Physica E: Low-dimensional Systems and Nanostructures 97 (2018) 239–249

Contents lists available at ScienceDirect

Physica E: Low-dimensional Systems and Nanostructures

journal homepage: www.elsevier.com/locate/physe

Theoretical studies of hydrazine detection by pure and Al defected MgO nanotubes

Alireza Soltani [a,b,*], Mohammad Ramezani Taghartapeh [c], Masoud Bezi Javan [d], Peter J. Mahon [c], Zivar Azmoodeh [e], E. Tazikeh Lemeski [f], I.V. Kityk [g]

[a] Golestan Rheumatology Research Center, Golestan University of Medical Science, Gorgan, Iran
[b] Young Researchers and Elite Club, Gorgan Branch, Islamic Azad University, Gorgan, Iran
[c] Department of Chemistry and Biotechnology, Swinburne University of Technology, Hawthorn, VIC 3122, Australia
[d] Physics Department, Faculty of Sciences, Golestan University, Gorgan, Iran
[e] Young Researchers and Elite Club, Behshahr Branch, Islamic Azad University, Behshahr, Iran
[f] Department of Chemistry, Gorgan Branch, Islamic Azad University, Gorgan, Iran
[g] Faculty of Electrical Engineering, Czestochowa University Technology, Armii Krajowej 17, 42-201 Czestochowa, Poland

ARTICLE INFO

Keywords:
N_2H_4
MgO nanotube
Al defected
Adsorption
UV spectrum
Thermodynamic parameter

ABSTRACT

Density Functional Theory (DFT) and time dependent density functional theory (TD-DFT) calculations using PBE and TPSS functionals have been performed to investigate the effects of the adsorption of hydrazine (N_2H_4) on the structural and optoelectronic features of the pure and Al defected MgO nanotubes. The calculated results for hydrazine/MgO systems reveal no remarkable changes with respect to optical and electronic features of the pure MgO after interactions. Consequently, the Al substitutions with Mg atoms placed in the middle and end sites have shown significant changes in values of the frontier molecular orbital space distribution and ground state dipole moment of states **V** and **VII** after interaction with hydrazine compared to those of hydrazine adsorbed onto pure MgO nanotubes. The quantum molecular descriptor and TD-DFT calculations show that electron transfers from the HOMO orbitals of Al-defected MgO nanotubes to LUMO, LUMO-1 and LUMO-2 orbitals of hydrazine. The study indicates that Al-defected-MgO nanotubes (states **X** and **Z**) as a sensor can facilitate the hydrazine detection over MgO nanotube, while the pure nanotube is not highly sensitive.

1. Introduction

Due to recent advances in nanotechnology, extensive efforts have been devoted to investigate the theoretical and experimental aspects of nano-sized structures. Particular interst is devoed to the optoelectronic features [1,2]. It was shown that the low-dimensional nanostructures are very important for modifications of the electron structured and corresponding optical susceptibilities. Taking the metal oxide nanostructures into account, magnesium oxide (MgO) nanoparticles were extensively studied as functional structures particularly as an inert material with a high melting point, which is suitable as a catalyst for chemical substances and composites. MgO clusters were examined using a couple theoretical [3–8] and experimental [8,9] methods. Ziemann and Castleman introduced a cube-like stable structure [3]. This was followed with several other structures for this metal oxide such as nanorods [10,11], MgO nanobelts [12], metal oxide nanowires [13,14] and nanofilms being considered. Furthermore, new structures such as MgO nanotube bundles [15], single-walled carbon nanotube reinforced magnesia films [16], as well as Ga filled MgO nanotubes [17] as promising candidates for many novel applications. In recent years, several studies have been performed on the structural, electronic and adsorption properties of MgO nanostructures after interaction with single molecules [18–20]. According to literature reports, the state energy of MgO nanotubes varied between 0.12 and 0.66 eV, which is higher than the cage and cubic isomers [21]. Valero et al. and Yang et al. have studied the adsorption of cobalt on MgO nanotubes [22,23].

