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Density Functional Theory calculations for graphene oxide, zinc oxide, and graphene oxide/zinc oxide composite structure

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Abstract

Graphene oxide is a complex material with important implications in both theoretical and practical fields. To investigate the potential of graphene oxide (GO) in reducing the high band gap of conducting materials, the electrical properties of the materials, including topography and band gap, were analyzed using density functional theory (DFT) calculations .The "B3LYP" approach was used, together with the "6-31G" (d, p) and "LanL2DZ" basis sets. Total energy (E), highest occupied molecular orbital energy (EHOMO), lowest unoccupied molecular orbital energy (ELUMO), energy gap (EH-L), hardness (η), softness (S), and global electrophilicity index (ω) are the quantum chemical parameters that have been calculated and found to be related to reduced efficiency. Potential locations for local reactivity were more easily evaluated by using the abbreviated Fukui function and abbreviated softness indicators. The findings indicate that the GO/ZnO composite has the highest total energy E, making it the most stable combination. The composite's EH-L was approximately 1.62, which indicates that it is more susceptible to photodegradation than ZnO under visible light.

Keywords:

DFT, graphene oxide, energy gap, hardness, and softness.

Introduction

Graphene oxide (GO), a two-dimensional material, has remarkable electrical, optical, and mechanical properties [1]. This material has found utility in a wide range of applications due to its unique structural and physical properties [2]. Theoretical studies aimed at improving understanding of the structure and behavior of GO under specific conditions have increased in recent years[3].The field of nanotechnology is currently undergoing a significant transformation within the realms of science and technology, exhibiting enhanced physical and chemical properties, allowing their use in a variety of device applications, including but not limited to flexible displays, sensors, and optical limiters.

Graphene oxide (GO) has variable electrical, mechanical, thermal, and optical properties [4]. The material under consideration exhibits a variety of properties that are dependent on the specific characteristics of the sample, making it a highly viable option for a wide range of nanodevices [5]. Graphene oxide (GO) can be obtained through experimental methods involving thermal and mechanical exfoliation of graphite oxide, resulting in the formation of nanosheets [6]. Expanded graphite is commonly used as the initial material in order to produce large graphene oxide (GO) sheets with lateral dimensions greater than 10 m [7].

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The ability of graphene oxide to generate intricate three-dimensional configurations is a particularly appealing feature. This has resulted in investigations into the topography and band gap of the material, which are important in understanding its inherent properties [8, 9]. Topography refers to a substance's physical configuration or structure, whereas band gap refers to the difference in energy levels that exists between the most energetically occupied molecular bands within a given material [10]. Investigations into the topographical properties and band gap of graphene oxide can provide valuable insights into its inherent properties and applications in future technological advancements [11]. In contrast, the use of molecular modeling principles and methodologies allows for the theoretical evaluation of the inherent characteristics of interactions between the constituent elements of a prospective sensor [12]. The primary goal of model construction is to use mathematical principles to improve and clarify the results of experimental work. This enables the investigation of the physical and biological properties of chemical structures using computer software codes. Such models frequently provide critical data in a variety of interdisciplinary fields of science [13, 14]. The use of theoretical models is not limited to situations in which experimental work is hampered due to ethical or situational constraints; rather, they are useful tools for providing plausible explanations for ongoing research by drawing on theoretical notions [15]. The hexagonal lattice structure of graphene oxide (GO) determines its topography, which is composed of carbon atoms interconnected in a honeycomb arrangement [16]. It is possible to gain knowledge in the fields of electrical, optical, and mechanical properties through the investigation of the topography of graphene oxide (GO) [17]. Furthermore, the band gap of graphene oxide (GO) can be quantified, which is an important characteristic in determining the material's suitability for various applications [18]. An examination of the topographical features and band gap of graphene oxide (GO) can provide a comprehensive understanding of its characteristics and potential applications [19]. The purpose of this study was to investigate the properties of graphene oxide (GO) using modeling and simulation techniques. According to our findings, graphene oxide (GO) has a hexagonal lattice structure and a band gap of 1.59 electron volts (eV). Furthermore, graphene oxide (GO) has been discovered to have a high level of structural stability, which is critical in determining its suitability for a wide range of applications. This study provides valuable insights into the properties of graphene oxide (GO) and its potential applications, thereby providing guidance for future research and development efforts in this field. To investigate the research question, the current study used a materials and methods approach.

