Density Functional Theory Study of Graphene-based Nickel Oxide Composites for Hydrogen Storage

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Hydrogen storage with high gravimetric density (GD) and volumetric density (V D) is a contem-porary challenge in utilizing hydrogen energy. Nano particles are ultimate suitable candidates for this purpose because of the large surface area which serves in storing hydrogen with high capac-ity. Accumulation of these nano-particles is a common problem in nano-catalysis, nano-electronics and hydrogen storage. Based upon its unique properties, graphene based serve as a miraculous materials with signi cant potential as a template to prevent the accumulation of nano particles. In this work, nitrogen-doped-graphene is employed in order to prevent the accumulation of the small NiO clusters. Two types of NiO clusters are examined; namely, $[NiO]_2$ and $[NiO]_3$. The two clusters exhibited considerable ability to store hydrogen; $[NiO]_2$ can store upto $6H_2$ molecules with average absorption energy of 0.27 eV, whileas $[NiO]_3$ can store upto $3H_2$ molecules with average absorption energy of 0.45 eV. The obtained simulated results indicated that though the number of hydrogen molecules stored on $[NiO]_3$ clusters is one-half the value for $[NiO]_2$, yet the adsorp-tion energy is 1.7 times greater. The charge transfer is reckoned to be the governing mechanism underlying this increase.

1. Introduction

Hydrogen has the highest energy per unit mass discovered so far; where 142 MJ of energy can be produced from only one Kg of hydrogen [1]. Such an amount of energy exceeds the petroleum energy by a factor of three [2]. On a volume basis, the density of liquid is 8MJ=L whereas the sensity of gasolin is 32MJ=L. Furthermore, hydrogen energy is clean, cheap and renewable. Hydrogen is not an energy source, rather, it is an energy carrier [3]. It could exist in nature in the form of water and hydro-carbons. It has a low critical temperature of 30 K [4]. Each kilogram of hydrogen in the gaseous phase has a volume of 12 M^3; which creates a space challenge for using hydrogen energy.

Moreover, hydrogen storage is currently a hot topic in contemporary scienti c projects. Fellow researchers are doing their best to develop, improve and enhance hydrogen storage materials. There are two important parameters

that can measure the e ciency of any hydrogen storage, the rst one is the Gravimetric Density (GD), which is de ned as the ration of hydrogen wight (W t%) to the total wight of the storing system, the second one is the Volumetric Density (V D), which is de ned as the ratio of stored hydrogen mass to the whole volume of the system [5]. Hydrogen can be stored in several techniques; which can be divided into several main categories, among them: compressed gas (at high pressure around 800 bar) [6][7], liquid hydrogen (at low temperature about 21K) [8][9], absorbed on materials in covalent or ionic bonds (chemisorption) [10][11] and adsorbed on host materials (physisorption) [12][13].

Metal clusters are more appealing as a topic for detailed studies. Their peculiar features are rather advantageous than the bulk form [14][15][16]. Parameters related to electronic and magnetic properties of metal clusters exceed the corresponding values of bulk structures; presented in a modi ed geometry [17]. Moreover, Ni clusters o er abundant opportunities declared in recent research articles [18][19].

The formation energy, binding energy as well as magnetic moment have been veri ed through several experiments [20] The manipulation of the DFT techniques = methodology through several geometrical modi cation initiated the visualization of the metal structure.

The gas adsorption on materials is based on the physisorption e ect i.e. vdW interac-tion. There are several physical properties governing the gas adsorption processes; such as magnetization, dipole moment and polarization [21].

Moreover, Li doped graphene sheets, as well as carbon nano-tubes, showed that at a 20 bar pressure and room temperature the hydrogen molecules can be adsorbed at 6.5 wt% capacity with doping ratio 1Li/3C. On the other hand, the average binding energy of hydrogen is 0.3 eV; hence the doping ratio changes to 1Li/6C and the capacity changes to 5 wt% [22] respectively. For Al doped graphene, two doping methods are frequently examined; namely adsorption and substitutional techniques. The Al doped graphene can store hydrogen at room temperature with average binding energy of -0.26 eV and capacity 5.13 wt% [23]. On the other hand, Li decorated double vacancy graphene proved to be potentially signi cant in storing hydrogen with capacity of 7.26 wt% and binding energy -0.26 eV [24].

