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Nanowire versus nanotube: A quantum mechanical approach to some ZnO nanostructures and Cu/ZnO surface

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ABSTRACT

Density functional theory with 6-31G basis set has been carried out in order to determine the geometric and electric structure of small ZnO nanostructures at room temperature. The calculations were done on ZnO nanowires and single-walled nanotubes with n atoms per periodic unit, where one periodic unit is made up of two hexagonal ZnO layers. The calculations show that, for small n , a single walled nanotube has lower energy than a nanowire but when the larger wire, have lower energy than SWNT. Also for large size of nanostructure the growth of nanowires in the z direction is more favorable than other x direction or x - y plane. Charge distributions of ZnO nanowire with 48 atoms are calculated, while top site adsorptions of Cu atoms on Zn or O atoms on the ZnO surface are considered. Optimized distances, charge transfers and binding energies associated with both types of adsorption processes are calculated. The interaction energies corrected by basis set super position error (BSSE) with the same level of calculation. © 2013 Trade Science Inc. - INDIA

KEYWORDS

Zinc oxide;
Nanowire;
Nanotube;
Hexagonal;
DFT calculation.

INTRODUCTION

Zinc oxide (ZnO), as an important functional oxide, is a direct wide band gap (3.37 eV) semi conducting and piezoelectric material having many useful properties, such as optical absorption and emission, conductivity, piezoelectricity, photo catalysis, and sensitivity to gases^[1-3]. Therefore, a large number of publications have been reported for the synthesizing of ZnO nanostructures with various shapes (nanowires, nanobelts, nanorings, nanotubes, nanodonuts, nanopropellers, etc.)^[4-7]. Among these various ZnO nanostructure, in the past few years have witnessed numerous reports of the synthesis of one dimension (1D)

ZnO nanomaterials; much current activity is directed toward achieving further decrease in nano crystal size, controllable and selective area growth, and the formation of aligned, high aspect ratio arrays of such nanostructures^[8-10].

In recent years, the combinations of increased computer power and improvements on the computational methods have allowed researchers to address, from first principles, very complex problems. Theoretical description of the non polar ZnO surface^[11-18] and adsorption of different molecules on this surface have been reported in the literature^[19-23]. Cu/ZnO based catalysts have received much attention due to interest in industrially important processes. A preliminary condition for a more

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extensive understanding of catalytic reactions on this surface is to unravel the details at an atomic scale. Taking advantage of these new developments we have carried out this theoretical work in order to investigate the following aspects: (i) determination of the structural properties and energy stability of some nanostructures of zinc oxide at the B3LYP/6-31G calculation level, and (ii) exploration modes of the Cu atom to simulate the Cu/ZnO surface. This provides a new guideline for making new one dimension nanostructure.

THEORETICAL SECTION

Computational details

(a) *Ab initio* molecular orbital calculation

All calculations were performed using the Gaussian 2003^[24]. The energies and geometries of all nanostructures were calculated and optimized by performing DFT calculations using the Beckes's three-parameter hybrid non-local exchange functional^[25] combined with the Lee-Yang-Parr gradient corrected correlation functional^[26], B3LYP, of which the most successful one is based on the hybrid functional method^[27]. The 6-31G basis set was employed for geometry optimization and energy calculation. Full optimizations of all the compounds studied without any symmetry constraint. The interaction energies were calculated at the same level and corrected with zero-point vibrational energies (ZPEs) and the basis set superposition error (BSSE) using the Boys-Bernardi counterpoise technique^[28]. The POP = NBO key word is used for a full natural bond orbital analysis spin density and atomic charge assignments^[29].

