

## **First-Principle Investigation of The Alkali Metal Interactions With MgO Armchair -Nanotubes**

Aqeel Mohsin Ali

Molecular Physics Group Laborotary (MPGL), Department of Physics, College of  
Science, University of Basrah, Basrah, Iraq. E-mail: [aqeel.ali@uobasrah.edu.iq](mailto:aqeel.ali@uobasrah.edu.iq).

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### **Abstract**

Encapsulation inside and adsorption of Lithium alkali metals (Li) on the surface of magnesium oxide armchair - nanotubes (MgONTs) with different diameters ( $3\times 3$ ,  $4\times 3$ ,  $5\times 3$ ,  $6\times 3$ ,  $7\times 3$  and  $8\times 3$ ) was investigated by using density functional theory. According to the obtained results, the adsorption on the oxygen site of tube surfaces with adsorption energies with energies in the range of  $-0.93$  to  $-1.11$  eV are most stable than the encapsulation complexes in the range of  $-0.51$  to  $-0.99$  eV. Energy gap (Eg) of the nanotubes dramatically decreases upon the encapsulation / adsorption of the alkali metal, resulting in enhancement of their electrical conductivity. The order of energy gap decrement caused by the metal encapsulation / adsorption is as follows: adsorption > encapsulation. Li - MgONTs are photoactives and they have high values of oscillator strengths. The results suggest that the MgONTs were transformed from semi - insulator to semiconductor upon the alkali metal encapsulation / adsorption. Increasing the tube diameter, the adsorption energies of the MgONT-Li complexes are stable and the encapsulation energies of the alkali metal are decreased.

### **المستخلص**

أجريت دراسة نظرية لحالة أحتواء أو أمتزاز ذرة الليثيوم في الأنابيب الصغيرة من مادة أوكسيد المغنيسيوم ذو الحلقة السداسية وبأصاف أقطار مختلفة ( $3\times 3$ ,  $4\times 3$ ,  $5\times 3$ ,  $6\times 3$ ,  $7\times 3$  and  $8\times 3$ ). أجريت الدراسة بالأعتماد على نظرية دالة الكثافة. بينت النتائج النظرية أن عملية الأمتزاز فوق ذرة الأوكسجين على سطح الأنابيب وبطاقات تتراوح بحدود  $-0.93$  to  $-1.11$  eV كانت أكثر أستقرارا منها في حال الأحتواء ذات طاقات بحدود  $-0.51$  to  $-0.99$  eV. تنخفض فجوة الطاقة للأنابيب الصغيرة في كلا الحالتين بوجود ذرة الليثيوم مما يحسن خاصية التوصيل الكهربائي. أن الأخفاض في قيمة فجوة الطاقة في حالة الأمتزاز هي أكثر منها في حالة الأحتواء. كانت الفعالية الضوئية في كلا الحالتين عالية وقيم كبيرة لشدة المتذبذب. توضح النتائج وجود حالة أنتقال للأنبوب الصغري من الحالة العازلة كهربائيا الى حالة أشباه الموصلات. تبقى طاقة الأمتزاز مستقرة مع زيادة نصف قطر الأنبوب الصغري في حين تنخفض طاقة الأحتواء

### **I. Introduction**

Nanotubes and nanowires are ideal building blocks for nanoscale electronic and optoelectronic devices.<sup>1</sup> Following the identification of carbon nanotubes,<sup>2</sup> nanotubes, nanowires, and nanoribbons of several other materials have been synthesized and studied experimentally and theoretically, including  $\text{MoS}_2$ ,<sup>3,4</sup>  $\text{GaN}$ ,<sup>5-8</sup>  $\text{AlN}$ ,<sup>9-11</sup>  $\text{AlGaIn}_2$ ,<sup>12</sup> boron,<sup>13-15</sup>  $\text{Mo}_6\text{S}_{6-x}\text{I}_x$ ,<sup>16,17</sup> imogolite  $[(\text{HO})_3\text{Al}_2\text{O}_3\text{SiOH}]$ ,<sup>18,19</sup>  $\text{InP}$ ,<sup>20-24</sup> and the material of the present study MgO although the experimentally studied systems often are thicker than those in theoretical studies. Compared to the crystalline materials, the electrons in nanotubes and nanowires are confined in two dimensions. Their properties can be modified in a more or less controllable way by varying material and / or the structure of the nanotube or nanowire. For

