Investigation of the influence of Br- and As-doped silica single-wall nanotubes: Hartree–Fock method

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Abstract. Synthesis of silica single-wall nanotubes was reported based on single-membered ring (single unit cell) with the element As. These results are supported by performing the Hartree–Fock/6-311G method. The electronic structure, optical band gaps, hardness (η) and softness (S) are discussed. No difference in the computed bond length and angle of doped silica was found. Doping of As and Br atoms leads to a decrease in the energy gap of pure silica. This will make the silica doped with Br and As molecules not require more energy to be excited.

Keywords. Silica nanotubes; HF method; Gaussian model; electronic and structural properties; optical band gaps; hardness.

1. Introduction

Cluster-derived Si nanotubes are encouraging candidates for different parts of forthcoming nanodevices [1]. Si nanotubes' low dimensionality causes quantum effects which are often harnessed to regulate the electronic digital properties [2–7]. This begins the route for most probable uses together with electronic digital devices, for example, nano-scale transistors [8–15], high levels of sensitivity, chemical and natural detectors [16–21] and optoelectronic procedures [22–25]. A number of theoretical investigations have led to the properties of SiNWs as a function of crystallographic development direction, radial measurements, chemical substance doping and surface renovation [2–5,26–36]. Many computational approaches have been formulated to treat structures of many systems containing semi-empirical methods [35], DFT-based limited binding (DFTB) assessments [45,50], DFT theory approximations [4–7,32,35,36], other than many-body disconcertion principles inside the GW methodology [32]. These investigations show that the quantum size of SiNWs smaller than 4 nm prevail in the results. Even it can be expected that by reducing the size of NWs brought about two results together with an increase in the band gap of the material, occasionally, by moving from an indirect to a primary space [3–5,37]. Theoretical studies on silica nanotubes (SiNTs) have recently emerged focusing on single-walled SP2 SiNTs, which form silicon analogues of CNTs [38–40]. The system structure was considered to be chirality-based mostly with the change from metallic to semi-conducting with regard to the chiral vector orientation, which is similar to the reason behind their carbon equivalents [38,39]. Further, it has been shown that a little distorted composition of single-walled locations where in fact the

Si–Si bonds have a relatively enhanced SP3 identity which is more steady compared to the pristine CNT-like composition [39,41–43]. In addition, determining the properties of SP2 SiNTs by using several hydrogenation techniques has been explored [43]. Apart from the SP2 model, prismane-like [44,45] SiNTs made of stacked and covalently bonded square, pentagonal and hexagonal silicon bands have predicted to be metallic in nature. Until now, the nature of Br and As element impurities in SiNTs has not been premeditated by molecular modelling techniques. The objective of this work is to fill the lacuna in this direction. This report shows that it is possible to compute the structure, energy band gaps and mechanical properties of SiNTs plus some of its derivatives that doped with Br and As elements by using the Hartree–Fock (HF) method/6-311G level.

2. Methodology

Silica single-wall nanotube potential predicated for one-membered ring (one unit cell) and its own doping instances by Br and As has been illustrated using quantum computations predicated on the HF method at the 6-311G level. We have based our understanding on molecules, structures and hardness of the examined silica single-wall structure nanotubes predicated on the one-membered band (one product cell) and its own doping instances by Br and As. This was executed by using the Gaussian03/W software package [49] to completely optimize the varieties individually in the gasification stage.

Hardness (η) of the fragment is given as [48]

$$\eta = -1/2(E_{\text{HOMO}} - E_{\text{LUMO}}) \quad (1)$$

Figure 1. Bond lengths of the member ring molecule SiO_2 , without and with interaction of guest molecules Br and As atoms, respectively (bond length in Angstrom).

Figure 2. Bond angles of the member ring molecule SiO_2 , without and with interaction of guest molecules Br and As atoms, respectively (bond angles in degrees).

Table 1. Structural factors for the silica single-wall nanotubes (experimental data [54,55]) and the calculated unit cell ring SiNTs.

