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Theoretical Study of the Electronic and Optical Properties of Polypyrrole (PPy) Polymer Nanoparticles Doped with TiO_2 and ZnO

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Abstract

Designing suitable nanoparticles of polymer Polypyrrole (PPy) backbones to improve doping efficiency can provide a new direction in enhancing electronic and optical properties by enhancing the efficiency of doping (ZnO) and (TiO_2). Objective: In this study geometry optimization in the gas phase, UV-visible, IR spectrum, and several electronic characteristics have been studied. All computations were based on density functional theory (DFT). Results showed the analysis of ultraviolet and visible spectra. A peak appears in the visible region, and this corresponds to transitions between electronic energy levels within the conjugated polymer chain. This peak is due to π-π^* transitions, and these transitions are sensitive to doping levels and oxidation states. The results show the spectroscopic analysis highlights the interactions between TiO_2 and PPy nanoparticles. TiO_2 particles are characterized by energy gaps that define the absorption edge of the electromagnetic spectrum and thus affect the absorption spectrum of the material as a whole. These effects lead to changes in the locations of the absorption peaks, and this explains changes in the electronic structure and optical properties of these compounds. Transmittance spectra, HOMO and LUMO refer to the highest occupied molecular orbital and the lowest unoccupied molecular orbital respectively band gaps of PPy, PPy/TiO_2, and PPy/ZnO polymer nanocomposites are 3.8, 3.3 eV and 3.2 eV, respectively. All (PPy/TiO_2 and PPy/ZnO) show a shift in the N–H peak of PPy. The change in stretched peak positions indicates the significant bond formed between PPy and TiO_2 as well as ZnO. The bonding of TiO_2 and ZnO with PPy polymers. Also observed TiO_2 and ZnO are significantly at about (1100, 1300) cm^{-1} and (1500, 1900) cm^{-1}, respectively.

Keyword: polymers • polyvinyl alcohol (PVA) • doping ZnO • TiO_2 DFT.

Introduction

Polypyrrole (PPy) is a heterogeneous organic conjugated polymer. It consists of a pentagonal ring with five carbon members, with one of the carbon atoms replaced by a nitrogen atom. PPy has good optical, electrochemical, mechanical, electrical, and biocompatible properties However, many of the physical and structural characteristics of PPy are poorly understood, and the available information is often contradictory. Due to the great interest in PPy, much literature describes research on applications in electronic and optical devices. Many of them have demonstrated the effect of doping of various materials on electronic and optical properties [1-3]. With the development of nanomaterials, PPy is considered a nanoscale component in a wide range of applications including sensors, fibers, coated foams, solar cells, corrosion protection, and electrocatalysis. To improve the PPy properties, nanoparticles were introduced into the PPy composition, such as some of metal oxide, namely ZnO and TiO_2, were added to develop nanocomposites.

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As is clear, conjugated polymers are used in sensors, solar cells, batteries, and light-emitting devices [4, 5]. These polymers are easy to synthesize and have controllable electrical effects, so they are used in biomedical applications [6].

PPy can be readily produced by chemical or electrochemical oxidative polymerization of pyrrole. As for PPy, it is insoluble and insoluble if it is industrially conductive, which prevents it from being processed and applied in other fields. It is considered a process for loading and releasing drugs and biomolecules based on the use of polymers that contain PPy. As for preventing metal corrosion, polymer blends based on PPy are used [7-9]. The synthesis of new organic materials has now received great interest in academic and industrial fields. Recently, organic materials based on conjugated structures have attracted interest due to their ease of synthesis and processing, ease of synthesis, and low cost. Some metallic and semiconducting properties appear in conductive polymers and these properties do not appear in any other material. Conductive polymers are mainly characterized by the existence of conjugated double bonds running along the backbone of the polymer, such as the structure of the polymer Pyrrole [10, 11].

Semiconductors are widely used in photocatalytic activity due to their improved stability and are excited by light energy [12]. Metal oxides such as CuO, ZnO, TiO_2, and ZrO_2 are considered specific types of semiconductors photocatalysts and have photocatalytic potential due to their ability to transfer electrical charges between the valence and conduction bands. ZnO and TiO_2 are important semiconductors due to their high binding energy and wide band gap [13, 14].

Pyrrole itself is the simplest member of the pyrrole family which has the molecular formula of $[H(C_4H_2NH)nH]$. It has many applications such as tissue engineering. PPy is stable in the oxidized form. It is considered an insulator in its neutral state. With these excellent characteristics, PPy has proven to be a possible candidate for many implementations [15, 16].