semiconductors, the electronic properties also can be modified through n- / p- type doping.<sup>25,26</sup> Moreover, the nanowires can be modified by incorporating quantum dots into the wire.<sup>27</sup> For nanowires, the growth direction and the diameter provide two additional parameters that can be varied, whereas for nanotubes one has one further structural degree of freedom, i.e., both an inner ( $R_i$ ) and an outer diameter ( $R_o$ ) of the tube. Through their variation, it is possible to change the properties from those of nanowires (vanishing inner diameter) to those of rolled-up sheets (large inner and outer diameters, but small values of the thickness  $t = R_o - R_i$ ).

Using the MgO nanotubes that were synthesized some few years ago as an example, it is the purpose of the present contribution to analyze the dependence of the material properties on the diameters for nanowires and nanotubes.<sup>28</sup> In particular we shall focus on stability, structure, and electronic properties. MgO may crystallize in either the rock salt or the wurtzite crystal structure. For crystalline MgO the rock salt structure is more stable than the wurtzite structure. However, very little is known about the structure of low-dimensional MgO structures like, e.g., clusters, nanowires, and nanotubes.

Recently, Finazzi et al. have systematically investigated experimentally and theoretically the properties of small amounts of alkali metal atoms (Li, Na, and K) deposited on different sites of MgO surfaces.<sup>29</sup> They showed that all of the atoms bind preferentially to the surface oxide anions, but the location of these anions differs as a function of the deposition temperature and the alkali metal. Beheshtian et al. have performed a theoretical study on the adsorption of alkali metal atoms (Li, Na, and K) on the surface of different MgONTs.<sup>30</sup> They showed a semi-insulator to semiconductor transition was seen for MgONTs upon the alkali metal adsorption, and preferable adsorption of the alkali metals on the oxygen atom of the tube surface rather than the Mg site can be attributed to their metal characteristic and therefore having the tendency of losing their valence electron to the electro-negative nonmetallic oxygen. Intercalation and encapsulation of the alkali metals in carbon nanotubes (CNTs) affect the electronic and structural properties of the tubes<sup>28</sup> and show a significant reduction of the work function<sup>31</sup>, resulting to the improvement of the emission properties. Soon after the discovery of CNTs, one of their isoelectronic structures, magnesium oxide nanotubes (MgONTs) were predicted by theoretical calculations<sup>32,33</sup> and then experimentally synthesized.<sup>34, 35</sup> MgONTs have recently attracted great interest due to the development of their synthesis methods and their remarkable properties. Pure MgONTs, as important metal-oxide quasi-one-dimensional nanostructures, are attractive for various applications in catalysis, as an additive in refractory and superconductor products.<sup>36</sup> Beheshtian et al. have shown that the MgONTs can selectively detect NO molecules in the presence of gaseous CO.<sup>37</sup>

Herein, it reported a theoretical study about the encapsulation / adsorption of an alkali metal of Li on the surface of MgONTs with different diameters through DFT calculations. In addition, it have studied structures obtained by rolling up a planar sheet of MgO with an assumed grapheme-like structure with, however, each Mg (O) atom surrounded by three O (Mg) neighbors. The interaction of the alkali metal with the oxide materials is relevant to a wide number of problems and applications and usually changes the electrical and conductivity of the materials. In some cases such as tungsten bronzes this may lead to an insulator-metal transition. It is noteworthy that the addition of alkali metals to the layered materials is essential for the preparation of ionic conductors and new generations of batteries.

The paper is organized as follows. Section II gives a brief description of the computational method, and the results are discussed in section III. Finally, the main conclusions are summarized in section IV.