RESULTS AND DISCUSSION

Optimization of nano tubes and nanowiers

The studied nanowires are fragments of wurtzite ZnO, cut along the (001) axis with period c . The optimized model of ZnO nanowires and single walled nanotubes with n atoms per periodic unit, where one periodic unit is made up of two hexagonal ZnO layers, Figure 1. The first nanowire with 12 atoms per unit cell and C_{3v} point group is also the first nanotube. The second nanowire (two honeycomb units, 20 atoms per cell)

with the C_{2v} point group is the starting point for the third nanowire and so on. To making the nanotube, we near two unit cells to each other in the z direction and optimize this two layers system. The released energy is about 11 kcal/mol that related to electrostatic interaction between Oxygen and Zn atoms. This method is continuing until 48 atoms. The result of the our calculations indicate that the nanowire with 48 atoms and C_{3v} point group is about 15 Kcal/mol more stable than the nanotube with the same number of atom and same point group. The relative energies of relaxed nanowires and nanotubes are plotted in Figure 2. As this Figure shows for ZnO nanostructures (≤ 36 atoms), the SWNT is energetically more stable than nanowire form. But large size of nanowire is more stable than nanotubes. This can be understood if we view ZnO bonds as covalent. The wurtzite ZnO crystal has σ bonds made from sp^3 hybrid orbitals. Small nanowires have dangling bonds on the surface that increase the energy. In the nanotube, π bonds resulting from sp^2 hybridization will form, lowering the energy. As the wire grows larger, the fraction of surface dangling bonds decrease and the fraction of saturated sp^3 σ bonds increases, so the wire will eventually have lower energy than the SWNT. These results are in agreement with Shen et al. DFT calculations^[30].

Larger ZnO nanostructure

The reaction pathways for the construction of nanostructure with 144 atoms from nanowire with 48 atoms have been shown in Figure 3. Comparisons between the stability energy of different nanostructures have been presented in TABLE 1. As the results indicate the "a path" is the most favorable pathway to form a nanostructure with 144 atoms. Since the growth of ZnO nanowire in the z direction lead to nanostructure with seven parallel nanotubes, A structure, that is 20 kcal/mol and 28 kcal/mol more stable than C and B nanostructures respectively with the same of atoms, Figure 3.

Cu/ZnO

Two models of Cu/ZnO surfaces, depicted in Figure 4, have been considered at the B3LYP/6-31G computational level. In "1" and "2" at full coverage, Cu atoms are located on top of Zn and O atoms belonging to one of the two sides of the nanowire with 48 atoms,

