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A THEORETICAL MODEL FOR CREATION OF ZnO NANOTUBES: A SEMI-EMPIRICAL THERMODYNAMIC STUDY

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ABSTRACT

The thermodynamic functions to test the ZnO nanotubes building were investigated by the semi-empirical method PM6 calculations. It was found that the priority to build tetragonal ZnO nanotubes is by tetragonal periodic units (I) and that tetragonal ZnO nanotubes with a N=4 length were more favourable than those constructed by the tetragonal periodic units and than those of one layer (I). Also, hexagonal ZnO nanotubes, which were built from the hexagonal periodic unit (VI), were more spontaneous since they have more spontaneity than the tetragonal ZnO nanotubes. The added part (II) to build the diameters of ZnO nanotubes was the most favourable. It was established that the entropy didn't have a real influence on these building processes.

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RESUMEN

***Spanish title**: Un modelo teórico para la creación de nanotubos de ZnO: un estudio semi-empírico termodinámico.* Las funciones termodinámicas para poner a prueba la construcción de nanotubos de ZnO fueron investigadas por el método de cálculos semi-empíricos PM6. Se encontró que la prioridad para construir nanotubos de ZnO tetragonales es por unidades tetragonales periódicas (I) y que los nanotubos de ZnO tetragonales con un N = 4 de longitud fueron más favorables que los construidos por las unidades periódicas tetragonales y que los de una capa (I). Además, los nanotubos de ZnO hexagonales, que fueron construidos a partir de la unidad periódica hexagonal (VI), fueron más espontáneos, ya que tienen una mayor espontaneidad que los nanotubos de ZnO tetragonales. La parte añadida (II) para construir los diámetros de los nanotubos de ZnO fue la más favorable. Se estableció que la entropía no tuvo una influencia real en estos procesos de construcción.

INTRODUCTION

The growing interest of nanomaterials was due to their molecular scale (≤100nm) and their significant physical and chemical characteristics. Furthermore, the nanomaterials have the potential for a great impact in the nano-medical fields. Among the best known are the carbon nanotubes (CNTs) which are the first nanotubes, with which Iijima stumbled on, and can be considered as graphite sheets wrapped into a cylindrical shape [1]. The magnesium oxide nanotubes (MgONTs), are other nanotubes over which some studies tried to establish the interaction of CO and NO on their surface [2, 3]. As well, others investigated about the use of doping impurities of the magnesium oxide nanotubes which enhanced their nucleophilic reactivity [4]. The studies of the Raman spectra (infra-red IR) and the nonlinear optical properties (NLO) of the MgONTs depend on the density functional theory (DFT). Where the DFT theory shows that the IR spectra are matched closely to those in the corresponding MgO cluster and bulk materials [4]. The structural information for neutral MgO clusters has been obtained by a comparison of their experimental vibrational spectra with predictions from theory. As well, the MgONTs (hexagonal) has structures same as the MgO rings (hexagonal) [5]. The new biological and medicinal applications were due to the ability of the nanotubes to penetrate into cells offering thus the potential of using them for delivery of drugs and antibiotic molecules without toxicity effects [6–11]. Likewise, the nanomaterials are as a biosensing, antigen recognition and DNA hybridization due to their unique properties. Wong et al. have shown that CNTs are the excellent probe tips for AFM due to their small diameter [12-14]. The CNTs will present big technological advances in bioengineering too [15]. However, there are few theoretical studies of the interaction mechanism between the CNTs and biomolecules [16] compared to an expectation of the broad applications of nanotubes, which try to describe the nature of this interaction with the nanotubes. However, Mavrandonakis et al. studied the interaction of the amino acid with CNTs [17, 18]. Moreover, the influences of other factors such as the diameters and lengths of the CNTs were considered too [19]. What is more, others studied interaction with the magnesium oxide nanotubes [20] and also with the boron nitride nanotubes (BNN) [21]. The nanotubes such as the boron nitride that are non-cytotoxic can be functionalized for interaction with proteins and cells [22]. Also, the fatty acid (butyric acid) interaction with the CNTs was studied [23]. Moreover, Boshra et al. introduced the thermodynamic view to the communication between the Tacrine, which is the drug for Alzheimer's disease, and the boron nitride nanotubes (BNNTs) [24]. Also, our previous work focused on the investigation the CNT as delivery for the anti-cancer drugs [25, 26], here Hesabi et al. studied the skin anti-cancer drugs with the CNTs [27]. Continuously, the researchers are continuing to find or design new nanotubes for many purposes.

