Molecular Modeling Analyses for Electronic Properties of CNT/TiO₂ Nanocomposites

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Research Article

Keywords: B3LYP/3-21g**, CNT/TiO₂, XRD, TEM, FTIR

Posted Date: April 14th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-372905/v1>

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Abstract

Electronic properties of carbon nanotube (CNT) is enhanced with the help of metal oxides which in turn paves the way toward functionality of CNT for many applications based on their electronic properties. Accordingly, density functional theory at B3LYP/3-21g** is utilized to model the decoration of CNT and TiO₂. 7 molecules of TiO₂ are interacted with the CNT surface as adsorb state and complex. As a result of this decoration, a change in the Mulliken atomic charges of a carbon atom which is interacted with the metal is recorded, changing both the total dipole moment and HOMO/LUMO bandgap energy. The molecular electrostatic potential is localized toward the left side for the adsorb state then up and down for the complex state, which enhances the probability of forming hydrogen bonding with the surrounding. The change in the physical parameters of the surface promotes the decorated CNT for many applications. For verification, CNT is prepared with homemade CVD then decorated with TiO₂. XRD, TEM, and TGA confirmed that TiO₂ is located on the surface. Finally, the FTIR spectrum indicated that the studied model is suitable for the investigated system regarding both accuracy and computational time.

1. Introduction

Among nano scale material located, the carbon family as well as their derivatives showing emerging applications. This family includes several members such as graphite, activated carbon, fullerene, carbon nanotubes (CNTs), mesoporous carbon, carbon nano onions, nano diamond, graphene nano ribbon as well as graphene (Elhaes et al. (2016)). In 1991, Sumiolijima discovered a byproduct of fullerene called nanotubes. They could be classified as single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). Starting with the MWCNTs, one can describe it as rolled-up one multiple graphene sheets, could be also described as many SWCNTs with growing diameters being arranged (like "Russian doll") in a concentric manner (Scharff et al. (1998)).

CNTs could be produced as mass production and/or in large amount by means of catalytic decomposition of hydrocarbon gas like acetylene in the presence of catalytic agents such as Co and/or Fe (Hernadi et al. (1996)). Carbon nano materials including CNT and fullerene (C₆₀) could be synthesized upon high-purity graphite using keVAr⁺ ion bombardment technique under controlled physical conditions. It is stated that, controlling the experiment conditions C₆₀ was changed into amorphous carbon then further transformed into CNTs (Wang et al. (1998)). More detailed experimental conditions describing this method is reported (Suchanek et al. (2001)). Since the discovering of CNTs, many synthesizing techniques have been reported, however some of them are less significant. The most forward and efficient reported methods include; laser ablation, arc discharge, and chemical vapor deposition (CVD).

Researchers pointed out that, some simple and easy handling techniques are required for the preparation of different forms of carbon nano materials. Among these techniques the CVD is the most suitable and forward for CNTs synthesizing. Using CVD one can transform fullerene into SWCNTs, controlling the diameter could be also possible with controlling the operational conditions (Maruyama et al. (2003)). It is

reported that, fullerene is continue to be the source for CNTs by controlling both pressure and temperature with the modified Liquid-Liquid Interfacial Precipitation method which is termed LLIP, detailed experimental procedure is described in which C_{60} -pyridine and isopropyl alcohol were illuminating with visible as well as ultraviolet radiations (Ringor et al. (2008)). A sonochemical/hydrothermal facile method was recommended as an excellent method for the production of MWCNTs with considerable amounts (Manafi et al. (2008)). Although CNTs is not recently discovered but still of interest for many researchers as they apply it in many applications according to their amazing and outstanding properties (Yu et al. (2000)), such properties are: extraordinary flexibility (Iijima et al. (1996)), excellent electrical and thermal conductivities, fantastic resistibility to acids and bases, (Cobden et al. (1998)) it is reported as excellent field emission agent (Jung et al. (2006)), moreover its characterized by high aspect ratio. This paves the way toward its possible applications as electron field emitter of display systems (de Jonge et al. (2002)), finiste and/or nanoscale electronic devices (Fennimore et al. (2003)), gas and biosensors (Huang et al. (2002)), effective hydrogen storage media (Liu et al. (1999)) and finally it show applications as effective fuel cell electrodes (Villers et al. (2006)). In spite of all of these outstanding properties; CNTs suffering from some drawbacks represented in hydrophobicity, insolubility in polar and nonpolar solvents, tendency to agglomeration, and poor adsorption selectivity. Despite that, these disadvantages can be overcome by means of grafting some functional particles to the surface of CNTs, or what is known as decorations. These particles could be inorganic, organic or even biological molecule. Decoration of CNT by metal oxides produces nanocomposites for many applications. Decoration could increase the ability for removing heavy metals from wastewater where it acts as active catalysts for inorganic pollution in the aquatic environment (Yu et al. (2005)). It is stated that decoration enhances the charge transfer and hence decorated CNT could be applied for supercapacitor applications (Kuan-Xin et al. (2006)). Decoration could also enhance the ability of CNT for field emitter material applications to act as emission devices (Yu et al. (2006)). CNT/CuO nanocomposites is applied as a sensor for volatile organic compounds (Zheng et al. (2012)). Palladium nano-crystallite decorated TiO_2 nanotubes show efficient performance as a photocatalytic agent with the application for the degradation of diclofenac (Cheng et al. (2013)). The same nanocomposite is modified for photo-electrocatalytic performance for the degradation of aspirin (Cui et al. (2016)). CuS/ TiO_2 nanotube arrays photoelectrode is adapted to work in UV-Vis for photo-electrocatalytic decomposition and mechanism of penicillin (Ma et al. (2018)).