The name hydrazine was coined by Emil Fischer in 1875 [24]. Hydrazine is a molecule with the formula N_2H_4 and has two amino (NH_2) groups connected by σ bonding as in N—N. Thus these functional groups can freely rotate around the N—N axis [25]. It has found use in a range of different industries due to its specific characteristics [26–28]. Hydrazine takes several forms of sp^3 structure [29] and the three main structures are

* Corresponding author.
E-mail addresses: Alireza.soltani46@yahoo.com, alireza.soltani@goums.ac.ir (A. Soltani).

https://doi.org/10.1016/j.physe.2017.11.021
Received 17 August 2017; Received in revised form 18 November 2017; Accepted 24 November 2017
Available online 26 November 2017

Gauch, Cis and Anti. Among the three structures, Gauch is more stable while Anti and Cis have higher energy, 0.12 and 0.37 eV, respectively. The dipole moment of Cis is larger and Anti does not have a permanent dipole moment. Due to the use of hydrazine in fuel cell technology, the interaction of metal surfaces with hydrazine has occurred in many laboratory studies with particular examples being Ni and Fe [6,30]. Alberas et al. [31] and Grunze [32] suggested hydrazine adsorbs on Pt and Fe surfaces, respectively. It shoud be emphasized that one of restraining factor for all the DFT simnualtons in oxides is an underestimation of energy gap with respect to the experimental data [33]. Another important factor is possible manifestation of the electron-phonon interactions which are not directly take into account the energy broadening and which are typical for different materials [34,35]. These factors shoud be taken into account during analysis for the simulation results and comparison with experiments [36,37]. Herein, we have performed the DFT and TD-DFT calculations to investigate the structural and optical including nonlinear ones, optoelectronic properties of Al-defected MgO nanotubes after interactions with hydrazine using PBE functional of calculations with further calculations using the TPSS functional over the most stable configurations determined by the first calculations.

2. Calculations

All the calculations including molecular dynamic geometry optimization, interaction energies, frontier molecular orbitals and transition state (TD-DFT) studies with pure MgO nanotubes (MgONTs) for Al substituted MgO nanotubes (Al_{subs} MgONT). Crucial is their interactions with hydrazine that have been performed without any symmetry constraints i.e. the symmetry was C_1. The use of reliable and common density functionals (DFT) of the generalized gradient corrected Perdew-Burke-Ernzerhof (PBE) [38] and Tao, Perdew, Staroverov, Scuseria (TPSS) [39] functionals with 6–311++G** basis set were implemented within a framework of Gaussian 09 suite of program [40]. The PBE and TPSS functionals have been shown to be the dependable and accurate when applied in the study of different MgO nanostructures [41,42]. The binding energy (E_b) has been extracted using following formula:

$$E_b = E[(\text{Hydrazine}) - \text{Pure}/Al_{subs}\cdot\text{MgONT}] - \text{E}[\text{Pure}/Al_{subs}\cdot\text{MgONT}] - E[\text{Hydrazine}] \quad (1)$$

where the first part elaborated is the final energy of interaction between hydrazine and the MgONTs, the second part stands for the energy of optimized pure or Al substituted MgONT and the third part shows the energy of optimized hydrazine molecule. The energy convergence was assumed to be 10^{-5} eV for all the optimized structures of MgO nanotube. Corresponding quantum molecular descriptors (QMD), partial density of states (PDOS), space overlap population DOS (OPDOS), electron localization function (ELF), and electron density plots have also been carried out. The space charge distributions were calculated and plotted for all the systems by molecular electrostatic potential (ESP) analysis.

