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DFT Studies of Suitability of Nanocomposite (ZnO/TiO2@polythiophene) in Photocatalyst Application

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Abstract: ZnO & TiO2 nanocomposites have experienced a rapid development and advancement due to the variety of potential applications. Their properties have been exploited in the development of solar energy storage, photocatalysts, as well as medicinal bio-mediated processes. This research based on density functional theory DFT studies of suitability of ZnO and TiO2@polythiophene oligomer for the development of an efficient photocatalysts. An important photocatalytic parameters such as geometry optimization & bonding energy interaction, optical & electronic structure properties and charge transfer mechanism are calculated at B3LYP functional and 6-31G (d,p) basis set. The calculated results showed that the bonding energy interaction of ZnO & TiO2 with 3PT oligomers have a strong bonding interaction which are electrostatic and hydrogen bonding and the interaction energy ΔEint for ZnO@3PT is (−389.058 kcal/mol) while the TiO2@3PT bonding interaction energy ΔEint is (−395.331 kcal/mol) with TiO2@3PT value higher than the ZnO@3PT. The electron–charge transfer mechanism are calculated with natural bonding orbital NBO analysis where ZnO & TiO2 act as electron acceptor and 3PT oligomer act as electron donor in the study composites. Also, the optical and electronic properties calculation revealed the excellent absorption properties of ZnO@3PT and TiO2@3PT in the visible region over 3PT oligomer due to red-shifting from the ultraviolet to visible to IR ray and this shows an evidences of excellent photocatalytic properties of the two study composites over 3PT oligomer.

Keywords: nanocomposite, ZnO & TiO2 nanoparticle, polythiophene oligomer, DFT, photocatalyst, bonding energy interaction

1. Introduction

Nanomaterial such as (TiO2 & ZnO) have experienced a rapid development and advancement due to the variety of potential applications in solar energy generation, photocatalytic water splitting, environmental cleaning, water purification, as well as medicinal bio-mediated processes [1, 2]. They have been intensively studied and characterized as suitable candidates for photocatalytic effluent treatments. These nanomaterial shows significant properties such as absorption range, surface warping, interface chemical stability, charge carrier recombination, and mobility [3, 4]. Due to their significant potentials applications in different branches of science, the development of new polymer composites represents a priority [5]. Conducting polymers with an extended π-conjugated electron system, are mostly p-type semiconductors which work as an electron donor in the p-n junction such as Polyaniline (PANI), polypyrrole (PPy), polythiophene (PT), polyparaphenylene (PPP), poly (3,4-ethylenedioxythiophene) (PEDOT), among other are prominent examples of conducting polymer which have high charge carriers mobility expressed through high absorption coefficients that varied from visible light to near infrared [6] are explored in this area [7]. Polymers based on nano-composites are considered as hybrid structures composed of inorganic nanomaterials coupled with polymers acting as matrices, such nano-composite structures exhibit distinctive chemical and physical

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properties with targeted functional properties due to p-conjugated systems which contain a high concentration of electron-rich species available for transfer in the semiconductor's conduction band [8]. These hybrid materials can be used in photocatalysis reactions, from degradation of organic pollutants to fine organic processes, the great benefit of this method consisting of the direct conversion of light energy into chemical energy, thus providing a green method to combating environmental pollution [9]. Therefore, hybrid composites are considered as suitable candidates for AOPs due to their unique physical and chemical properties induced by the formation of the interphase region. The advanced oxidation process (AOP) is considered as a promising alternative for the complete decomposition of organic pollutants due to its ability to generate oxidative and super-oxidative species when a catalyst is irradiated with light [10]. During irradiation (hv), the composite interface behaves as a synergic active area where the photogenerated electrons (e−) migrate from the lowest unoccupied molecular orbital (LUMO) polymer level to the metal oxide conduction band (CB), while the photo-induced holes (h+) are transferred from the valence energy band (VB) of metal oxide directly on the highest occupied molecular orbital (HOMO) polymer level [11, 12].