To investigate the electronic properties of CNT and decorated CNT, molecular modeling at density functional theory (DFT) level is consulted. It is stated that DFT, as well as other classes of computational work, is leading the investigation aiming to understand molecular structures and properties of many systems and molecules (Omar et al. (2021); Bayoumy et al. (2020a); Bayoumy et al. (2020b); Nguyen et al. (2014); Srivastava et al. (2018)). The main aim of this study is to synthesize the CNTs/ TiO_2 nanocomposite experimentally, then studying its molecular structure and electronic properties through building appropriate model molecule. Since TiO_2 is a multipurpose material that has been utilized in different applications, we thought it relevant to analyze the electronic and structural properties of the CNTs/ TiO_2 nanocomposite.

The present work is conducted to study the effect of the decoration with TiO_2 on CNT using B3LYP/3-21g**. The investigated model is compared with experimental results in which CNT/ TiO_2 is prepared and characterized with XRD, TEM, TGA, and FTIR respectively.

2. Materials And Methods

2-1. Calculation details

All model molecules were calculated using Gaussian 09 program (Frisch et al. (2010)) at Spectroscopy Department, National Research Centre, Egypt. Model molecules of CNTs and CNTs decorated with TiO_2 were optimized with DFT at B3LYP/6-31g** (Becke et al. (1993), Lee et al. (1988) and Miehlich et al. (1989)). The bandgap energy is calculated as the difference between the highest occupied molecular orbitals and lowest unoccupied molecular orbitals (HOMO/ LUMO) using the same model. Total dipole moment (TDM) and electrostatic potential (ESP) were calculated for the studied structures at the same level of theory. For comparison with experimental results, vibrational spectra were calculated and assigned with the help of the software at the same level of theory.

2-2. Chemicals and reagents

To prepare CNT/ TiO_2 nanocomposite the following chemicals are purchased: Ferrocene was purchased from Sigma Aldrich, Germany. Sulfuric acid 95-98%, extra pure was purchased from Scharlau, European Union. Xylene technical grade was purchased from El-Nasr Pharmaceutical Company, Egypt. Nitric acid 55% was purchased from El-Salam Chemical Industry, Egypt. Titanium tetra isopropoxide (TTIP) was purchased from Sigma Aldrich, Germany. Ethanol, HCl, H_2O_2 and acetic acid were purchased from El-Nasr Pharmaceutical Company, Egypt. All of these chemicals were used as they are without any further purification.

2-3. Production of CNT and CNT/ TiO_2

A modified home-made CVD is used to produce CNT using ferrocene and Xylene as catalyst and hydrocarbon source respectively, as described earlier in our previous method (Morsy et al. (2014)). As synthesized CNTs have been refluxed in a mixture of 3:1 (V/V) HNO_3 and H_2SO_4 to impart function group to the surface of CNTs. Then CNT is further utilized to produce TiO_2 -decorated CNT. The CNT/ TiO_2 was prepared using simple precipitation route. In brief 30 mg of MWCNTs were dispersed in 50 ml of ethanol using ultrasonic homogenizer. Then TTIP (10 ml) were dissolved in a proper amount of ethanol in an ice bath. Functionalized MWCNTs suspension was added to the TTIP solution during stirring at low speed at room temperature.