MATERIALS AND METHODS

Computational Details: The Density Functional Theory (DFT) serves as the foundational framework for understanding numerous chemical principles used in various domains of chemistry using computational chemistry software. To assess the agreement between theory and experiment, the Gaussian-09 software package was used to perform quantum chemical computations with extensive geometry optimizations. Geometry optimization was carried out with the "B3LYP" functional, the "6-31G" (d,p) basis set, and the (DFT) methodology. Recently, the (DFT) application has been used to examine graphene oxide

(GO) in order to elucidate its structural properties. Density functional theory (DFT) has shown significant efficacy in establishing a theoretical framework for widely accepted qualitative chemical principles such as hardness (η), softness (S), and the Fukui function (F(r)), all of which are important concepts in the field of chemistry. Understanding these variables is critical for understanding molecule reactivity and properties. The Par, Donelly, Levy, and Palke (36) basic correlation connects the chemical potential (DFT) with the first derivative of energy with regard to the number of electrons, resulting in a negative electro negativity value [20].

$$\mu = \left(\frac{\delta E}{\delta N}\right) V = -\chi \quad (1)$$

"μ is the electronic chemical potential E is the to total energy"
" N is the number of electrons"

"ν(r) is the external potential of the system."

The equation (1) represents the mathematical relationship between the chemical potential (μ), (ΔE) in term of the change in electron number (ΔN) at constant volume (V), and the negative of the isothermal compressibility (χ). The second derivative of (E) in term of the number of electrons (N) can be used to determine the quality of hardness (η), while considering the v(r) function. A molecule's stability and reactivity are gauged by its hardness, and it is defined within the framework of (DFT) as described by Equation (2) [21].

$$\eta = \frac{1}{2}\left(\frac{\delta \mu}{\delta N}\right) V(r) \quad (2)$$

The equation (2) can be expressed as follows: η = 1/2 * (δμ/δN)

The practical and approximative meanings of the previously mentioned quantities are the ionization energy and electron affinity. As shown by the following equation [22], these two numbers may be combined to give the electronic chemical potential:

$$\mu = -0.5(I + A)$$
$$\eta = 0.5(I - A)$$

"I is the ionization potential A is electron affinity of the system"

On a rougher estimate: I= -ε HOMO and A= -ε LUMO. As a result, the correlations shown below can be utilized to indicate global hardness and chemical potential [23].

$$\mu = 0.5(\varepsilon HOMO + \varepsilon LUMO) \quad (5)$$

$$\eta = 0.5(\varepsilon LUMO - \varepsilon HOMO)$$

The softness(S)is the inverse of the hardness(η)as expressed by following[24]

$$S = \frac{1}{\eta}$$

A molecule's reactivity in electrophilic reactions is directly proportional to its greater (ε_{HOMO}), whereas a (ε_{LUMO}) is

crucial for molecular interactions involving nucleophiles. The utilization of electronegativity, hardness, and softness parameters has proven to be significantly advantageous in the realm of chemical reactivity theory. The parameter denoted as hardness (η) is indicative of the energy difference between (HOMO) and the (LUMO). The size of the HOMO-LUMO orbital energy gap directly relates to the molecule's hardness. There has been a historical association between hardness and the stability of chemical systems. The maximum hardness principle, as coined by Parr and Pearson, is grounded on the observation that molecules have a tendency to organize themselves in a manner that maximizes their hardness. Pearson states that hardness is primarily a measure of a molecule's ability to resist alterations in its electron distribution. Index of the electrophilicity ω, which has global significance, was initially suggested by Parr [24, 25]. It is determined by the utilization of two fundamental parameters, namely the electronic chemical potential "μ" and the chemical hardness (η) [25](Eq.8).