It was experimentally veri ed that nikel-oxide cathode in the Ni-Cd batteries can store hydrogen with ultimate capacity, namely 400 $Kg=m^3$ which is equivalent to 20.1 wt%. These reported values exceed all of traditional methods used for the same purpose. Moreover, this data was obtained from 5-years-life time batteries; which indicates the signi cant potential of NiO for hydrogen storage process. In this study, NiO clusters are utilized in order to comprehend this experimental data.

2. Computational Method

The Density Functional Theory (DFT) [25] is a computational method based on quantum mechanics that is used in several branches of science, namely physics and chemistry as well as technical sciences. Consequently,the DFT became a standard tool in investigating the ground state electronic structure of many-body systems. The DFT can also calculate the band structure of di erent materials, as well as the binding energies of molecules within the condensed phase of materials.

In this study, all calculations have been carried out by plane wave Quantum Espresso package [26] that based on DFT. Spin polarization has been considered in all calculations. The functionals of exchange and correlation have been described by generalized gradient approximation in the scheme of ultrasoft pseudo-potential and P erdew Burke Ernzerhof (PBE) [27].

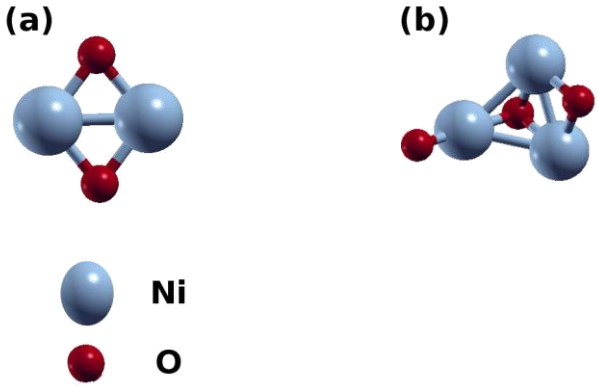

Fig. (1): Optimized geometrical structure of $[NiO]_2$ (a) and $[NiO]_3$ (b) with average Ni-O bond lengths of 1.77 A and 1.80 A for $[NiO]_2$ and $[NiO]_3$, respectively.

3. Results

A. Hydrogen Storage On Nickel-Oxide Clusters

Two types of Ni-O clusters, namely, $[NiO]_2$ and $[NiO]_3$ have been examined. The rst cluster $[NiO]_2$ consists of two Ni atoms and two O atoms; the average Ni-Ni bond length is 2.18 A, the average O O bond length is 2.79 A and the Ni O average bond length is 1.77 A. Moreover, the second cluster $[NiO]_3$ consists of Three Ni atoms and three O atoms with 2.35 A and 1.80 A average bond lengths for Ni Ni and Ni O, respectively (g.1).

Figure (2) represents the density of states (DOS) of $[NiO]_2$ (L.H.S) and $[NiO]_3$ (R.H.S). The DOS shows that NiO_2 has a spin band gap of 0.6 eV and this band gap value is reduced to one-half of its value in case of $[NiO]_3$ because

of creating more states near the Fermi-level. Consequently, $[NiO]_2$ can store upto $6H_2$ molecules with average adsorption energy (E_{ads}) of 0.27 eV and $[NiO]_3$ can store upto $3H_2$ molecules with average E_{ads} of 0.45 eV ; Table (1) shows the corresponding values of E_{ads} per H_2 molecule.