PPy has these properties due to the difference in polymerization conditions. Its properties can be dynamically controlled by applying an electric field. In addition, semiconductors have wide use in the field of photocatalysis due to their low cost and improved stability. Metal oxide compounds are specific types of semiconductors CuO photocatalysts, such as ZnO and TiO_2, which are excited by light energy [12, 17]. The electronic and optical properties of some substitutes or activators were studied theoretically.

Materials and Methods

All calculations were obtained using the program Gaussian 09 and constructed nanocompounds structures using the Gauss view program, based on DFT theory, the Becke–Lee–Yang–Parr (B3LYP) method, and the basis set 6-311G (d, p) for the elements (Zn, N, H, O, C). For the transition element (Ti), the LANL2DZ basis set was used because its atomic number was greater than the rest of the elements used. Finding theoretical methods provides a great deal in finding the molecular structure, molecular parameters, and vibrational spectra. First, the geometric shapes of the PPy, PPy/ZnO, and PPy/TiO_2 in the gas phase, structures were calculated to obtain more stable and lower energy structures. The TD-DFT theory was used to calculate vibration frequencies. In addition, the infrared and ultraviolet spectra, binding energy, thermodynamic calculations, and some linear and nonlinear parameters were calculated. The quantum descriptors, the electronic affinity, the ionization potential, and the atomic partial charges [13, 18-21]. In this paper, DFT was used to achieve spectral and electronic properties such as the ultraviolet, visible, and infrared spectra. **Figure 1** represents the nano compounds polymer pyrrole before and after doping with ZnO and TiO_2.

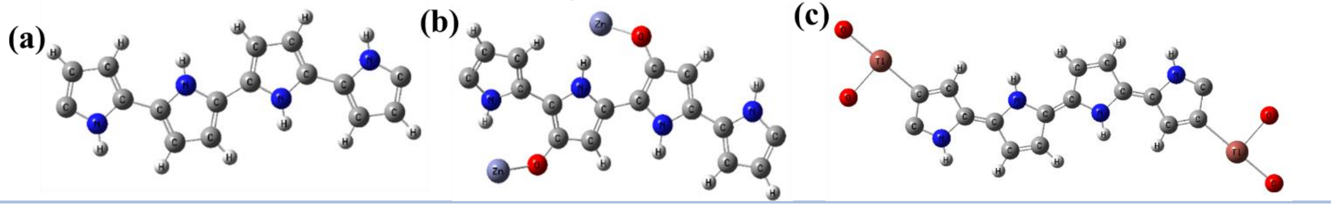

Figure 1. Geometry optimization of (a) PPy, (b) PPy/ ZnO, and (c) PPy/ TiO_2.

Results and Discussion

Transmittance Spectrum

The optical properties of the material and its potential applications can be determined through the transmittance spectrum. PPy is considered a good conductor, that is, it has high optical absorption in the visible and near-infrared regions of the electromagnetic spectrum. The transmittance is low in the visible range and increases in the infrared region.

Transmittance spectra were performed for the three nano compounds to identify the main peaks of (a) PPy, (b) PPy /ZnO, and (c) PPy /TiO_2 as in **Figure 2**. In Figure 2a, the primary spectrum of polypyrrole (PPy) reveals several distinct features. Firstly, a prominent peak appears at 1090 cm^{-1}, indicating the stretching of N-C bonds within the pyrrole ring present in the polymer. This peak occurs from the reaction of the carbon atom with the nitrogen present in the pyrrole unit of the polymer. Furthermore, a signal is evident at 3300 cm^{-1}, attributed to aromatic amines' N–H bond characteristics. Another significant peak at 1550 cm^{-1} originates from stretching the five-membered PPy rings. Additional observable bands at 1098 cm^{-1} and 800 cm^{-1} correspond to the out-of-plane stretching of PPy and the deformation of C–H bonds within the plane. Moreover, peaks within the ranges of 1330 cm^{-1}, 1370 cm^{-1}, and 1422 cm^{-1} are associated with C-H and CH_2 bending vibrations. Finally, discernible modes include C-C stretching at 800 cm^{-1} and CH2 rocking at 600 cm^{-1} [22-24]. In contrast, when PPy is combined with ZnO, notable changes occur in the spectrum. A distinct absorption band emerges at 1734 cm^{-1}, indicating C-O carbonyl stretching. Additionally, a broad peak at 3280 cm^{-1} suggests the vibration of O-H stretching. However, vibration peaks at 435 cm^{-1}, 910 cm^{-1}, and 700 cm^{-1} signify the bending and stretching modes of Ti-O, (Figure 2c). These outcomes amazingly coordinated with the results obtained [25][28]. All (PPy/TiO_2 and PPy/ZnO) show a shift in the N–H peak of PPy. The change in stretched peak positions indicates the significant bond formed between PPy and TiO_2 as well as ZnO. Other studies have also reported the bonding between conductive polymers and metal oxides, such as the bonding of TiO_2 and ZnO with PPy polymers. Also observed TiO_2 and ZnO are significantly at about (1100, 1300) cm^{-1} and (1500, 1900) cm^{-1}, respectively [26].