The aim of this study is to give an investigation of the theoretical creation for the ZnO nanotubes (ZnONTs). The lengths and the diameters of these tubes were adopted. Gibbs, enthalpy and entropy were used to prove this theoretical investigation.

Computational details

Intending to studying the length of the zinc oxide nanotubes ZnONTs theoretically that shown in Fig.1a, where we depended on two kinds of the periodic units (tetragonal and hexagonal) to build these two nanotubes. Four tetragonal periodic units were adopted with 1, 2, 3 and 4 layers respectively, as shown in Fig.1b, during this theoretic construction of the tetragonal ZnONT. Four periodic units with different layers were chosen in order to make the role of the periodic units be recognised on them well. Likewise, the four hexagonal periodic units with 1, 2, 3 and 4 layers were adopted (see Fig.1b) to the theoretic construction of the hexagonal ZnONTs.

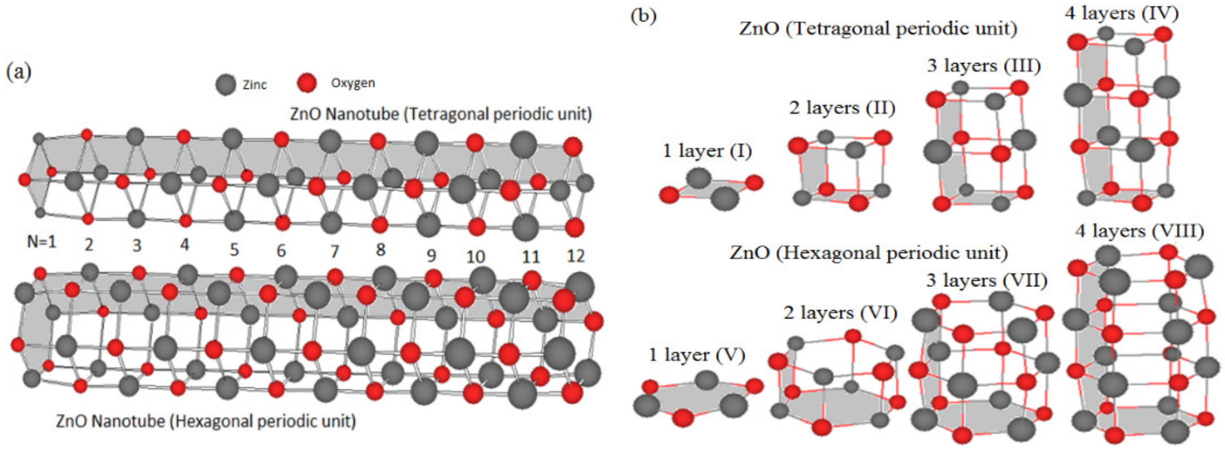

Figure 1. *(a) The ZnO nanotubes (tetragonal and hexagonal) and (b) the periodic units' structures from ZnO that used to build the ZnONTs.*

To study the ZnONTs diameters, it was started with the tetragonal ZnONT (5 layers) as shown in Fig.2a; part (I) was added (5 layers) in order to increase the ZnONT diameter. At the first step, we used the part (I) (5 layers) in addition to increase the diameter of the ZnONT and then it was continued with the same addition until it reached the longest diameter. At the next step, the part (II) was added which was three times bigger than the one utilised in the first step as appeared in Fig.2b. In the end, the part (III) was added, see Fig. 2c. We chose three parts additions (with same layers) in order to the role of the added different parts are recognised well during the ZnONTs building.