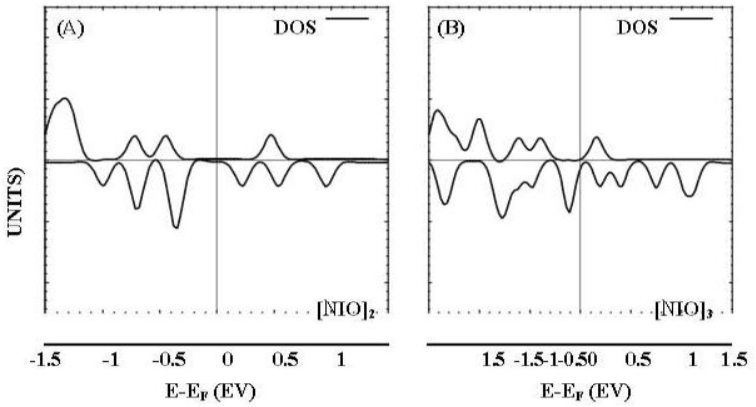

Fig. (2): Density of states (DOS) of $[NiO]_2$ (L.H.S) and $[NiO]_3$ (R.H.S), respectively.

Table (1) : Adsorption energies of H_2 molecules on $[NiO]_2$ and $[NiO]_3$.

E_{ads} (eV)		
nH2	$[NiO]_2$	$[NiO]_3$
$1H_2$	0.74	0.65
$2H_2$	0.80	0.70
$3H_2$	0.03	0.01
$4H_2$	0.03	-
$5H_2$	0.02	-
$6H_2$	0.02	-

The e ect of H_2 molecules on the DOS of $[NiO]_2$ is shown in gure 3 (L.H.S). Upon adding the 1st hydrogen molecule, a 0.5 eV band gap appeared in the DOS. The Fermi level shifted to the right by adding the second H_2 molecule and some states are created below the Fermi energy level. Furthermore, adding more hydrogen molecules did not a ect the DOS due to their low adsorption energies (Table 1).

Though $[NiO]_3$ can store only $3H_2$ molecules with average E_{ads} of 0.45 eV (this energy is 1.7 times greater than the corresponding value of $[NiO]_2$) the number of H_2 stored is 50% less than for $[NiO]_2$. Fig. (4) Represents the DOS of adsorbed $1H_2$ and $3H_2$ on $[NiO]_3$; the Fermi-level shifted to the right and more states are created in the spin up component upon adding the 2nd hydrogen molecule. Adding the 3rd hydrogen molecule caused no signi cant e ect due to its low adsorption energy.