UV – Visible Spectrum

UV-vis spectrum analysis is an important technique for identifying the optical properties of materials, especially polymers and their nanocompounds. This technique provides information about the characteristics of transmittance and absorption across these regions within the electromagnetic field. Figure 3 indicates PPy. A peak appears in the visible region, and this corresponds to transitions between electronic energy levels within the conjugated polymer chain. This peak is due to π-π^* transitions, and these transitions are sensitive to doping levels and oxidation states. As for PPy/TiO_2 nanocompounds, the spectroscopic analysis highlights the interactions between TiO_2 and PPy nanoparticles. TiO_2 particles are characterized by energy gaps that define the absorption edge of the electromagnetic spectrum and thus affect the material's absorption spectrum as a whole.

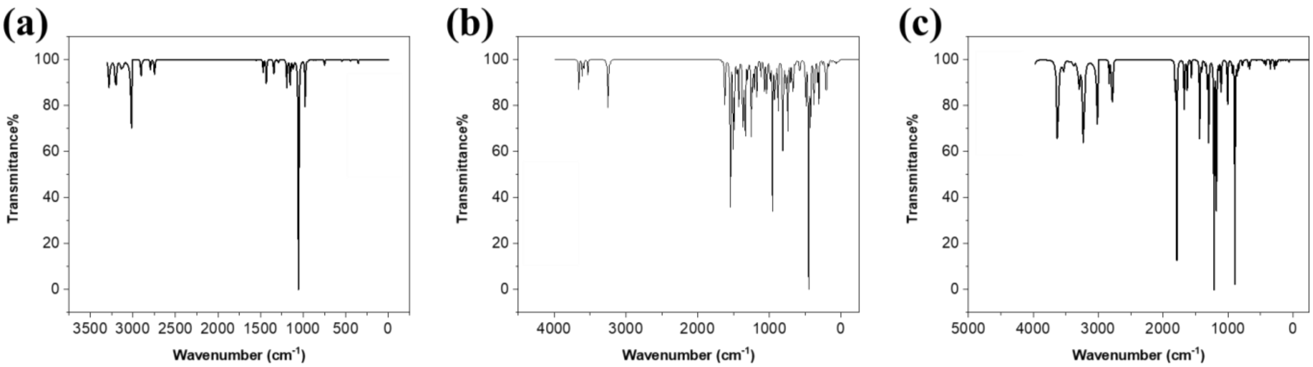

Figure 2. Transmittance spectrum of (a) PPy (b) PPy /ZnO and (c) PPy /TiO_2.

These effects lead to changes in the locations of the absorption peaks, and this explains changes in the electronic structure and optical properties of these nanocompounds. In addition, it was observed that the second and third bands of PPy /TiO_2 and PPy /ZnO indicate a dipolar state in these compounds. The peaks of PPy/TiO_2 and PPy/ZnO show a shift compared to PPy, and this indicates the redshift, that is, the longest wavelength and lowest frequency [27]. In contrast, PPy/ZnO and PPy/TiO_2 nanocomposites show absorption peaks in the range of 416 and 1584, respectively.

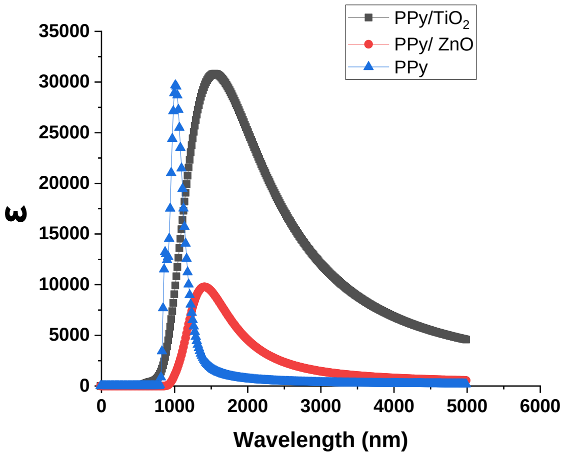

Figure 3. UV–vis spectra of PPy, PPy /ZnO, and PPy /TiO_2.