Recently, it has be found that nano-composites convert dye molecules into harmless compounds, in an attempt to reduce the toxic effects of these molecules on the environment [13]. Although, experimental study of nano-composite as a photocatalyst is reported but facing lower photocatalytic efficiency which is due to lack of theoretical investigation [14]. Computational simulation and theoretical studies can provide some valuable insights such as optimized geometry, optical & electronic structure, surface and charge transfer interactions between the nanoparticles and a reactant molecule, is essential to tailor and improve the photocatalytic activity of the nanocomposite. [15]. This research based on DFT study of important photocatalytic parameters such as (i) geometry optimization & bonding energy interaction of TiO2/ZnO nanoparticles with PT oligomers (ii) optical & electronic structure properties (iii) charge transfer mechanism for efficient performance.

2. Computational Method

Optimized structures, charge transfer, electronic and optical properties of model polythiophene (PT) oligomers (n = 3) (Figure 1) treated with ZnO and TiO_2 nanoparticles are performed with the help of density functional theory (DFT). All DFT calculations [16, 17] were carried out on GAUSSIAN 09 software [18] and the results were visualized using GaussView [19]. ZnO and TiO_2 are added to the oligomeric backbone of PT (n = 3) and then the model structures are optimized using DFT theory at B3LYP/6-31G(d,p) level and time-dependent DFT (TD-DFT) calculations were performed at B3LYP with the same basis set for the determination of optical and electronic structure properties of ZnO@3PT and TiO_2@3PT as an efficient photocatalyst. The bonding interaction energies (ΔE_{Int}) of the two composites are calculated from equations 1 [20].

$$\Delta E = E_{nano} + E_{3PT} - E_{nano@3PT} \quad 1$$

Where ΔE_{Int} is the bonding interaction energies, E_{nano} is the energy of nanoparticles, E_{3PT} is the energy of polythiophene oligomer and $E_{nano@3PT}$ is the total energy of the ZnO@3PT and TiO_2@3PT.

3. Results and discussion

3.1. DOPANTS

It has been widely reported that TiO2-polyanililne emeraldine salt composite form type II junction. It has been well reported dopant that m-cresol solution of camphor sulphonic acid doped polyanilinegives metallic conductive polyaniline film. The origin of the metallic conductivity had been attributed to secondary dopingby MacDiarmidand Epstein (A. G. MacDiarmid 1994; MacDiarmid and Epstein 1995b, 1995a). They explained that a secondary dopant is anapparently "inert" substance (usually solvents) which, when applied to a primary-doped polymer, induces conformational changes that will result in enhancement of conductivity of a doped (with a primary dopants) polyaniline. They explained further that a doped polyaniline chain is a essentially a polyelectrolyte, interaction of the secondary dopant with polyelectrolyte and the counter anion caused the polyelectrolyte chain to change from compact coil to expanded coil and the conformational change can persisteven upon complete removal of the secondary dopant. This secondary doping phenomenon depends on primary/secondary dopant combination.

Based on the explained secondary doping phenomenon camphor sulphonic acid was selected as reference dopants. Other dopants used in this work were conceived such that they have structural resemblance to camphor sulphonic acid and also have donor moiety to enhance hole conductivity of the resulting doping trianiline. The dopants were obtained by alkylation of donor moieties (diphenylamine, carbazole and phenothiazine) with 2-bromoethane sulphonic acid. The structures of the resulting dopants are shown in Figure 4.2. Success of the alkylation reactions were confirmed from FTIR studies. All the donor moieties have N-H fragment, thus N-H Stretch vibration band was exploited to confirm successful alkylation.