Acetic acid was added drop wise to the above solution and refluxed under continuous stirring at 140 °C for 2hrs; the overall solution was cooled to room temperature then left overnight. A two-layer solution was formed, the upper layer being the organic byproduct, and the lower one was a gray precipitate. The precipitate was filtered, washed then dried at 100 °C overnight. The obtained powder was calcinated at 500 °C for 3 hrs to get a pure anatase TiO₂ nanoparticles loaded on the surface of MWCNTs. The schematic diagram of the CNT/TiO₂ synthesizing method is represented in fig. 1

2-4. Characterizing techniques

X-ray diffraction (XRD) pattern was carried out with an Philips XRD Powder diffractometer (PW3050/60) with CuK_{α} radiation ($\lambda = 0.15406$ nm) .

High-Resolution Transmission Electron Microscopy (HR-TEM) for the examination of the morphology was conducted on a Philips (FEI Tecnai G2 S-Twin) which is operated at 200 kV.

Thermal analysis data were recorded with thermal analyzer STD-Q 600, under air atmosphere with a flow rate of 30 mL/min from room temperature up to 800 °C

Fourier Transform Infrared Spectroscopy was carried out on FTIR (Vertex 70, Bruker Optik GmbH, Germany) at the spectroscopy Department, National Research Centre, Egypt.

3. Results And Discussion

3-1. Molecular modeling calculations

A model for CNT is indicated in figure 2 with different views. CNT is optimized at B3LYP/3-21g** level of the theory then the HOMO/LUMO band gap is calculated as indicated in Fig. 3a. The molecular electrostatic potential (ESP) contour is calculated at the same level of theory and plotted in Fig. 3b. TiO₂ is supposed to interact with the surface of CNT following two schemes, the first form is adsorbed state as shown in Fig. 4a. Then HOMO/LUMO band gap energy is calculated as shown in Fig. 5b., while Fig. 4c shows the calculated molecular ESP.

Fig. 5a presents the second form of interaction between 7 TiO₂ and the surface of CNT which is through the complex form. Fig. 5b shows the HOMO/LUMO and Fig. 5c shows the molecular ESP. Before discussing the band gap and ESP, it is important to follow up on the physical changes in the surface of CNT as a result of TiO₂ surface interaction either through adsorb and/or complex state. Table. 1 presents the B3LYP/3-21g** Mulliken atomic charges, TDM, and HOMO/LUMO band gap energy. The Mulliken charges are charges based on the local electron density (charge density) that depends strongly on the basis set and function because it is sensitive to the probability density. In this work, the function and basis set is the same for the studied structures (B3LYP/3-21g**). The Mulliken atomic charges are

followed on one of the carbon atoms with which TiO_2 is going to interact. The value of the charge is calculated before and after the interaction between CNT and TiO_2 . Mulliken atomic charges as listed in table 1 is 0.028287 for CNT, then changed as TiO_2 interacted with CNT to be -0.084450 corresponding to adsorb state and -0.226259 corresponding to complex state. This is an indication for changing the charge upon the carbon atom as a result of the interaction with TiO_2 in either adsorb state or complex state.

Table 1

Calculated B3LYP/3-21g** Mulliken atomic charges (MAC), total dipole moment (TDM) as Debye, HOMO/LUMO band gap energy (ΔE) as eV, for Carbon nanotube, Carbon nanotube with 7 TiO_2 as complex state and Carbon nanotube with 7 TiO_2 as adsorb state.

Structures	MAC	TDM				ΔE
		X	Y	Z	Total	
Carbon nanotube (CNT)	0.028287	0.0759	0.5694	-0.0085	0.5745	0.245
CNT/7 TiO_2 as adsorb state	-0.084450	-1.7088	1.9695	10.4649	10.7849	0.543
CNT/7 TiO_2 as complex state	-0.226259	-1.6525	-0.2346	11.9222	12.0385	0.633

Regarding the TDM with x, y and z distribution for CNT, the TDM is 0.5745 Debye. Changing the charge upon carbon is expected to make redistribution process which is already regarded as a result of the interaction, which is, in turn, changing the values of the dipole moment in x, y, and z. This is the reason for changing the TDM to 10.4649 Debye for adsorbing state and 12.0385 Debye for the complex state.