Energy Gap

The band gaps of various materials, including PPy, ZnO, TiO_2, PPy/ZnO, and PPy/TiO_2, were determined by assessing the energy disparity between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) [28]. This parameter is important for understanding stability and interaction dynamics in compounds. These values are summarized in **Table 1** of this study. Furthermore, the observed band gaps of PPy, PPy/TiO_2, and PPy/ZnO polymer nanocomposites are 3.8, 3.3 eV, and 3.2 eV, respectively. In particular, the band gaps of the (PPy/ZnO) and (PPy/TiO_2) polymer composites were wider than the pure PPy polymer. It has also been shown that many polymer nanocomposites exhibit the same behavior. By using equation 1 to determine the band gap [29].

$$Energy\ gap = Homo - Lumo \qquad \ldots (1)$$

Table 1. HOMO, LUMO, and energy gap for PPy, PPy /TiO_2, and PPy/ ZnO.

System	HOMO (eV)	LUMO (eV)	Energy Gap (eV)
PPy	4.8	1.02	3.8
PPy/TiO_2	9.7	-6.38	3.3
PPy/ZnO	11.7	-8.5	3.2

Electronic Properties and Chemical Descriptors

The energy levels of PPy will be affected when TiO_2 and ZnO nanomaterials are added to the PPy chain, so new energy levels appear within the energy range of the PPy polymer. These new levels change the positions of HOMO – LUMO. Several factors play a fundamental role in the interaction of TiO_2, and ZnO with PPy, including the electronic properties, surface chemistry, and a change in the energy gap of the nanocomposite materials [30]. **Figure 4** shows that the energy gap of PPy, which is (3.8 eV), decreases upon the addition of TiO_2 and ZnO to become (3.3eV) and (3.2eV), respectively, and ZnO has a major effect in the decrease in the energy gap.

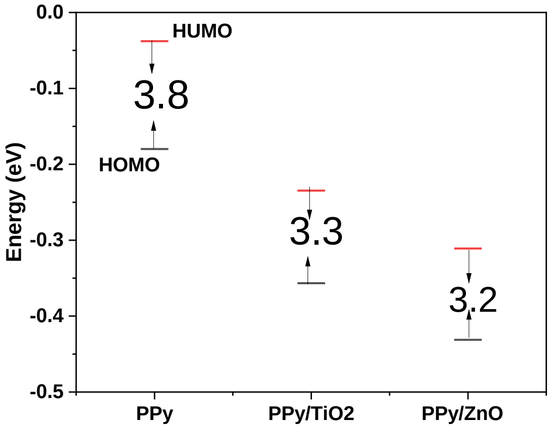

Figure 4. Indicates HOMO - LUMO and energy gap for the three compounds.

Ionization Potential

Understanding the energy of the HOMO and LUMO is very important to determining a molecule's chemical reactivity. Electron donors are connected to the ionization potential (IP) through their energy, which the HOMO indicates. On the other hand, LUMO acquires electrons and its energy is related to the electron affinity (EA) in molecular interactions [31]. By applying Koopmans' theorem (Koopmans 1993), we can derive the two electronic parameters, which are given by equation 2 and 3 [32].

$$IP = -E_{HOMO} \qquad \text{... (2)}$$

$$EA = -E_{LUMO} \qquad \text{... (3)}$$

Other important parameters can be used to discuss the reactivity and stability of molecules and can be obtained using the following equations, available in several publications as follows [33-35]:

The chemical potential (μ) and electronegativity (χ) can be obtained as follows:

$$\mu = -\chi = -\frac{IP + EA}{2} \qquad \text{... (4)}$$

We used the following equations to calculate electrophilicity (ω) and nucleophilicity(υ):

$$\omega = \frac{\mu^2}{2\eta} \qquad \text{... (5)}$$

$$\upsilon = \frac{1}{\omega} \qquad \text{... (6)}$$

where η represents the chemical hardness and is given by:

$$\eta = \frac{IP - EA}{2} \qquad \text{... (7)}$$

And the softness given by:

$$S = \frac{1}{\eta} \qquad \text{... (8)}$$

We can accurately determine the maximum amount of charge that can be transferred in a given system.

$$\Delta N_{max} = -\frac{\mu}{\eta} \qquad \text{... (9)}$$

Polypyrrole has carbon-carbon double bonds that create a conjugated system, and the π- electrons are delocalized along the system, which helps in the electrical conduction of polypyrrole. The doping (PPy) with (ZnO) and (TiO_2) contributes to the introduction of additional charge carriers (electrons and holes) into the polypyrrole structure. This promotes the delocalization of electrons, causing specific changes in the system. **Table 2** displays all the parameters above when ZnO and TiO_2 are added to (PPy).