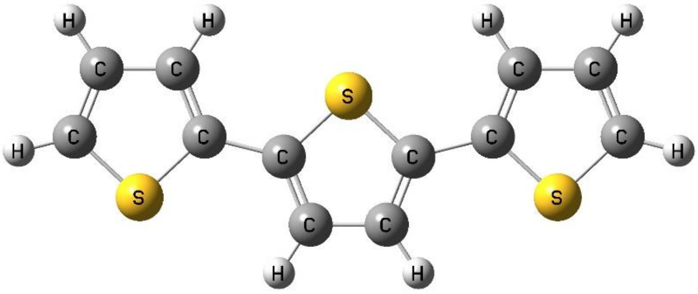


Figure 1. Model structure of polythiophene (3PT) oligomer

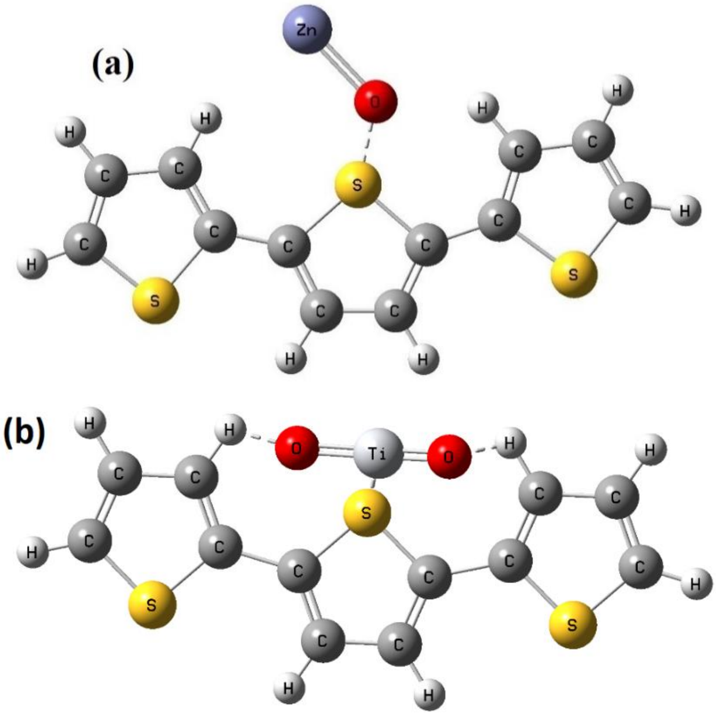


Figure 2. Optimized structure of (a). ZnO@3PT and (b). TiO_2@3PT

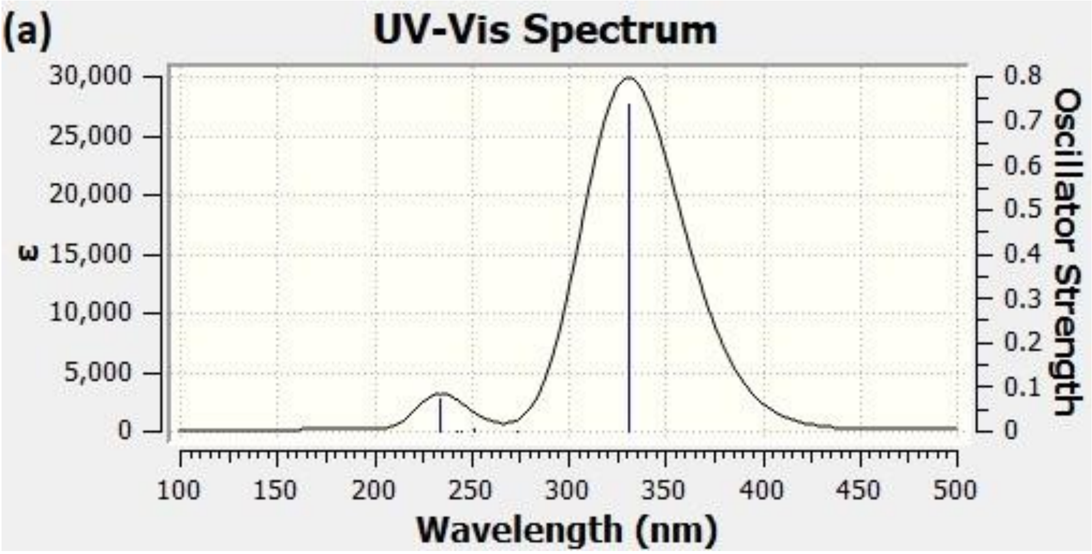
3.2. Geometry and Bonding Interaction Energy