$$\omega = \frac{\mu^2}{2\eta} \quad (8)$$

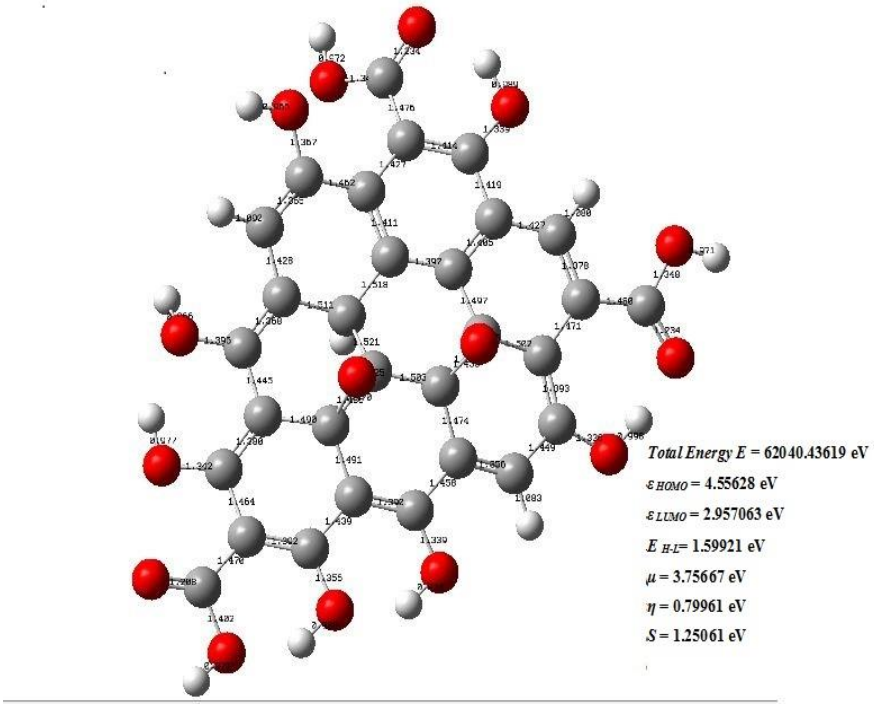
Although an electrophile with higher μ and ω values is considered more reactive, a nucleophile with lower μ and ω values is seen to be more reactive. According to the description provided, this index evaluates a chemical species' inclination to receive electrons.

Results and discussion

Several parameters define optimal geometries, reactivity, and stability. These consist of the electronic chemical potential (μ), global softness (S), global hardness (η), frontier molecular orbital energy gap (EH-L), and total energy (E). The computed values of the global electrophilicity index "ω" and bond length for graphene oxide, zinc oxide, and the composite material ZnO/graphene oxide are shown in the figures in the present study. These calculations were performed using the density functional theory (DFT) at the "B3LYP" and "6-31G"* levels of theory. The graphene oxide findings are shown in Figure 1, the zinc oxide results are shown in Figure 2, and the ZnO/graphene oxide composite results are shown in Figure 3. This study used density functional theory (DFT) calculations with the "B3LYP 6-31G" basis set to compare and assess the efficacy of three different approaches in the analysis of reactivity descriptors. The DFT estimated reactivity descriptors, namely E, μ, I, η, ω, and E_{H-L}, exhibit a high degree of similarity in their values. These descriptors demonstrate a noteworthy level of concordance with the corresponding experimental reactivity outcomes. Based on the calculated values of "E, μ, I, η, ω, and E_{H-L}", it can be inferred that GO/ZnO exhibits greater stability and reactivity compared to both GO and ZnO, making it a more suitable choice for photocatalyst applications. This conclusion provides confirmation for the experimental evidence pertaining to the differential reactivity and stability exhibited by ZnO and GO/ZnO composites.

Theoretical outcomes from molecular orbital analysis and the reactivity indices of the Fukui function line up perfectly with the observed reactivity of these compounds, indicating a high level of reactivity in the GO/ZnO composite when subjected to nucleophilic attack for compounds.

Figure (1): presents the results of“Density Functional Theory” (DFT) calculations conducted for GO