Parameter	HF/6-311G	Experimental	Previously calculated
Si–O (1) (Å)	1.670–1.671	1.6034 ^a	1.6056 ^a
Si–O (2) (Å)	1.667–1.668	1.6026 ^a	1.6062 ^a
Si–O–Si (deg.)	176.417–178.552	146.5 ^a	145.8 ^a
O–Si–O (deg.)	101.377–101.866	109.4 ^b	100.84 ^b

^aReference [54].^bReference [55].

and softness (S) as

$$S = 1/\eta, \quad S = -2/(E_{\text{HOMO}} - E_{\text{LUMO}}). \quad (2)$$

Chemical substance hardness simply is the level of resistance to the distortion or polarization of the substances under a small disorder of chemical reaction; more the hardness more the sizable energy gap molecule [47].

3. Results and discussion

The minimum energy structures for doped SiNTs by replacing silicon with Br and As are presented in figures 1 and 2.

From these figures and table 1, it can be seen that Si–O the bond lengths and $\angle\text{O–Si–O}$ or $\angle\text{Si–O–Si}$ bond angles of the studied nanotube rings using the model are close to those of experimental and previous calculation measurements.

It is clear that the geometric structures of Br- and As-doped SiNTs do not present dramatic changes compared with pure silica. To clearly show the guest molecule positions relative to pure SiO₂ rings, the cross-view is depicted in both figures 1 and 2.

Energy gap = the lowest unoccupied molecular orbital – the highest occupied molecular orbital (DE = LUMO – HOMO), in electron volts. The energy gap is an indication of the stability of molecules [50,51]. A small energy gap indicates low stability, because it is energetically acceptable to add electrons to the LUMO and to accept electrons from the HOMO [50–52]. The energy levels of SiO₂ and SiO₂ doped with Br and As are presented in figure 3, respectively.

The molecular orbital density plots for SiO₂ and SiO₂ doped with Br and As, respectively, are shown in figure 4. The frontier orbitals of the member ring molecule SiO₂ are relatively delocalized and spread above the complete surface of molecules. However, the frontier orbitals of the doped molecules become localized clearly because of the incidence of dopant atoms.

HOMO, LUMO, the energy gap DE, hardness and softness are illustrated in table 2.

Figure 3. Energy level diagrams for SiO₂ and SiO₂ doped with Br and As, respectively.

Figure 4. HOMO, LUMO and DE for SiO_2 and SiO_2 doped with Br and As, respectively.

Table 2. Calculations of HOMO, LUMO, DE, η and S for SiO_2 and SiO_2 doped with Br and As, respectively.

Molecule	E_{LUMO}	E_{HOMO}	DE	η	S
SiO_2	0.966	-9.287	10.254	5.127	0.195
SiO_2/Br	0.914	-6.208	7.122	3.561	0.2801
SiO_2/As	0.936	-8.390	9.326	4.663	0.215

For these calculations from table 1 and as shown in figures 3 and 4, we observed that the substitution of Br and As atoms on silica single-wall nanotubes affects the HOMO and LUMO. The calculated energy gaps of all these silica doped with Br and As clusters are reduced compared with the energy gap of pure silica. This means that in any excitation process silica doped with Br and As molecules needs more energy than that of pure silica. It suggests that electrons in all silica doped with Br and As molecules are easier to excite from the HOMO to LUMO levels than in pure silica. One might particularly assume to have a broad selection of new semiconductors because a number of spaces

are formed with regard to the substituents and the range of substitution.

In summary, the stability for each group is decreased by substitution with Br and As atoms. Table 2 shows the same behaviour with respect to hardness and the opposite behaviour for softness.

4. Conclusion

The structure, energy band gaps and mechanical properties were computed for SiNTs, in addition to some of their derivatives that doped with Br and As elements by executing the HF method/6-311G level. We have seen that all obtained results with respect to the geometric structures of pure SiNTs are in good agreement with the related experiment and no change in the computed bond lengths and bond angles of doped silica. The As and Br atoms led to a decrease in the DE of pure silica. The silica doped with Br and As molecules does not require more energy to be excited.

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