Optimized geometric structures of Zn@3PT and TiO_2@3PT are given in Figure 2. Two different types of inter-molecular bonding are observed in the case of the TiO_2@3PT nanoparticles; where (Ti–S) has strong electrostatic bonding and (O–H) has hydrogen type of bonding. The bond distance of (S-Ti) and (H-OTiO-H) at the B3LYP/6-31G (d,p) level of theory is found to be 1.21 Å and (1.31 & 1.25 Å) respectively. For ZnO@3PT composite, strong electrostatic bonding is observed and the bond distance of (S–OZn) at the B3LYP/6-31G (d,p) level of theory is found to be 1.62 Å. ZnO has a little effect on the ground state geometry upon interacting of ZnO, the bond distance of (S-C) ring increase from 1.67 to 1.75 Å and the bridging bond decrease from 1.54 to 1.44 Å. While TiO_2 does not have effect on the bond distance of PT oligomer. The bonding interaction of ZnO & TiO_2 with 3PT oligomers shows a good bonding interaction which are electrostatic and hydrogen bonding, calculated from interaction energy (ΔE_{int}) equation 1. The ΔE_{int} for ZnO@3PT is (−389.058 kcal/mol) while the TiO_2@3PT bonding interaction energy is (−395.331 kcal/mol) with TiO_2@3PT value higher than the ZnO@3PT. Moreover, the strong bonding interaction of Zn@3PT composite can be attributed to the fully relaxed geometric structure, which allows ZnO to orient around PT oligomer compared to TiO_2@3PT (Fig. 2). The result of this bonding inter-molecular interaction between the nano-composites proved that a very strong bonding interaction exit between these two species which led to the confirmation of stable composite [20].

3.3. Optical and Electronic structure properties

3.3.1. UV-Visible absorption

The absorption properties (UV–Vis spectra) of 3PT oligomer, ZnO@3PT and TiO_2@3PT are calculated in the vaccum phase at TD-DFT/B3LYP level. Two absorption band peaks are found in the UV–Vis spectra of 3PT oligomers with calculated absorption band at ca. 234 nm and a strong at ca. 331 nm in the UV region (Figure 3 and Table 1). The 3PT oligomers is unable to absorb in the visible region, where the high wavelengths one is referred as λmax. The Interaction of ZnO with 3PT oligomers cause a red-shifting absorption peaks of 370 & 648 nm wavelength in ZnO@3PT (Figure 3 and Table 1). This red-shifting in λ_{max} of 3PT oligomer indicate the n-type nature of ZnO. In the case of TiO_2@3PT composite, shows a range of absorptions peaks the minimums light absorption is at 729.30 nm and the maximum light absorption is at 2737.36 nm wavelength which evidences the establishment of strong bonding, it can be observe that it light absorption reaches the range of infrared (IR). If the TiO_2@3PT composite is capable of absorbing IR ray, thus, the TiO_2@3PT composite is also capable of absorbing in the UV- visible range [21]. The dominant IR ray is produced during the day and evening. It means that the TiO_2@3PT composite in photo-catalyst application is capable of absorbing light during the day or night time [21]. The ZnO@3PT and TiO_2@3PT have excellent absorption properties in the visible region over 3PT oligomer due to red-shifting from the ultraviolet to visible to IR ray and this shows an evidences the excellent photocatalytic properties of the two study composites over 3PT oligomer.