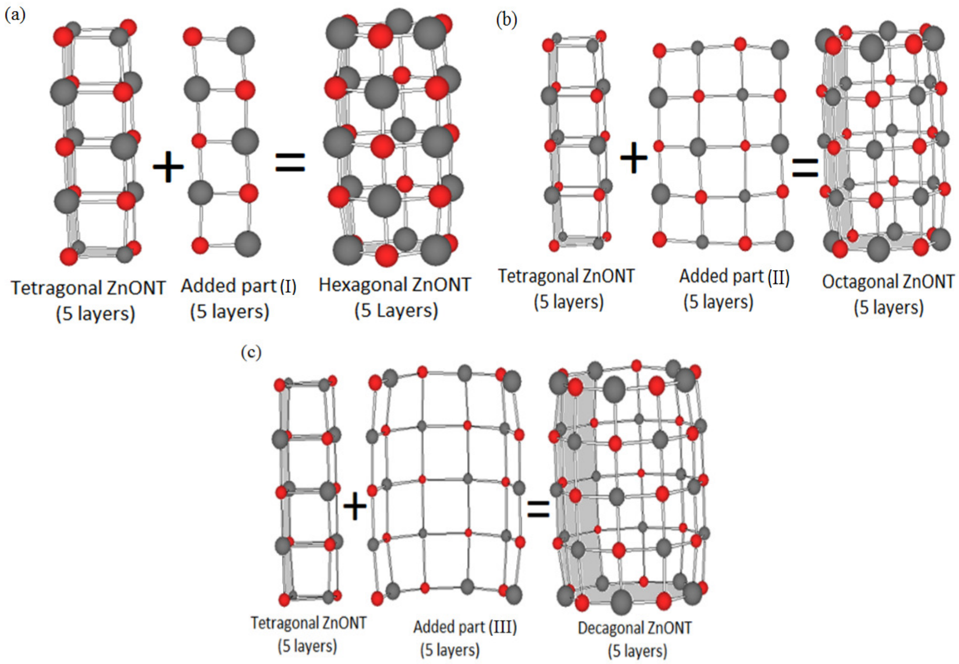

Figure 2. *Shows the added parts (a) I, (b) II, and (c) III that we used to make the ZnONTs diameters.*

The semi-empirical method PM6 (Parameterization Method 6), which is a recently developed semi-empirical method that follows in the tradition of other NDDO methods such as MNDO, AM1, PM3, AM1, and PM5, was used to optimize the studied models [28]. This method is implemented in the Gaussian 09 programme package [29]. Furthermore, frequency calculations were carried out to obtain thermochemical functions, where the frequency calculations were performed at 1 atm and 298.15 K. In all building steps during this paper, the thermodynamic functions (ΔG, ΔH, ΔS) were computed by subtracting the reactants from the products. We used the following model for the ZnONTs lengths: $\Delta G^N = G^N - (G^{N-1} + G^{\text{periodic unit}})$, $\Delta H^N = H^N - (H^{N-1} + H^{\text{periodic unit}})$, $\Delta S^N = S^N - (S^{N-1} + S^{\text{periodic unit}})$. While for the ZnONTs diameters: $\Delta G^N = G^N - (G^{N-1} + G^{\text{added part}})$, $\Delta H^N = H^N - (H^{N-1} + H^{\text{added part}})$, $\Delta S^N = S^N - (S^{N-1} + S^{\text{added part}})$.