## II. Computational Methods

It considered different type of structure. Although crystalline MgO is formed from rock salt coordinated atoms, we considered here rolled - up graphene - like sheets with 5-fold coordinated atoms. These structures have the advantage that no dangling bonds occur and have, moreover, been found relevant for nanotubes of similar materials like Si<sup>38</sup> and GaN.<sup>5</sup> Geometry optimizations were performed on different armchair MgONTs including 3 × 3, 4 × 3, 5 × 3, 6 × 3, 7 × 3 and 8 × 3 types and their alkali metal – adsorbed complexes at the spin - unrestricted local density approximation (LDA) level of theory. All of the energy calculations, charge, density of state (DOS) analyses and spectra were done using double zeta (DZ) basis sets with the same functional. In terms of nomenclature, the first number is referred to the numbers of atoms locating at the open end of the tubes and the latter is referred to the numbers of atom layers (Fig. 1).

The definition of the encapsulation / adsorption energy (E) of the alkali metal as follows:  $E = E(\text{Li} / \text{MgONT}) - E(\text{MgONT}) - E(\text{Li})$  where  $E(\text{Li} / \text{MgONT})$  is the total energy of the Li atom encapsulated / adsorbed on the pristine MgONT surface, and  $E(\text{MgONT})$  and  $E(\text{Li})$  are the total energies of the pristine MgONT and the lithium, respectively. By the definition, negative values of E correspond to the exothermic encapsulations / adsorptions. All calculations reported here were carried out using a locally modified version of the ADF electronic structure program.<sup>39</sup>

## III. Results and Discussion

Alkali Metal encapsulation / adsorption on the armchair MgONT. At first, optimized the structure of the pure MgONT as a model. The calculated Mg-O bond length of the tube surface (Fig. 1(a)) was found to be about 1.95 Å and 1.98 Å according to the center and the end of MgONT. A smoothed surface was obtained for the optimized structure; the more electronegative atoms (O atoms) have lied in parallel with the more electropositive ones (Mg atoms). Then, the alkali metal atom Li has been considered to be encapsulated / adsorbed on the outside surface of the MgONTs. Based on our first - principle calculations, the metal atom was exothermically encapsulated / adsorbed on the outside surface of the MgONT with negative E. However, in the bare tube some charges are transferred from the Mg atoms to the O atoms; when Li atom is placed in the vicinity of an O atom of the tube surface it competes with the Mg atoms for giving the electron to the O atom. According to the obtained results, the E values are high. This observation may be explained based on the Pearson's hard - soft acid – base theory (HSAB), states that the soft acids react strongly with the soft bases and in contrary, the hard acids react strongly with the hard bases, when all other factors being equal.<sup>30</sup> The Li atom is a hard acid with smaller size, and is weakly polarizable. Therefore, it tends to interact more preferably with oxygen which is known as a hard base.

Therefore, upon the metal interaction,  $E_g$  of the tube dramatically decreases in the all encapsulation / adsorption cases which would result in an electrical conductivity change of the nanotube according to the equation

$$\sigma \propto \exp\left(\frac{-E_g}{2kT}\right)$$

where  $\sigma$  is the electric conductivity, k is the Boltzmann's constant and T is the temperature.<sup>40</sup> According to the equation, smaller values of  $E_g$  at a given temperature lead

to larger electric conductivity. The largest decrement of  $E_g$  belongs to the case of the adsorption (encapsulation) of Li atom, in which the  $E_g$  reduces by 75% (53%) so that the tube is transformed from semi-insulator to a narrow  $E_g$  semiconductor compound. More inspection of the DOS reveals that in all of the cases the LUMO levels are nearly constant and the HOMO levels shift toward higher energies due to the charge transfer from the alkali metals to the tubes. It is also well known that the change of  $E_g$  influences the nanotube chemical reactivity so that a smaller  $E_g$  typically leads to a higher reactivity. As shown in Table 1, the encapsulation energy is increased by decreasing the tube diameter. This might be due to the fact that upon the encapsulation process, the oxygen atoms have to project in; while the thermodynamic driving force of this phenomenon is higher in the case of smaller diameter tubes because of the larger surface curvature. The results do not show a straightforward relation between the diameter of the studied tube and the change of the  $E_g$  upon the encapsulation process.