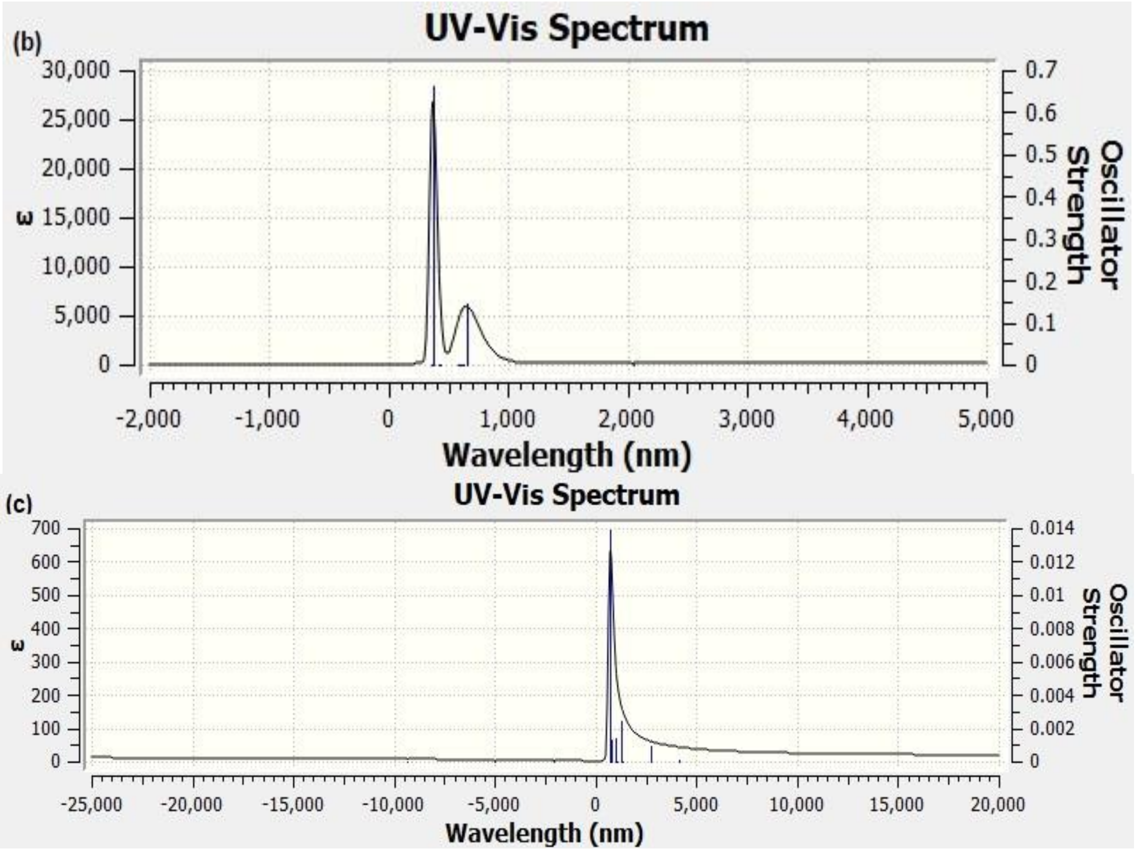


Figure 3. Calculated absorption spectra of the (a) 3PT oligomer, (b) ZnO@3PT and (c) TiO_2@3PT at TD-DFT/B3LYP level

Table 1. Calculated absorption wavelength (λ nm), total dipole moment (TDM), HOMO-LUMO and band gap energy (ΔE) as eV at B3LYP/6-31G (d,p) level for 3PT oligomer, ZnO@3PT and TiO_2@3PT.

Compound	λ (nm)	Total Dipole moment (Debye)	HOMO (eV)	LUMO (eV)	ΔE (eV)
3PT oligomer	234-331	0.4843	-7.16	-1.49	5.67
ZnO@3PT	665	3.1136	-3.74	-1.009	2.731
TiO_2@3PT	1261.27	4.5555	-2.38	-0.125	2.225

3.3.2. Electronic structure

The electronic structure (HOMO/LUMO) and total dipole moment (TDM) of 3PT oligomer, ZnO@3PT and TiO2@3PT are calculated in the vaccum phase at TD-DFT/B3LYP level (table 1 & 2). The HOMO of ZnO@3PT is localized on the polythiophene oligomer ring and that of TiO2@3PT is localized on the polythiophene oligomer ring and TiO2. In contrast, the LUMO of ZnO@3PT is delocalized over the ZnO orbital and the bond middle ring of 3PT oligomer. For TiO2@3PT, the LUMO delocalized over the entire TiO2 orbital and the 3 ring of 3PT oligomer.