RESULTS AND DISCUSSION

In the study of tetragonal ZnONTs lengths (see Fig. 3a), the Gibbs free energy (ΔG), as a function of the tetragonal ZnONTs lengths, was computed and the results were depicted in Fig.3b. According to the negative values of the Gibbs energy, this building would be spontaneous. This spontaneity decreases slightly as the length increases. When the tetragonal periodic unit II (which formed from two layers as shown in Fig.1b) is used, it’s spontaneously and will be lower than the first case (see Fig.3b). Fig. 3b shows the relationship between ΔG and the length of tetrahedral ZnONTs (N). It can be seen from the figure above (or below) that the DG increases as N increases for all cases. A significant increase was seen for tetragonal periodic unit (I). Fig.3c displays the entropy (ΔS) as a function of the tetragonal ZnO nanotubes lengths. According to the negative value of the entropy, for all four issues (I, II, III and IV) were exothermic, so the use of the tetragonal periodic unit of the one layer gave more favourable among these four issues. The processes that release heat are more likely to occur than those in which heat is required. Therefore, the tetragonal ZnONTs, which was built from the tetragonal periodic unit (I) is expected to occur more than the others. With a note that the tetragonal ZnO nanotube has a length (N=4) may be built by the tetragonal periodic units that form from one layer (I) or two layers (II) with the same ΔH approximately, see Fig.3c. Also, the two curves for III and IV have closed around. The entropy (ΔS) was negative for all ZnONTs lengths as shown in Fig. 5d, which is an unfavourable condition during the theoretical creation of the ZnONTs for different lengths. The negative entropy, which decreases as the tetragonal ZnO nanotube's length increases, is predicting less likely to occur. The four curves for I, II, III and IV are interfering together approximately. The entropy results are little negative values so that it did not show a high effect on Gibbs energy (ΔG) in comparison to the enthalpy (ΔH). However, its negative value will not have real influence on the Gibbs free energy.