In order to consider the influence of metal encapsulation / adsorptions on the electronic properties of the tube, it has drawn the DOS plots for the pristine  $3\times 3$  MgONT and metal encapsulated / adsorbed atoms shown in Figure 2. From the DOS plot of the bare MgONT in this figure 2, it can be concluded that it is a semi-insulator material with a wide HOMO-LUMO gap ( $E_g$ ) of 2.26 eV. As shown in the subplot, the DOSs for the encapsulated / adsorbed lithium configurations have a distinct change near the conduction level compared to that of the pristine tube, so that a local energy level appears after the encapsulated / adsorbed of the metals.

As it can be seen in Figure 2, the alkali metal encapsulation / adsorption induce a local structural deformation to the MgONT; the bond length of Mg-O of the tube surface is significantly increased from 1.95 Å in the free MgONT to 2.04 Å in the Li-adsorbed form, indicating their strong interaction. The latitudinal O-Mg-O angle is changed from 120° to 119°. Further indication of the degree of deformation after the adsorption process is given by the bond reorganization energy ( $E_{br}$ ), calculated as the energy difference between the geometry of the tube after adsorption and the full relaxed one. The calculated  $E_{br}$  is in the range of 0.26 - 0.31 eV, confirming high strength of the interaction.

#### **IV. Electronic Excitation spectra**

The absorption of energy between the valence and conduction bands can to interpret the response and activity of the material toward an electric field, chemical stress and photocatalytic action. Figures 3 to 8, show the oscillator strength as a function of energy of the electronic excitations of pristine and encapsulated / adsorbed Li-MgONTs. The spectra of pristine tubes are presented in the subplots because of their oscillator strengths are very low (in order of  $10^{-3}$ ).

According to this, the pristine tubes are photo-passive and unreactive toward light absorption. Their energy gaps which identified from the excitation spectra have the same values that calculated from LUMO-HOMO gap, and this reflects the property of direct band gap of all these tubes. The encapsulated / adsorbed Li atom shifted the electron excitations toward lower energies, and this enhances the MgONTs photo activity. The absorption thresholds have magnitudes that equal to the LUMO-HOMO gaps.

The oscillator strengths of their transitions are very high values which may predict that these complexes have good photoactivities. Spectra of all the encapsulated / adsorbed Li-

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MgONTs have more broadened than these of pristine tubes. This broadening occurred by the distortion in the bond lengths of Mg-O and latitudinal O-Mg-O angles that caused by the interaction with lithium atom. Also, the Li-MgONTs spectra have many peaks in compared with their pristine tubes which reflect the different inter-nuclear distances of tube surface atoms which induced after lithium atom interaction. The LUMO level distributed over the whole tube complexes, so the different bond lengths cause more than single excitation of HOMO-LUMO transition. According to this, the properties of relaxation emission are expected for these complexes.

### V. Conclusions

A theoretical study has performed on the encapsulation / adsorption of alkali metal atom (Li) on the surface of different MgONTs. Lithium atom prefers to bind the O atom of the tube surface. Upon the metal encapsulations / adsorptions, the  $E_g$  of the tubes considerably decreases in all of the encapsulation / adsorption cases which would result in an electrical conductivity increment of the nanotubes. A semi-insulator to semiconductor transition was seen for MgONTs upon the alkali metal encapsulations / adsorption. By increasing the tube diameter the adsorption energies are stable, while the encapsulation energies of the alkali metals are decreased. The electronic excitation spectra reflect the HOMO-LUMO energy gaps, and they have many transitions for the single HOMO-LUMO transition which related to different bond lengths between tube atoms after Li atom encapsulation / adsorption operations.