The HOMO-LUMO band gap energy (ΔE) of 3PT oligomer is 5.67 eV which is higher than the ΔE values of ZnO@3PT and TiO2@3PT composites, the value of ΔE for 3PT oligomer decreased from 5.67 to 2.731 eV for 3PT treated with ZnO and 2.225 eV for 3PT treated with TiO2 (table 1). However, the values of TDM for 3PT oligomer is 0.4843 and increased to 3.1156 Debye for ZnO@3PT when treated with ZnO nanoparticle, this indicates that ZnO@3PT composites have TDM higher than TDM for 3PT oligomer but less than the values of TiO2@3PT which is 4.5555 Debye (table 1).

3.3 Natural Bonding Orbital Charge transfer

The main aspect of charge transfer analysis is to provide a clear picture of the electron transfer and charge distribution mechanism from the donor to acceptor orbital of both ZnO@3PT and TiO_2@3PT nano-composites structure [22]. The NBO charge analysis was performed based on the optimized geometries of their ground state. The charge transfer mechanism between the (ZnO, TiO_2) and 3PT oligomer are calculated at the B3LYP/6-31G (d,p) level of theory. The calculated NBO results are tabulated in (Table 3). In connection with bonding interaction sections, (ZnO and TiO_2) interacts with 3PT oligomers through strong electrostatic (ZnO-S) and (Ti-S). The analysis of NBO calculation indicates that ZnO-S bond is the main charge transferring paths for ZnO@3PT and Ti-S for TiO_2@3PT composites. For all nano-composites study, the positive (green) value reveal the total NBO charge, which act as an effective electron-donor part. Contrarily, the negative (red) value reveal the NBO charges which electrons are trapped in the electron-acceptor part (table 3 & figure 4). The positive (green) value (1.199) on the sulfur atom on the PT rings act as a transporter for the electron-transfer mechanism from PT oligomer to oxygen atom of ZnO with negative (red) value (-1.119). In the case of TiO_2@3PT composite, the sulfur atom on 3PT oligomer act as donor and has positive charge values (1.90) and the Ti of TiO_2 act as acceptor part with a negative (red) charge (-1.09).

Table 2. The optimized structure and HOMO-LUMO of ZnO@3PT and TiO_2@3PT at B3LYP/6-31G(d,p) level.

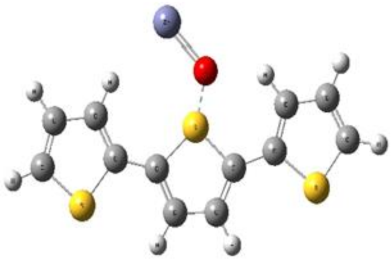
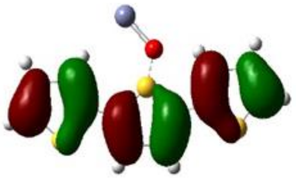
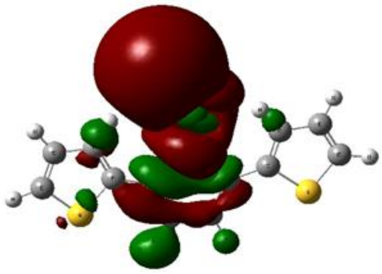
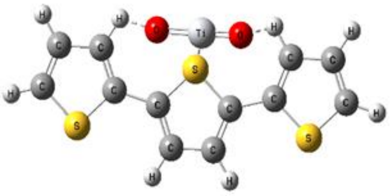
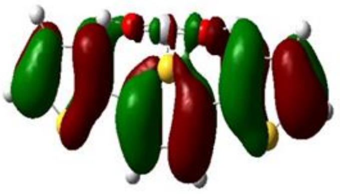
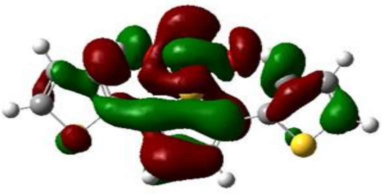
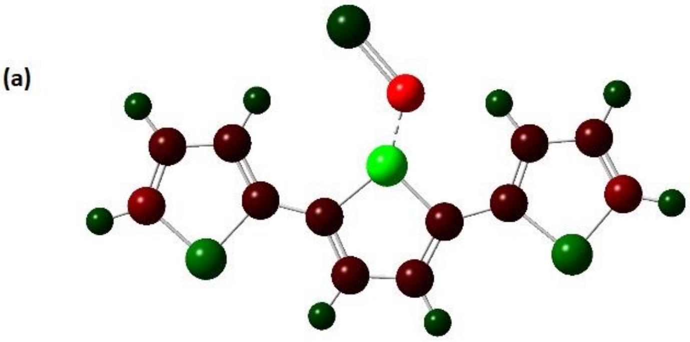
Optimized Structure	HOMO	LUMO
		