The correlation between the Mulliken atomic charges and TDM could be also tried for HOMO/LUMO bandgap energy. As listed in table 1, the bandgap is changed from 0.245 eV to 0.543 eV then 0.633 eV ongoing from CNT to adsorb state to complex state. Changing the surface properties of CNT as a result of interaction with TiO_2 dedicates its surface for many applications. Another important physical parameter that describes the surface of a given structure is the molecular ESP which is plotted for the studied structures as indicated in Fig. 4c, 4-c and Fig. 5c respectively. The contour of ESP is a useful tool necessary for describing the surface of a given structure as it determines the sites for both electrophilic and/or nucleophilic reactions. In other words, the ESP could be very effective to determine the ability to form hydrogen bonding (Politzer et al. (1981)). This ESP contour is describing the charge distributions for the studied CNT and CNT/7 TiO_2 throughout colors. It was stated earlier that, the colors are ranging from negative to positive on going from red and yellow to blue. In other words, the following decreasing order

is describing the increase in potential namely red < orange < yellow < green < blue (Politzer et al. (1985); Politzer et al. (1996)).

The electrophilic reactivity is always related to red then electrophilic reactivity is correlated with blue. Fig. 3b presents the ESP contour of CNT indicating that there is a uniform distribution of ESP. Regarding the CNT/TiO₂ adsorb state, the electrophilic active regions (negative regions) are localized on the left side as indicated in figure 4-c. This is also confirmed by the distribution of HOMO/LUMO as shown in figure 4-b. While ESP for CNT/TiO₂ complex state is localized uniformly up and down inside the CNT as indicated in figure 5-d. This is also confirmed by the distribution of HOMO/LUMO as shown in figure 5-b.

3-2. Comparison with experimental results

For verifications of the model the CNT is prepared by CVD using ferrocene and Xylene as catalyst and hydrocarbon source respectively, and then characterized tested with different characterization techniques. X-ray is one of the most powerful and nondestructive techniques for crystal structure identification. Fig. 6 shows the XRD pattern of MWCNTs decorated with TiO₂. The pattern shows three characteristic diffraction peaks at $2\theta = 25.5^\circ, 37.9^\circ, 47.79^\circ, 55^\circ$ and 62° . These diffraction peaks are corresponding to (101), (0 0 4), (2 0 0), (211) and (204) crystal planes of the pure anatase TiO₂ phase (JCPDS Card No. 86-1157) (Kalaierasi et al. (2018), Morales et al. (2012), Wang et al. (2014)). It was noticed that the XRD peaks are broad which confirm the nano size of the TiO₂ particles. No diffraction peaks of CNT has been detected in the CNT/TiO₂ nanocomposite, which can be due to that the main characteristic diffraction peak of CNT (002) at 26.2° is perhaps shaded by the (101) peak at 25.3° of anatase TiO₂.

No other diffraction peaks belonging to any other impurities have been recognized indicating a pure anatase phase. These results of this morphology suggest that the model which describes the interaction between CNT surface and TiO₂ could be through the surface as indicated earlier in the molecular modeling part.

As indicated in Fig. 7(a,b), the HR-TEM images indicate the morphology and structure for CNT/TiO₂. They revealed that the as-prepared TiO₂ nanoparticles look like spherical dark black dots and appear like agglomerated particles over the surface of CNTs. The amount of loaded TiO₂ nanoparticles is not so high and distributed over all the external surface of CNTs. The TiO₂ nanoparticles grown out the surface of the nanotubes indicating the weak force between TiO₂ nanoparticles and CNTs. Moreover the HR-TEM revealed that the CNTs are of multiwall type with thick wall and narrow cavity. Fig. 8 presents the TGA as thermal analysis which is well known as an effective tool to describe the amount of nano-metal oxide on the surface of CNTs which is sometimes known as the loading ratio. TGA was performed in the air from room temperature up to 800 °C at a scanning rate of 10 °C/min. The TGA thermogram exhibited two mass changes at 372 °C and 503 °C. The first mass change is a shoulder peak at 372 °C which may be attributed to the complete oxidation of the remaining non-oxidized Ti ions. This may be an indication that

not all the metals are complexed and may exist as adsorb state. The second mass loss is due to the CNTs consumption (Chen et al. (2015)). The amount of loaded TiO_2 nano particles has been estimated from TGA thermogram to be approximately 75%. The TGA results confirmed the both of XRD and HR-TEM results.