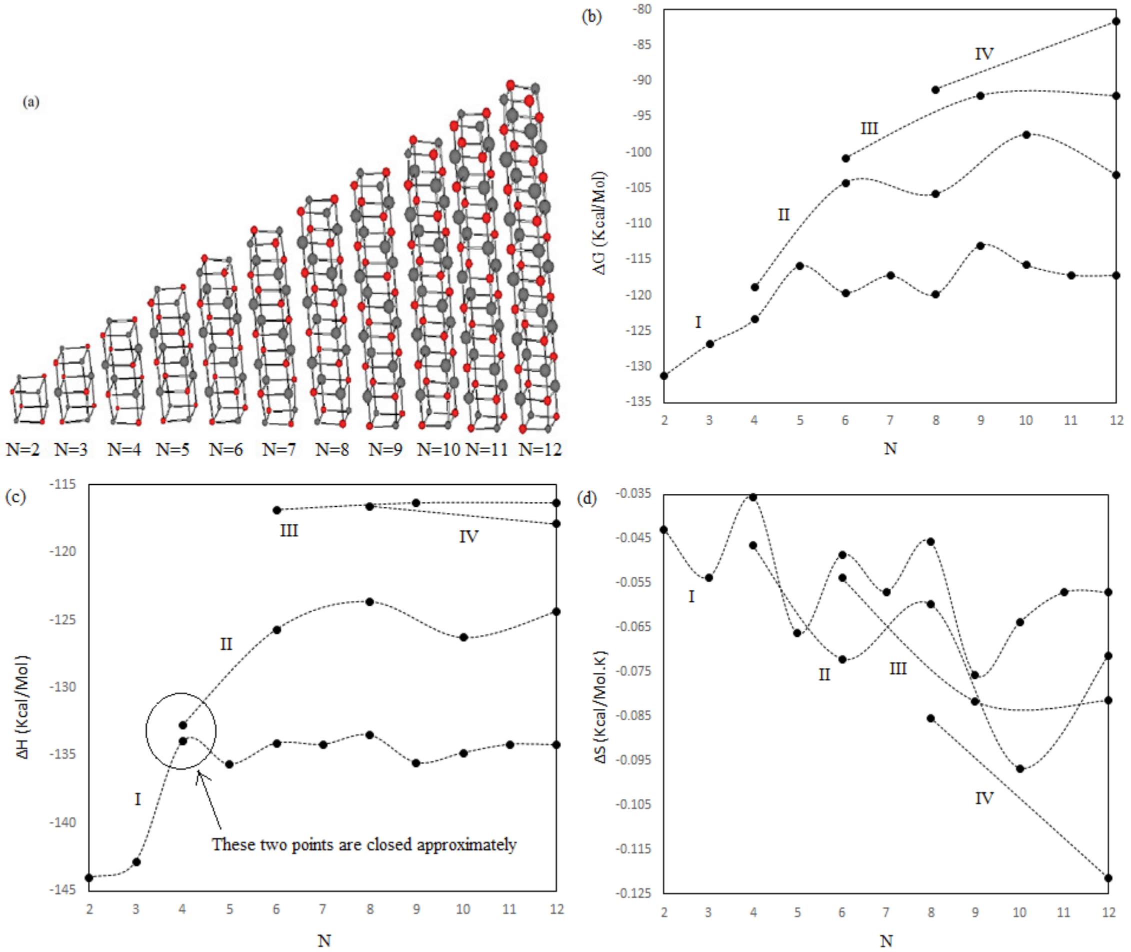

Figure 3. *Gibbs free, enthalpy and entropy as a function of the tetragonal ZnO nanotubes lengths with the tetragonal periodic units: (I) 1 layer, (II) 2 layers, (III) 3 layers and (IV) 4 layers.*

The results of the Gibbs free energy, enthalpy and entropy as a function of the hexagonal ZnO nanotubes length (see Fig.4a) were shown in Fig.4b, c and d respectively. As can be seen from Fig 4b the hexagonal periodic unit (VI) has more negative ΔG than others. Hexagonal is more spontaneous, in comparison with tetragonal (Fig. 3b and Fig. 4b). The results of ΔH for the hexagonal ZnONTs show the same behaviour, see Fig.4c. As can be seen from Fig. 4d and 3d, the ΔS for the hexagonal ZnONT have a similar trend to the tetragonal ZnONT.

To examine the ability of build the ZnONTs with many different diameters, the Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) as a function of the ZnONTs diameters were computed and the results were depicted in Fig.5b,c,d. According to the negative values of the Gibbs energy, the building of the ZnONT's diameter occurs spontaneously. It can be seen from Fig.5b that the spontaneity of curves (I, II, III and IV) decreases as the ZnONTs diameters increase. Then curves stayed constant for few diameters before they came back to rise again. The addition of part (III) increased the ΔG significantly. This case leads spontaneity to be less than those of the part I and II additions. Also, it can be noticed that the two curves I and II at N=7 are identical. The use the part (II) addition to building ZnONT with many different diameters was easier than the two other additions. The behaviour of the enthalpy in Fig.5c was not much different from the conduct of the Gibbs free energy. All enthalpy values were negative values, and all these diameters were exothermic. Also, the second part (II)addition, which was used to build ZnONT diameters, was more favourable than the other additions. The entropy was negative for all ZnONTs diameters as shown in Fig. 5d, which is an unfavourable condition during the theoretical creation of the ZnONTs for different diameters. The entropy's results were similar to the results of the ZnONTs lengths. Consequently, there was no significant effect of its negative on the Gibbs free energy.