Table 2. shows the electronic parameters of undoped and doping polymers.

Table 2. The electronic parameters of undoped and doping polymers.

System	IP (eV)	EA (eV)	μ (eV)	χ (eV)	η (eV)	S (eV^{-1})	ω (eV)	υ(eV^{-1})	ΔN_{max}
PPy	4.894	1.029	- 2.962	2.962	3.865	0.258	1.134	0.881	0.766
PPy/ ZnO	9.706	6.383	- 8.044	8.044	3.323	0.300	9.736	0.1027	2.420
PPy/ TiO_2	11.7	8.5	-10.1	10.1	1.6	0.625	31.87	0.031	6.31

Thermochemical Preparties

The thermochemical properties of polymers can be determined using some analytical methods. These properties such as Zero-point (ZOP), total energy (E_{tot}), Enthalpy (Hcorr), and Gibbs free energy are important for understanding the behavior and stability of polymers during synthesis. The Enthalpy (H_{corr}) was determined using equation (11- 12), all at (1.0 atmospheres and 298.15K). To obtain values for thermochemical properties, theoretical methods can be used, such as quantum chemistry calculations based on density functional theory (DFT) for the nanoparticles polymer polypyrrole and ZnO\PPy, PPy/TiO_2. The enthalpy (Hcorr) measures the system's heat content at constant pressure and temperature. When the polymer is formed or transformed, the Gibbs energy (G) combines the enthalpy and entropy of the system and gives information about its stability. Tables 3 and 4 show how these results can generate various chemical properties for (PPy/ZnO, PPy, and ZnO) and (PPy TiO_2, PPy, and TiO_2).

Table 3. Analyze various chemical profiles for PPy, ZnO, and PPy/ZnO).

System	ZOE	E_{tot}	H_{corr}	G_{corr}
PPy	0.710684	0.724686	0.725630	0.669465
ZnO	-138.939907	-138.936425	-138.935480	-138.963767
PPy/ZnO	-4542.91982	-4542.89786	-4542.89691	-4542.9763

Table 4 shows how these results can be used to generate.

Table 4. Generate various physicochemical data for PPy, TiO_2, and PPy/TiO_2 nanocomposites.

System	ZOE	E_{tot}	H_{corr}	G_{corr}
PPy	0.710684	0.724686	0.725630	0.669465
TiO_2	-0.228673	-0.224148	-0.223203	-0.248219
PPy/TiO_2	0.645649	0.667355	0.668299	0.590173

$$\Delta_r H°(289K) = (\Delta_f H° products) - (\Delta_f H° reactant) \qquad \text{... (10)}$$

$$\Delta_r H°(289K) = [(PPy/ZnO) - [(PPy + ZnO)]] \qquad \text{... (11)}$$

= - 4681.105 × 627.51= - 2937440.45 Kcal / mol

$$\Delta_r G°(289K) = [(PPy/ZnO) - [(PPy + ZnO)]] \qquad \text{... (12)}$$

= - 4681.27 × 627.51 = - 2937543.73 Kcal / mol [36].

It can be concluded that the reaction of the polymer with (ZnO) is exothermic, while the reaction of the polymer with (TiO_2) is endothermic.

Conclusions

Adding titanium dioxide and zinc oxide with the polymer PPy means that these nanocompounds interact with the polymer strongly, and this is demonstrated by the analysis of the UV-visible spectrum and transmittance. It was found that the absorption band of the pure polymer shifted to longer wavelengths after the addition, that is, towards a redshift. The energy gap of the polymer was also calculated before the addition. It was large, but after the addition, it became smaller. Various applications, including sensors, solar cells, and light-emitting diodes, can benefit from the improved electrically or optically properties of the polymer. Thermal properties showed that the reaction of the polymer with (ZnO) is exothermic, while the reaction of the polymer with (TiO_2) is endothermic.

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Declaration of Competing Interests

The authors affirm that the publication of this paper is not impacted by any conflicts of interest.

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