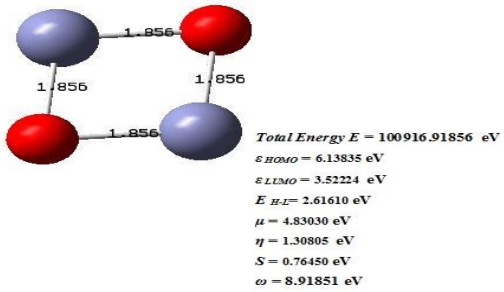


Figure 2 presents the results of “Density Functional Theory” (DFT) calculations

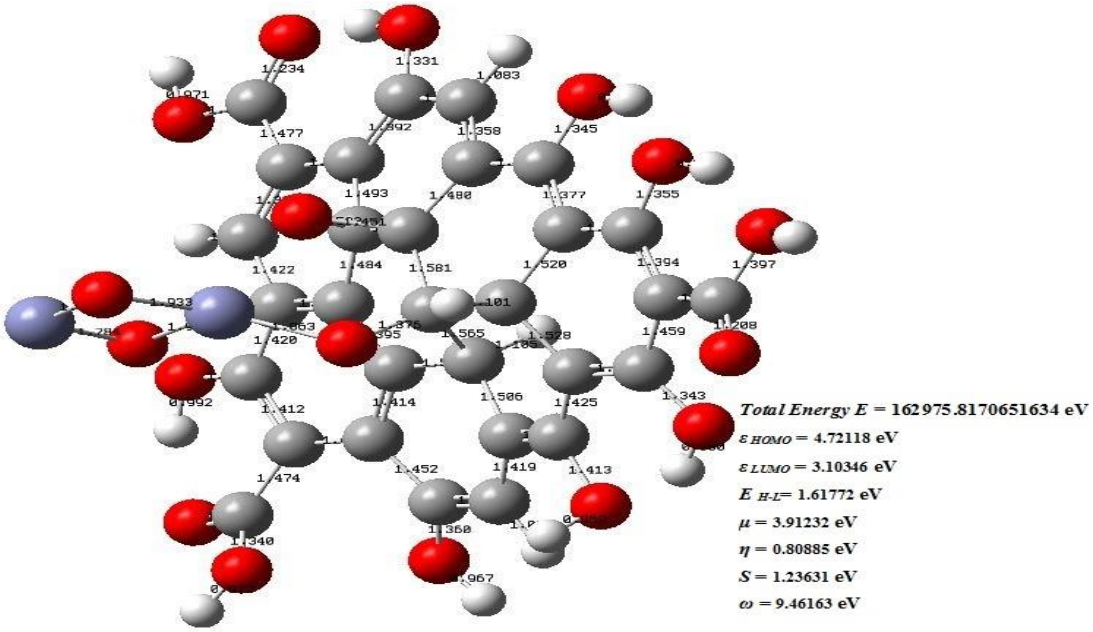


Figure 3 presents the results of "Density Functional Theory" (DFT) calculations conducted for GO/ZnO composite

Table 1 the electronic properties of GO, ZnO and GO/ZnO composite

Properties Material eV	E_{Total}	E_{HOMO}	E_{LUMO}	E_{H-L}	μ	η	S	ω
GO	62040.43619	4.55628	2.95706	1.59921	3.75667	0.79961	1.25061	8.82469
ZnO	100916.91856	6.13835	3.52224	2.61610	4.83030	1.30805	0.76450	8.91851
GO/ZnO	162975.81707	4.72118	3.10346	1.61772	3.91232	0.80885	1.23631	9.46163

Table 1 presents the electrical characteristics of graphene oxide (GO), zinc oxide (ZnO), and the GO/ZnO composite. This study showcases the notion of graphene oxide. The geometric properties associated with a circle.The carbon structures under investigation were selected in order to mitigate any potential anisotropic effects that could arise from variations in the modeled structure's size while simultaneously taking a particular orientation. It is imperative to acknowledge that the aforementioned model has been effectively employed for the analysis of the physical characteristics of two-dimensional carbon and other material sheets [26].There have been reports of higher gap energy values for graphene oxide in the literature, which can be attributed to either high oxidation states (3.2 eV) or low oxidation states (1.4-1.5 eV). Consequently, a semi-metal behavior has been acknowledged [27]. Based on the model under investigation, it is evident that the computed band gap (1.59 eV) exhibits a rather low oxidation state.The computed energy (E) values for graphene oxide (GO), zinc oxide (ZnO), and the GO/ZnO composite, obtained using (DFT) at the "B3LYP 6-31G"* level, provide

