Figure 3 shows more compact and intricate peaks in the case of ZrO2 @ GO, indicating enhanced charge transfer compared to GO alone. The energy gap of graphene oxide is measured at 3.34 eV, while $ZrO_2@GO$ exhibits a reduced gap of 1.16 eV. This reduction in band gap signifies that metalling GO with ZrO_2 transforms them into materials similar to semiconductors, suggesting potential applications in various industrial sectors for charge transfer. The determination of the tendency to escape can be elucidated through the evaluation of chemical potential values.



Figure S2. Showing the FMOs of GO and ZrO₂@GO.

1.3 NON-LINEAR OPTICAL PROPERTIES

Table S1. Tabulated the NLO of ZrO₂@GO.

Parameter	B3LYP/6-	Parameters	B3LPYP/6-311++G(d,p)
	311++G(d,p)		
μ _x	6.1072	β _{xxx}	966.8746
μ _y	-7.6988	β _{yyy}	-343.1096
μ _z	2.1919	β _{zzz}	25.4102
μ(D)	10.0685	β_{xyy}	224.0290
α _{xx}	-287.5149	β_{xxy}	-523.2959
$\alpha_{\rm vv}$	-331.4414	β _{zxx}	82.4247
α_{zz}	-314.4438	β _{xzz}	-101.7347
α _{xy}	-65.2811	β _{yzz}	27.4093

α_{xz}	-27.7604	β_{zyy}	46.6350
α_{vz}	26.4152	β _{xyz}	114.1339
α_0 (e.s.u)	-46.11×1024	β_{tot} (e.s.u)	11952.37×10 ⁻³³

The features of NLOs are also of interest in current communication technologies and optical signal processing materials. NLO features indicate a tendency for intra molecular charge delocalization in clusters of donor electrons. Furthermore, NLO characteristics are linked to increased mobility and electron transport efficiency from donor to acceptor. That is, NLO parameters should only be used to estimate and evaluate the efficiency of electron charge transport in organic systems. To Know the non–linearity behavior , the polarizability, and the hyperpolarizability of the GMO were done at B3LYP functional using a 6-311G (d, p) basic set. The computed values are listed and can be determined by the equation below-

 $\dot{\alpha}_{total} = (\dot{\alpha}_{xx} + \alpha_{yy} + \alpha_{zz)/3}$

$$\begin{split} ^{\beta}_{total} =& (\beta_{x}^{2} + \beta_{y}^{2} + \beta_{z}^{2})^{1/2} \\ Where \ \beta_{x} =& \beta_{xxx} + \beta_{xyy} + \beta_{xzz} \\ \beta_{y} =& \beta_{yyy} + \beta_{yzz} + \beta_{yxx} \\ \beta_{z} =& \beta_{zzz} + \beta_{zxx+} + \beta_{zyy} \end{split}$$

therefore the $\dot{\alpha}_{total}$, β_{total} value reported for MO@G was found to be-46.11×10⁻²⁴ e.s.u, 11952.37×10⁻³³ e.s.u computed using DFT/B3LYP/6-311G (d,p). The larger hyper polarizability value corresponds to charge transfer (ICT) properties from electron donor to electron acceptor.

1.4 RE-ORGANIZATION ENERGY

The geometric relaxations that take place during electron injection and dye regeneration are measured using the reorganization parameter (ΔG_{reorg}). For an electron transfer procedure to be successful, lower reorganization energy levels are necessary. We determined the total reorganization energy for each sensitizer (Table 2). Lower reorganization values from Eq. 6 suggest efficient electron transport across the intra molecular interface, according to Marcus'

Model. The calculated reorganization energies are in the following order: -40.28 < 1.09 for ZrO2@GO < GO.

S.No	λ_{e}	λ _h	ΔG_{REORG} (λ total)
1. GO	0.54 eV	0.55 eV	1.09 eV
2. ZrO ₂ @GO	20.13 eV	19.86 eV	-40.28 eV

Table S2: Re-Organization energy table GO and ZrO₂@G.

The geometry relaxations that take place during electron injection are evaluated using the reorganization parameter (Δ Greorg). It's a useful approach to assessing molecule potency. It's a significant factor in determining the electron/hole transit of the molecule. For an electron transfer procedure to be successful, lower reorganization energy levels are necessary. We determined the overall reorganization energy for each molecule (Table 2). Lower reorganization values, in Marcus' theory, denote efficient electron transmission across the intra molecular interface.

Therefore, the greater the value of chemical potential greater the tendency to escape the electron, and the chemical potential seems to increase on metallation (ZrO_2) substitution. The chemical hardness defines the reactivity and stability of a molecule. The smaller the chemical hardness, the more stable the chemical species. Metalleted (ZrO_2) on GO was having a small chemical hardness, therefore, the molecule is more stable. The electrophilicity index measures the propensity of chemical species that accept an electron. Thus, the $ZrO_2@GO$ was found to have less value than the GO indicating a good nucleophile. This result has proven that metalation has a positive impact on the optoelectronic properties of Graphene nano-composites, but stability an invaluable tool in the production of the optoelectronic device is proven counterproductive with the same process.

1.5 Choice of DFT functional and basis set (B3LYP/6-311G)

B3LYP is widely used for its good balance between accuracy and computational cost. It incorporates both exchange-correlation energy contributions from local, gradient-corrected, and Hartree-Fock methods, making it suitable for a broad range of chemical systems.

6-311G Provides a good balance of accuracy and computational efficiency with additional polarization functions compared to the 6-31G basis set. It is often used for systems requiring a detailed description of electron distribution.

Therefore, B3LYP/6-311G is well-suited for general-purpose calculations where a balance of accuracy and efficiency is needed. This benchmarking provide a comprehensive overview of how B3LYP/6-311G stacks up against other methods and highlight where it fits within the broader spectrum of computational approaches.

Limitations: May not be sufficient for highly accurate calculations in systems requiring diffuse functions or more extensive polarization.

It may not be as accurate for systems with significant dispersion interactions or for excited states due to its lack of long-range dispersion corrections.

Reference:

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