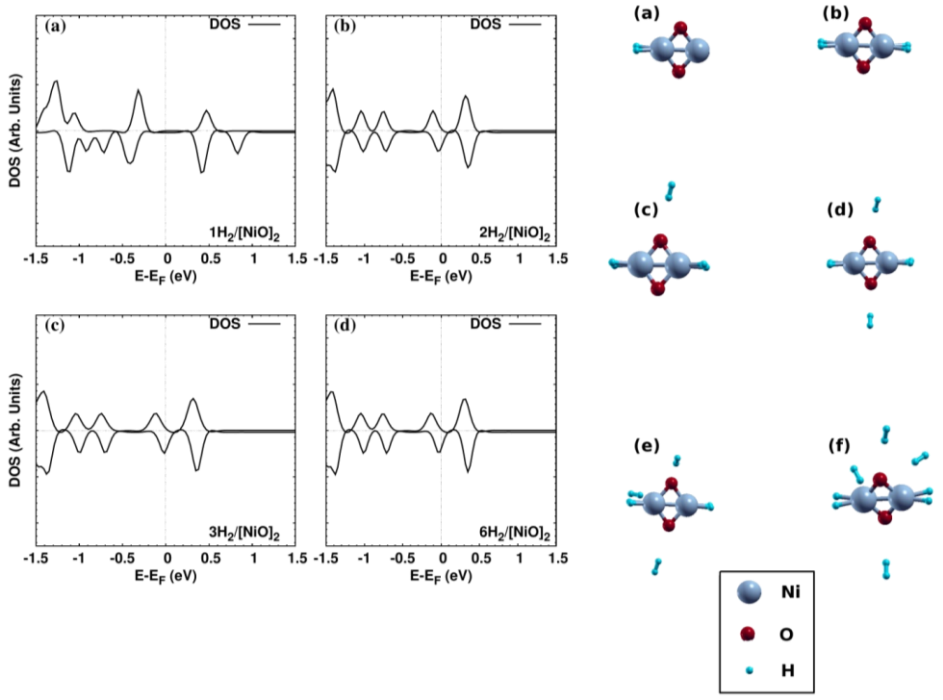

Fig. (3): Density of states (DOS) of $1H_2$, $2H_2$, $3H_2$ and $6H_2$ adsorbed on $[NiO]_2$ (L.H.S) and the Optimized geometrical structure of 1 (a), 2 (b), 3 (c), 4 (d), 5 (e) and 6 (d) H_2 molecules adsorbed on $[NiO]_2$ (R.H.S), respectively.

B. Hydrogen Storage On Graphene-based Nickel Oxide Clusters

In order to prevent the accumulation of small clusters a graphene sheet is introduced. A 4x4 super-cell of graphene with 32 C atoms is adopted; the band structure and the DOS are examined; in satisfactory agreement with the results reported in ref.[28]. Both clusters are adsorbed to graphene sheet with binding energy less that 0.5 eV. For enhancing these binding energies, a substitutional doping of graphene occurred by replacing one carbon atom by a nitrogen atom. Fig. (g.5) represents the DOS of pristine graphene (a) and nitrogen doped graphene (b); in case of N G, a 0.38 eV band gap has been created due to the symmetry breaking upon doping by nitrogen.

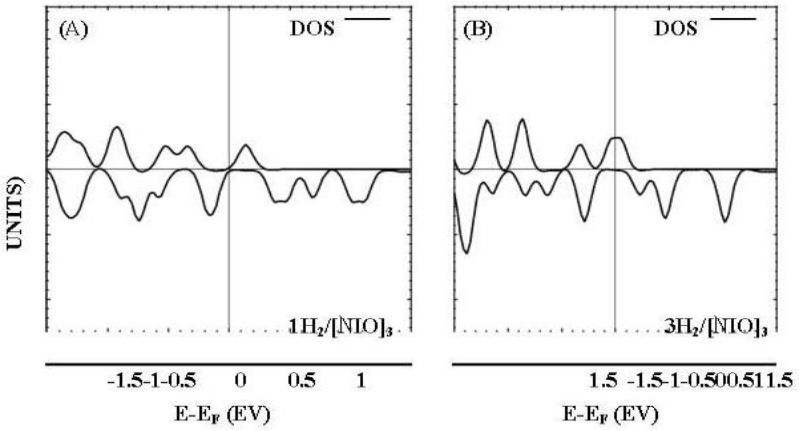

Figure (4): Density of states (DOS) of $1H_2$ (a) and $3H_2$ (b) on $[NiO]_3$.

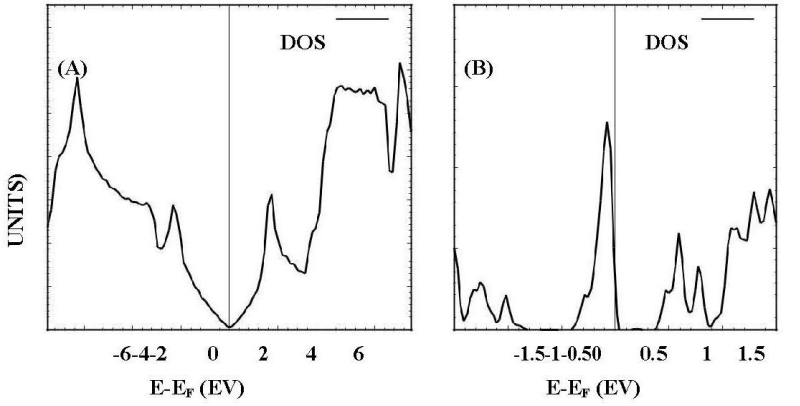

Figure (5): Density of states (DOS) of graphene (a) and graphene doped nitrogen (b).