confirmation that the GO/ZnO composite exhibits the highest stability among these modules. This enhanced stability, along with its notable height value, renders the GO/ZnO composite a promising candidate for many applications as a semi-metal composite.The results presented in Figures 1, 2, and 3, as well as Table 1, indicate that the combination of graphene oxide (GO) and zinc oxide (ZnO) in photocatalyst applications under visible light exhibits enhanced reactivity. This enhanced reactivity can be attributed to the inherent hardness of the composite material and the energy difference between (HOMO) and (LUMO) of ZnO. Based on the empirical observations, the GO/ZnO combination demonstrates notable reactivity and catalytic properties in the degradation of several dyes under visible light conditions. In comparison to the GO/ZnO combination, ZnO demonstrates distinct reactivity tendencies related to photocatalysis and exhibits decreased chemical reactivity under same conditions [28-30]. In comparison to ZnO, the GO/ZnO composite exhibits a wider HOMO-LUMO energy gap and hardness (η), resulting in enhanced energetic reactivity and stability.These three compounds are shown to have nucleophilic properties based on their calculated global electrophilicity index values according to the reference's understanding [31]. The measured values for zinc oxide (ZnO) and graphene oxide (GO) exhibit a high degree of similarity. The GO/ZnO complex demonstrates a higher energy value of 0.54312 eV in comparison to ZnO. Based on this observation, it may be hypothesized that the GO/ZnO composite is more prone to engage in reactions with nucleophiles when compared to ZnO and GO individually [32,33].

Experimental calculations

Our findings indicate that the ZnO/GO composite's band gap EH-L is around 1.8e.v. in the UV region at a wavelength of λ = 385 nm, which is in close agreement with theoretical calculations.

$$\text{Eg (eV)} = \text{hv} = 1240/\lambda\ \text{nm} \quad (9)$$

By plotting (hv)2 versus the photo engry (hv) using the kubelka-munk function, the following equation is obtained:

$$\alpha\text{hv} = \text{A(hv} - \text{Eg)}^{n} \quad (1$$

Where, $\boldsymbol{\alpha}$ is the absorption coefficient(a function of light frequency), $\boldsymbol{\nu}$ is light frequency, h is Planck's constant (*hv* is the energy of a photon with frequency$\boldsymbol{\nu}$),Eg is the band gap energy, A is a certain frequency-independent constant, n is a constant, that is an indirect band gab for n=2 and a direct band gab for n=$^{1}/_{2}$.

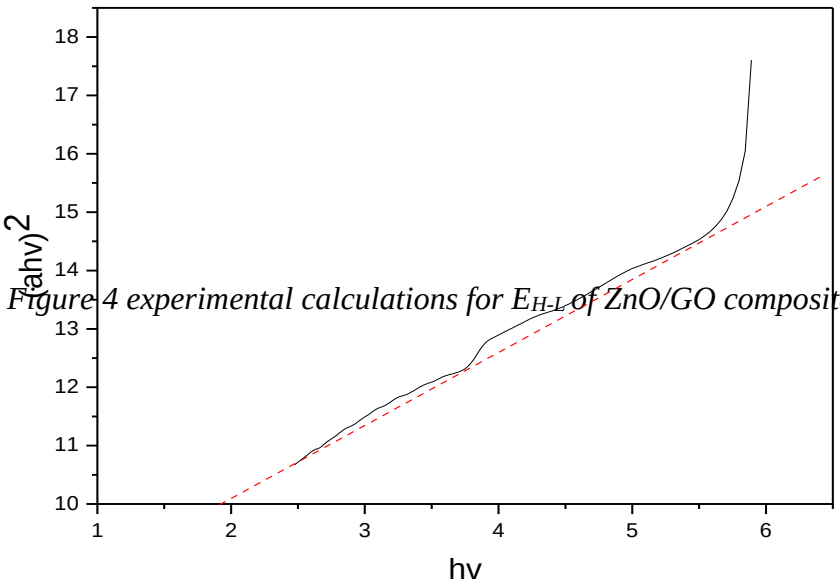


Figure 4 experimental calculations for $E_{H\text{-}L}$ of ZnO/GO composite

Conclusions

The stability and reactivity of the GO, ZnO, and GO/ZnO composite structures were investigated theoretically at the (DFT) calculation level. The differences in reactivity between the three compounds were determined and used by determining and utilizing global descriptors such as ionization energy (I),molecular hardness (η), electrophilicity (ω), frontier molecular orbital shapes and energy gaps "EH-L", local ionization energy, and electrostatic potential energy surfaces. The use of reactivity indices derived from (DFT) calculations has shown to be beneficial in improving our understanding of chemical reactivity. In general, there is a strong concordance between theoretical conclusions and observed experimental reactivity.

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