Table. 2 presents the FTIR spectrum for CNT/ TiO_2 . The band at 3437 cm^{-1} could be assigned for the OH stretching from carboxyl groups, which can be ascribed to the oscillation of carboxyl groups ($\text{O}=\text{C}-\text{OH}$ and $\text{C}-\text{OH}$). It is also the band at which the water and/or the moisture could appear during the measurements. The two CH- bands at 2920 cm^{-1} and 2850 cm^{-1} are assigned for symmetric and asymmetric bands respectively of CH_2 . These two bands are an indication of the fact that the methylene structure of carbon nanotubes is not destroyed. While the band at 2358 cm^{-1} can be associated with the OH stretching from strongly hydrogen-bonded $-\text{COOH}$ group (Hussain et al. (2011)). The band at 1728 cm^{-1} is assigned for carboxyl groups and that at 1160 cm^{-1} is assigned for carbonyl group; both of which are formed in the modification stage (Saleh et al. (2012)). The band at 1580 cm^{-1} is assigned for the stretching of the carbon nanotube backbone, while the band at 1397 cm^{-1} is the O-H deformation of the $\text{C}-\text{OH}$ group. Finally, the band at 660 cm^{-1} is the characteristic band for TiO_2 (Sun et al. (2011)). For comparison with theoretical IR, only two bands are chosen; one for CNT and the other for the interaction between a metal oxide and CNT as indicated in Table. 3. As listed in table 2, the experimental band for stretching of CNTs was at 1580 cm^{-1} while that of TiO_2 interacted with CNT was at 660 cm^{-1} . The calculated B3LYP-3-21g** values for the same bands were 1517 cm^{-1} and 652 cm^{-1} respectively. Gathering the accuracy of the method together with the computational time, one can conclude that the studied level of theory is suitable for studying the CNT/ TiO_2 regarding the computational time.

Table 2

FTIR band frequencies and their assignment for CNT/ TiO_2 nanocomposites.

Frequencies	Assignment
3437	O-H stretching of the carboxyl group coupled with that of the hydroxyl group
2920	Symmetric stretching of CH ₂
2850	Asymmetric stretching of CH ₂
2370	OH stretching from strongly hydrogen-bonded -COOH group
1728	Carboxyl group
1580	Stretching of the carbon nanotube backbone
1397	O-H deformation of C-OH group
1160	Carbonyl group
660	MO

Table. 3

FTIR spectrum of CNT/TiO₂ as compared with the calculated DFT:B3LYP/3-21g** spectrum.

FTIR	Cal	Assignment
1580	1517	Stretching of the carbon nanotube backbone
660	652	MO

4. Conclusion

CNT as well as decorated CNT (CNT/7TiO₂) as complex or adsorb states are subjected to DFT calculations at B3LYP/3-21g**. Mulliken charge on the carbon atoms is changed as a result of decoration for both adsorb and complex states. This change affected the TDM and HOMO/LUMO bandgap energy. Correlation between the change in Mulliken charge and ESP existed where it is related to the total electron density which changes ESP contour. The effect of decoration was changing the potential of the CNT which dedicated the surface of CNT for sensing phenomena as the decorated CNT surface could perform hydrogen-bonding based on the electrophilic active regions found as a result of decoration. The simple wet chemical route was used experimentally for the decoration of the surface of CNTs with TiO₂. XRD, TEM, and TGA confirmed that the metal is decorated on the surface of CNT. FTIR confirmed the suitability of the B3LYP/3-21g** model for studying the decorated CNT with acceptable accuracy within appropriate computational time.

Based on the studied theoretical and experimental data the studied composite is a successive candidate for sensing phenomena it could be act as gas as well as volatile organic compounds sensor.

Declarations

Acknowledgment

The authors extend their appreciation to the Scientific Research Deanship at King Khalid University and the Ministry of Education in KSA for funding this research work through the project number IFP-KKU-2020/10.

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Figures

Figure 1

Schematic diagram of CNT/TiO₂ preparation method

(a)

(b)

Figure 2

Optimized structure of carbon nanotube which calculated at DFT:B3LYP/3-21g** level of theory with different views.

(a)

(b)

Figure 3

Optimized structure of carbon nanotube which calculated at DFT:B3LYP/3-21g** level of theory, a- HOMO/LUMO, b- the molecular electrostatic potential contour.

Figure 4

DFT:B3LYP/3-21g** calculated optimized structure of a- Carbon nanotube with 7TiO₂ as adsorb state and b- HOMO/LUMO orbitals, c- Molecular electrostatic potential.

Figure 5

DFT:B3LYP/3-21g** calculated optimized structure of a- Carbon nanotube with 7TiO₂ as complex state and b-HOMO/LUMO orbitals, c- Molecular electrostatic potential.

Figure 6

XRD pattern for CNT/TiO₂.

Figure 7

Typical TEM images for CNT/TiO₂.

Figure 8

TGA for CNT/TiO₂.