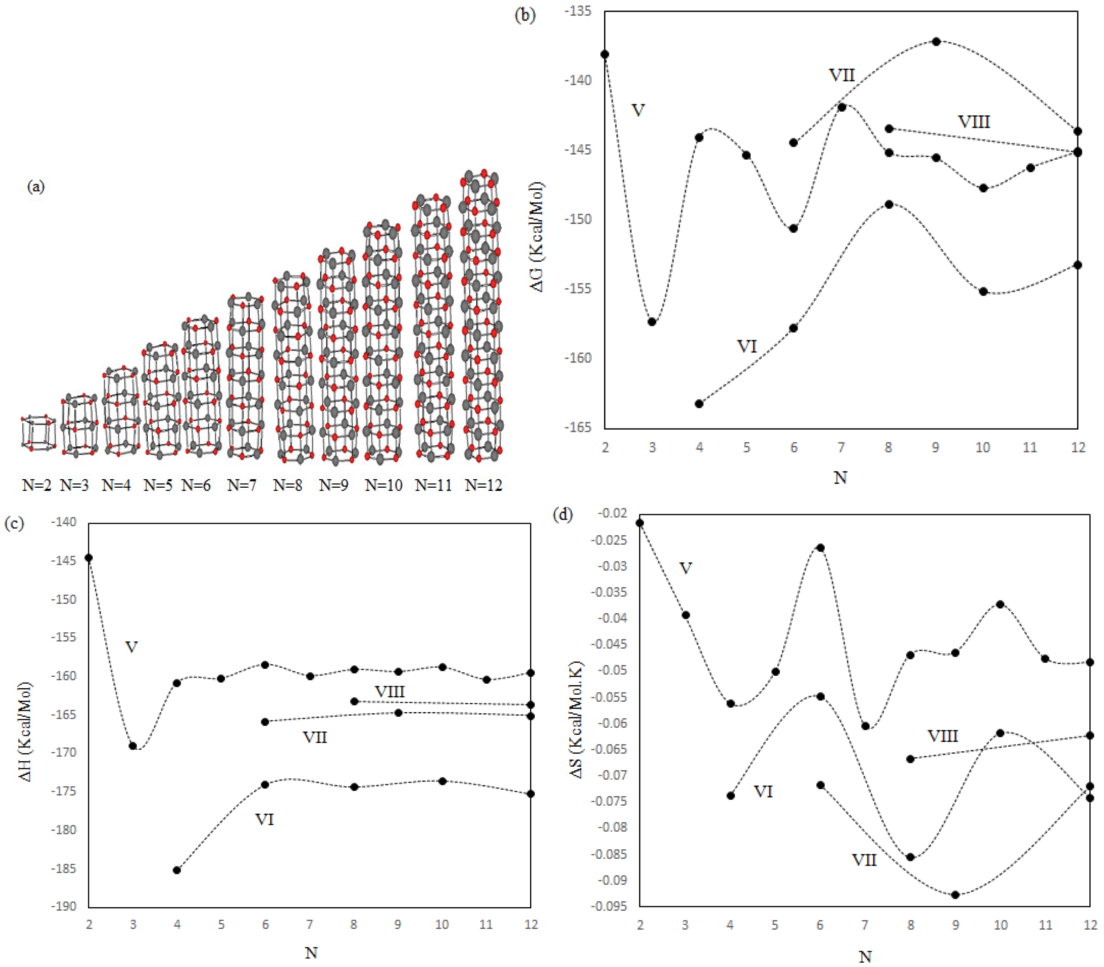

Figure 4. *Gibbs free, enthalpy and entropy as a function of the hexagonal ZnO nanotubes lengths with the tetragonal periodic units: (V) 1 layer, (VI) 2 layers, (VII) 3 layers and (VIII) 4 layers.*

CONCLUSIONS

In summary, we have performed the thermodynamic functions to study the ZnONTs building by the PM6 semi-empirical method. The theoretical models which were adopted here are summed up as follows:
a- Lengths of ZnONTS:
1- Consequently from the Gibbs free energy and the enthalpy, the priority to build the tetragonal ZnONTs will be by tetragonal periodic unit (I).
2- The tetragonal nanotube of ZnO has a length (N=4) and can be formed by the tetragonal periodic units that form from one layer (I) or two layers (II).
3- The hexagonal ZnONT, which is built from the hexagonal periodic unit (VI), will be more spontaneous compared to other cases.
4- The hexagonal ZnONT has more spontaneity than the tetragonal ZnONT.
5- The entropy's results didn't have a real influence on the Gibbs free energy during the building of ZnONTs lengths.
b- Diameters of ZnONTS:
1- All ZnONT's diameters will be spontaneous and exothermic.
2- The use the added part (II) to build the ZnONTs diameters is the most favourable.
3- The entropy's results didn't have a real influence on the Gibbs free energy during the building of diameters of ZnONTs