3. Results and discussion

3.1. Structural analysis of N_2H_4

The optimized structural parameters of N_2H_4 which corresponds to a minimum of total energy calculated by PBE and TPSS functionals in the gas phase is summarized in Table 1. The length of N—N chemical bond is found to be about 1.491 Å by PBE and 1.499 Å by TPSS functional, which is in agreement with the theoretical value of 1.484 Å and the experimental value of 1.449 Å [43]. Calculated bond angles for H—N—H (102.6°) and N—N—H (103.8°) by PBE functional and H—N—H (102.8°) and N—N—H (103.5°) by TPSS functional are also close to that of experimental results H—N—H (106.6°) and N—N—H (112°), respectively. Therefore, we have found that the PBE functional is more suitable (due to its better agreement with experimental data) than the TPSS functional with respect to the accuracy of geometry optimizations taking into account the above mentioned underestimation of the energy gap and contribution of the phonons. We have observed that the charges of N and H atoms are −0.755 and 0.377 |e| by PBE functional, whereas is −0.753 and 0.378 |e| using TPSS functional, respectively. The dipole moment magnitude for N_2H_4 is about 0.007 Debye and 0.006 Debye following PBE and TPSS functionals, respectively, which is in agreement with results mentioned by Agusta and Kasai [44,45].

3.2. Structural analysis of N_2H_4 loaded onto MgONT

In this work we used a MgONT formed by 30 atoms and 5 polygons with an overall length of 7.99 Å. MgONT and C_3h symmetry. Two types of Mg—O bonds were found in the MgO nanotube, one with the bond length of 1.93 Å and the second 1.99 Å in parallel with the tube axis, and the diagonal to the tube axis bonds have the lengths of 2.06 Å and 2.05 Å by PBE and TPSS functionals, respectively [46]. Kakkar et al. calculated the average interior Mg—O distances of about 1.975 Å, while the outer ones are almost 0.02 Å longer, i.e., 1.994 Å [40]. The calculated dipole moments of the pure MgO nanotube is about 0.13 Debye and based on the ESP charge analysis, a net charge of 1.2 e is transferred from Mg to O atoms in the tube surface, indicating high ionic nature of the MgONT [47]. We first considered the most possible conformations of hydrazine adsorption in the gas phase on the outer surface of MgONT. The bond lengths and bond angles for both hydrazine and MgONT have not experienced any significant changes during the interaction process as can been seen in Table 1. The binding energy of the first four configurations varied appreciably, starting at −0.94 eV (2.23 Å) for state **II** to −1.39 eV (2.19 Å) for state **III** as the most stable state with the chemical nature of this interaction. Moreover, about 0.31 and 0.22 electrons were transferred from hydrazine to MgONT in states **II** and **III**, respectively. The importance of the bond reorganization energy (E_{br}) for the deformation degree in the geometry of MgONT for the hydrazine adsorption was computed. The E_{br} value for hydrazine adsorbed on the MgONT surface were estimated to be −0.08 (state **III**) and −0.07 eV (state **IV**), forming the electrostatic interaction between the tube's low dimensional surface and hydrazine molecule (See Table 2). Applying TPSS functional to study

Table 1
Computed bond length and angle of hydrazine and MgO nanotube before and after interaction at PBE functional.

Property	N—N/Å	N—H/Å	Mg—O/Å	Al—O/Å	O—Mg—O/°	O—Al—O/°	H—N—H/°
MgO	–	–	1.93	–	95.66	–	–
State I	1.449	1.04	2.14	–	87.69	–	106.43
State II	1.446	1.03	2.07	–	88.92	–	106.81
State III	1.456	1.04	2.00	–	92.59	–	106.72
State IV	1.446	1.03	2.01	–	92.69	–	106.71
State X	–	–	2.15	1.91	81.63	94.17	–
State V	1.44	1.03	2.09	1.89	82.51	91.25	106.03
State VI	1.44	1.02	2.04	1.85	79.21	94.81	108.51
State Z	–	–	2.05	1.87	90.31	96.11	–
State VII	1.45	1.02	2.19	1.81	82.01	102.16	106.83
State VIII	1.44	1.03	2.13	1.82	81.12	97.44	109.83