The binding energies are 1.75 and 0.03 for both clusters $[NiO]_2$ and $[NiO]_3$, respectively. The binding energy of $[NiO]_3$ is too small to prevent accumulation, hence only $[NiO]_2$ is considered in this process. Fig. (6) represents the optimized geometry of $[NiO]_2$ adsorbed on graphene ($[NiO]_2$@G) with average Ni C bond length of 1.84 A; the Ni O average bond length is slightly elongated to 1.81 A. The $[NiO]_2$@G can store upto 4 H_2 molecules with average E_{ads} of 0.33 eV; this value exceeds the corresponding value of $[NiO]_2$ by a factor of 1.22. Table II shows the E_{ads} for each hydrogen molecule; ranging between 0.5 to 0.01 eV. Being a template, the graphene avor appeared in the band structure though it did not contribute in the DOS distribution. The enhancement in the DOS change seems therefore to be signi cantly governed by adding the nH_2 molecules.

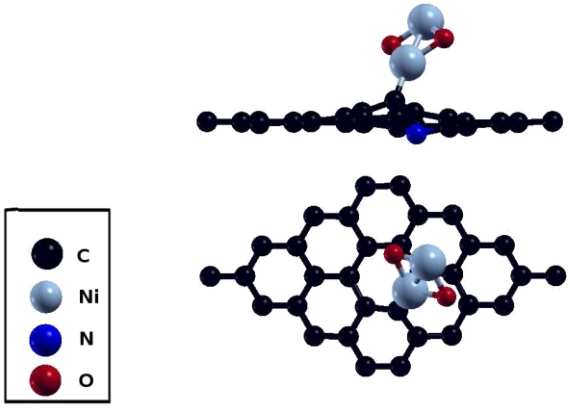

Figure (6): Top and side view of optimized geometrical structure of $[NiO]_2$@G.

4. Conclusions

Two NiO clusters are studied namely, $[NiO]_2$ and $[NiO]_3$; they both have a signi cant potential for hydrogen storage. The rst cluster can store upto $6H_2$ molecules with average absorption energy of 0.27 eV. On the other hand, the second cluster can store upto $3H_2$ molecules with average absorption energy of 0.45 eV. Though this number of hydrogen molecules is reduced to one-half the corresponding value in the case of $[NiO]_2$, yet the ad-sorption energy increased to 1.7 times. In an attempt to form a network of these small clusters and prevent their accumulation, a graphene sheet is utilized as a template; the binding energies of both clusters on the pristine graphene is less than 0.5 eV. A substitu-tional doping of graphene occurred by replacing one C atom by an N atom to form nitrogen doped graphene with concentration of 1N=31 C. The binding energies of the two clusters are 1.75 and 0.03 for $[NiO]_2$ and $[NiO]_3$, respectively. The $[NiO]_3$ clusters accumulate due to their small binding energy, whereas only $[NiO]_2$ clusters take part in the storing process. Moreover, $[NiO]_2$@G has the ability to store upto 4 H_2 molecules with average adsorption energy of 0.33 eV; this value is 1.22 times higher than the corresponding value of isolated $[NiO]_2$. These results indicate that the metal oxide composites on nitrogen doped graphene have a signi cant potential in hydrogen storage, which paves the road for an innovative trend in this research eld.

Table (2): Adsorption energies of H_2 molecules on $[NiO]_2$ and $[NiO]_3$.

E_{ads} (eV)	
nH2	$[NiO]_2$@G
$1H_2$	0.50
$2H_2$	0.69
$3H_2$	0.15
$4H_2$	0.01

5. Acknowledgment

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