		

Table 3. The NBO charge (e) of the nano-composites in the ground state at the B3LYP/6-31G(d,p) level of theory

Composite	Acceptor (negative)	NBO color charge	Donor (positive)
ZnO@3PT	-1.119	🟥⬛🟩	1.199
TiO_2@3PT	-1.09		1.90



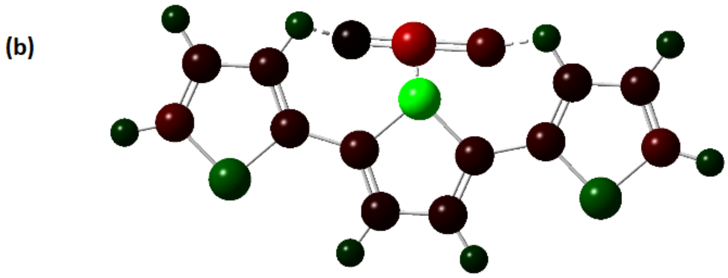


Figure 3. Natural Bonding Orbital (NBO) distribution charge for (a) ZnO@3PT and (b) TiO_2@3PT.

Among the two nano-composites investigated, TiO_2@3PT composite has the highest total NBO charge values of the donor and acceptor (Table 3). These results prove that the electrons are probably transferred efficiently from the donor part of 3PT oligomer to the acceptor part of (ZnO & TiO_2) through the electrostatic bond in the two investigated composites, which leads to injection into the conduction band of ZnO and TiO_2. From this NBO charge transfer analysis it can be easily concluded that, in the nano-composites, ZnO and TiO_2 will causes oxidation and the 3PT oligomer will causes reduction. Based on the above context, the two composites have an optimum for the designing of an efficient photocatalyst [20].

4. Conclusions

Density functional theory (DFT) investigation of suitability of ZnO and TiO_2@ polythiophene composite are explored for the development of an efficient photocatalysts. The DFT calculation results showed that bonding interaction of ZnO & TiO_2 with 3PT oligomers have a strong bonding interaction which are electrostatic and hydrogen bonding; where (S–OZn) and (Ti–S) have strong electrostatic bonding and (O – H) has hydrogen type of bonding. Optical and electronic structure properties such as (Uv-Visible spectra, TDM and HOMO-LUMO) calculation indicate the excellent absorption properties of ZnO@3PT and TiO_2@3PT in the visible region over 3PT oligomer due to red-shifting from the ultraviolet to visible to IR ray and this shows an evidences of excellent photocatalytic properties of the two study composites over 3PT oligomer. The electron–charge transfer mechanism are calculated with natural bonding orbital NBO analysis where ZnO & TiO_2 act as electron acceptor and 3PT oligomer act as electron donor in the study composites. However, this study may aid in the optimum design of improved (ZnO and TiO_2) nanocomposites as a promising and good candidate for photocatalysts application.

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