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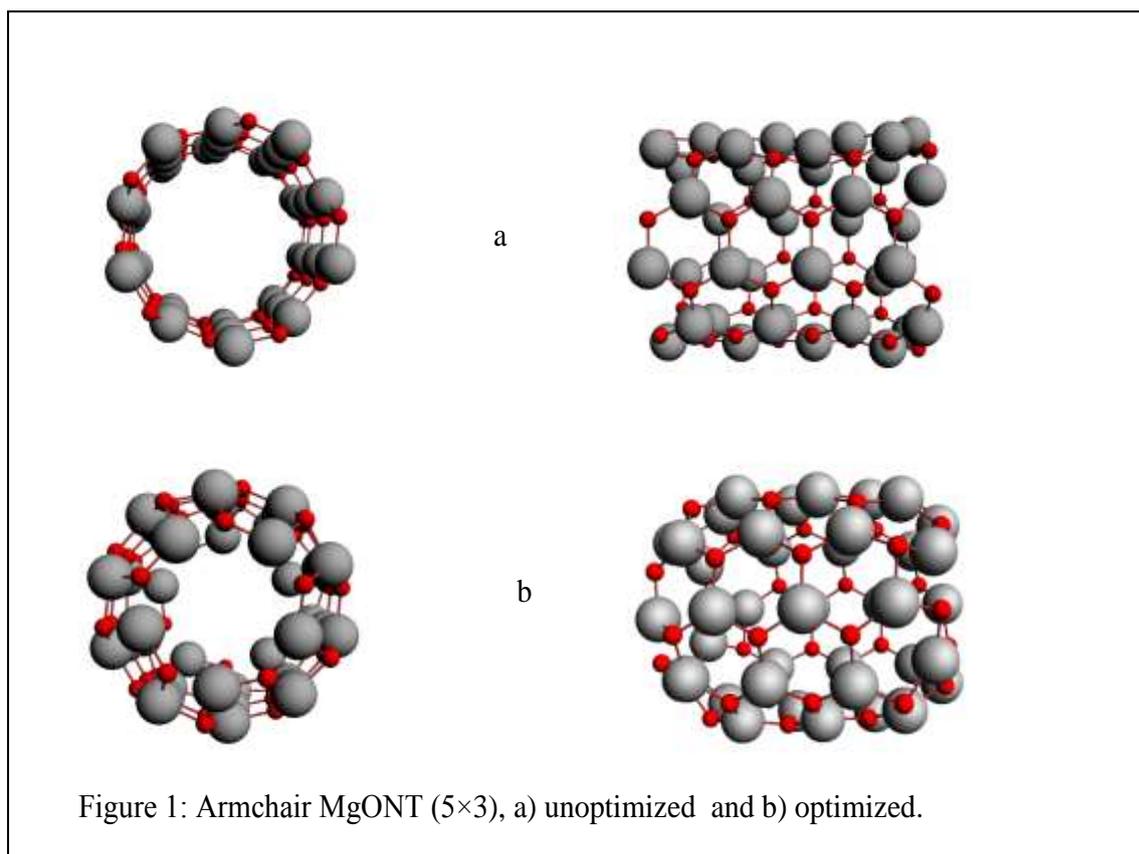


Table 1. Calculated structural parameters and encapsulation/adsorption energies of lithium-MgONT

ube	Li	E (eV)	Q (C)	$E_g$ (eV)	$\Delta E_g$ %
<b>3 × 3</b>	En	-0.99	0.23	0.82	64
	Ads	-0.95	0.19	0.57	75
<b>4 × 3</b>	En	-0.99	0.21	1.14	53
	Ads	-1.00	0.19	0.54	77
<b>5 × 3</b>	En	-0.71	0.21	1.33	53
	Ads	-0.96	0.18	0.63	78
<b>6 × 3</b>	En	-0.54	0.23	1.20	57
	Ads	-1.11	0.19	0.68	72
<b>7 × 3</b>	En	-0.53	0.21	1.20	53
	Ads	-0.95	0.22	0.61	75
<b>8 × 3</b>	En	-0.51	0.22	1.09	54
	Ads	-0.93	0.21	0.30	76

Encapsulation/adsorption energy per atom. Q is defined as the total Mulliken charge on the lithium atom.  $E_g$  HOMO-LUMO gap of the tube after metal encapsulation/adsorption. The  $E_g$  of bare 3 × 5 to 8 × 5 nanotubes is 2.26, 2.4, 2.8, 2.42, 2.53 and 2.42 eV respectively.  $\Delta E_g$ % the percentage change of  $E_g$  (eV) upon the metal encapsulation/adsorption.