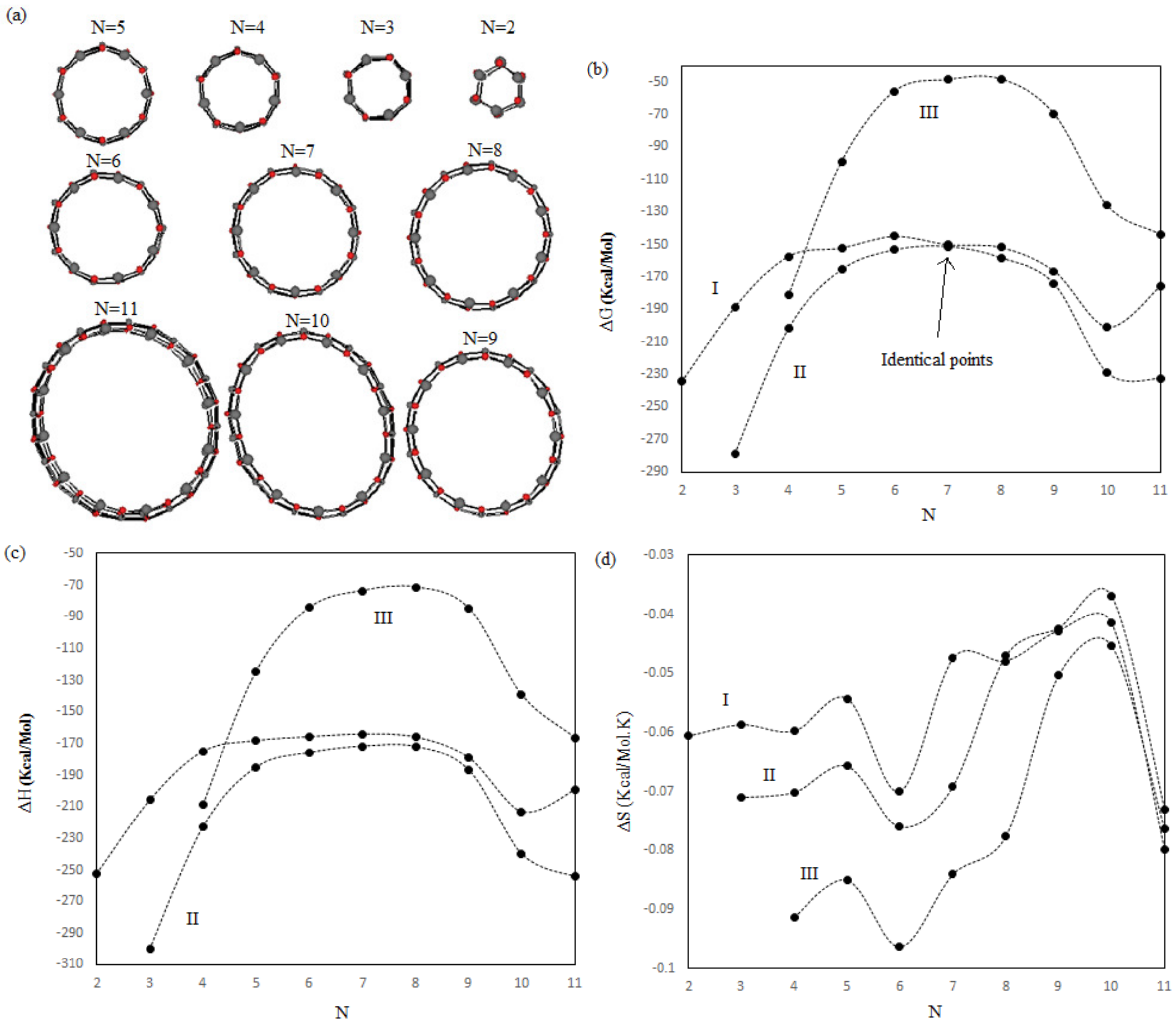

Figure 5. *Gibbs free, enthalpy and entropy as a function of the ZnO nanotubes diameters with three different sizes of the added parts (I, II and III).*

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