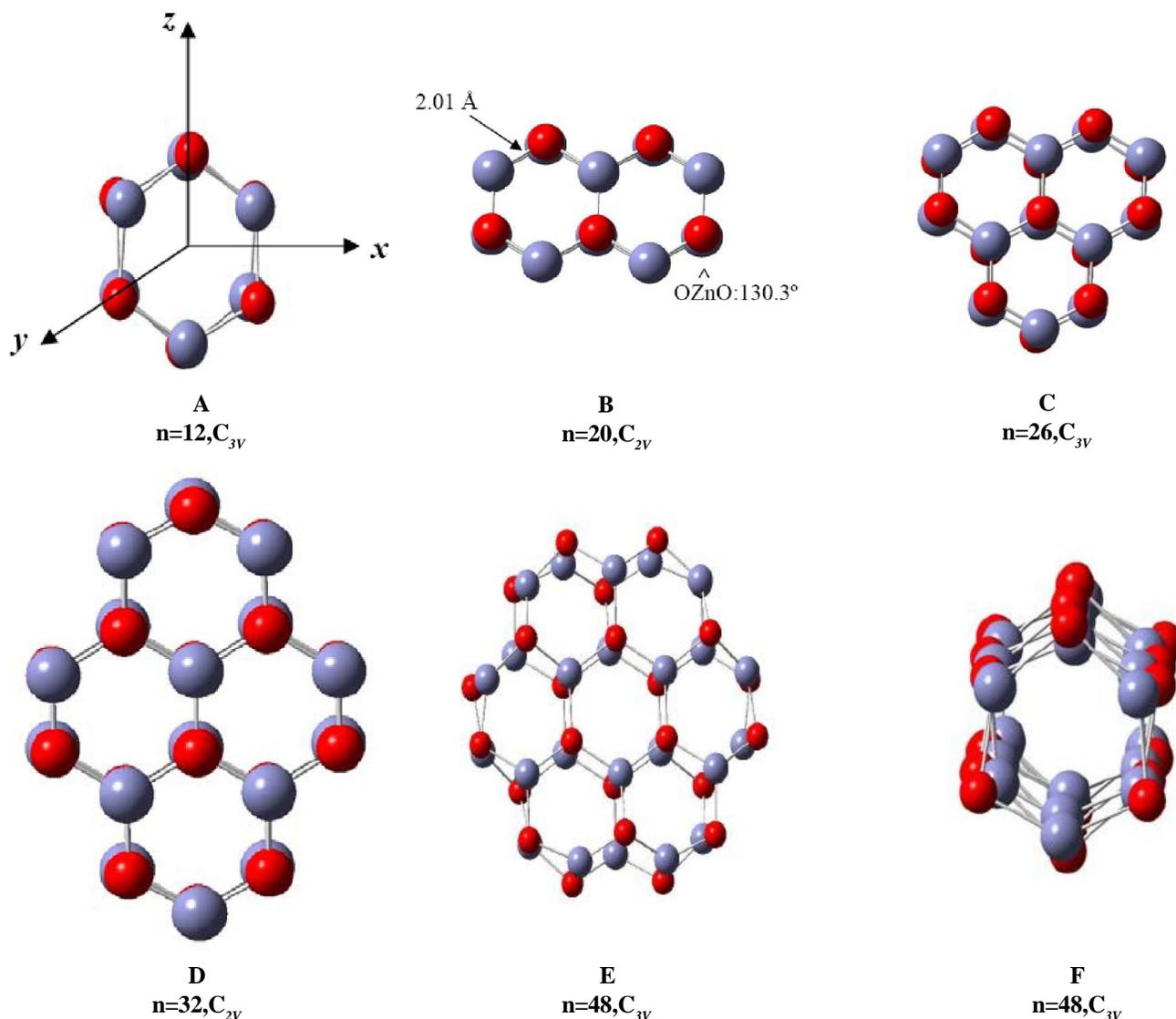


Figure 1 : Optimized structure of nanowires, A-E, and nanotube, F, The purple balls represent Zn atoms, and red balls represent O atoms.

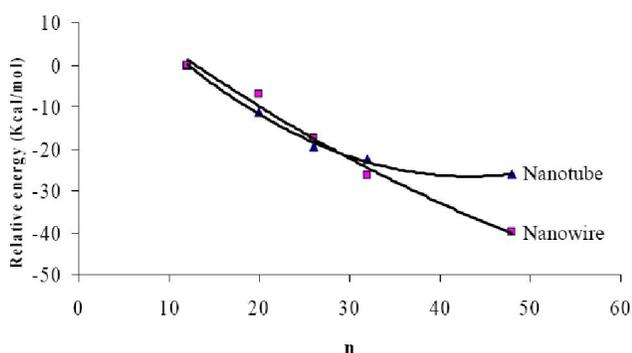


Figure 2 : Relative energy for SWZONTs and nanowires from DFT results.

respectively. In these processes, the ZnO surface remains unchanged at the previous relaxed geometry. This procedure has been employed by Person and

Ojamäe^[31], Minot et al.^[32] and Beltrán et al.^[33] on related systems with acceptable results. The optimized Cu-Zn distance is 2.26 Å in the system a while the distance Cu-O of the system b is 1.98 Å, “2” being energetically favorable, by 9.81 kcal/mol, with respect to “1”. The binding energy, BE, has been estimated by the following equation:

$$BE = -[E(\text{Cu/ZnO}_{\text{nanowire}}) - (E(\text{ZnO}_{\text{nanowire}}) + E(\text{Cu}))]$$

Here, $E(\text{Cu/ZnO}_{\text{nanowire}})$, $E(\text{ZnO}_{\text{nanowire}})$ and $E(\text{Cu})$ represent the total optimized energy (heat of formation) of the $\text{Cu/ZnO}_{\text{nanowire}}$, $\text{ZnO}_{\text{nanowire}}$, and Cu atom, respectively.

The computed binding energy have been corrected for basis-set superposition error (BSSE) using the coun-

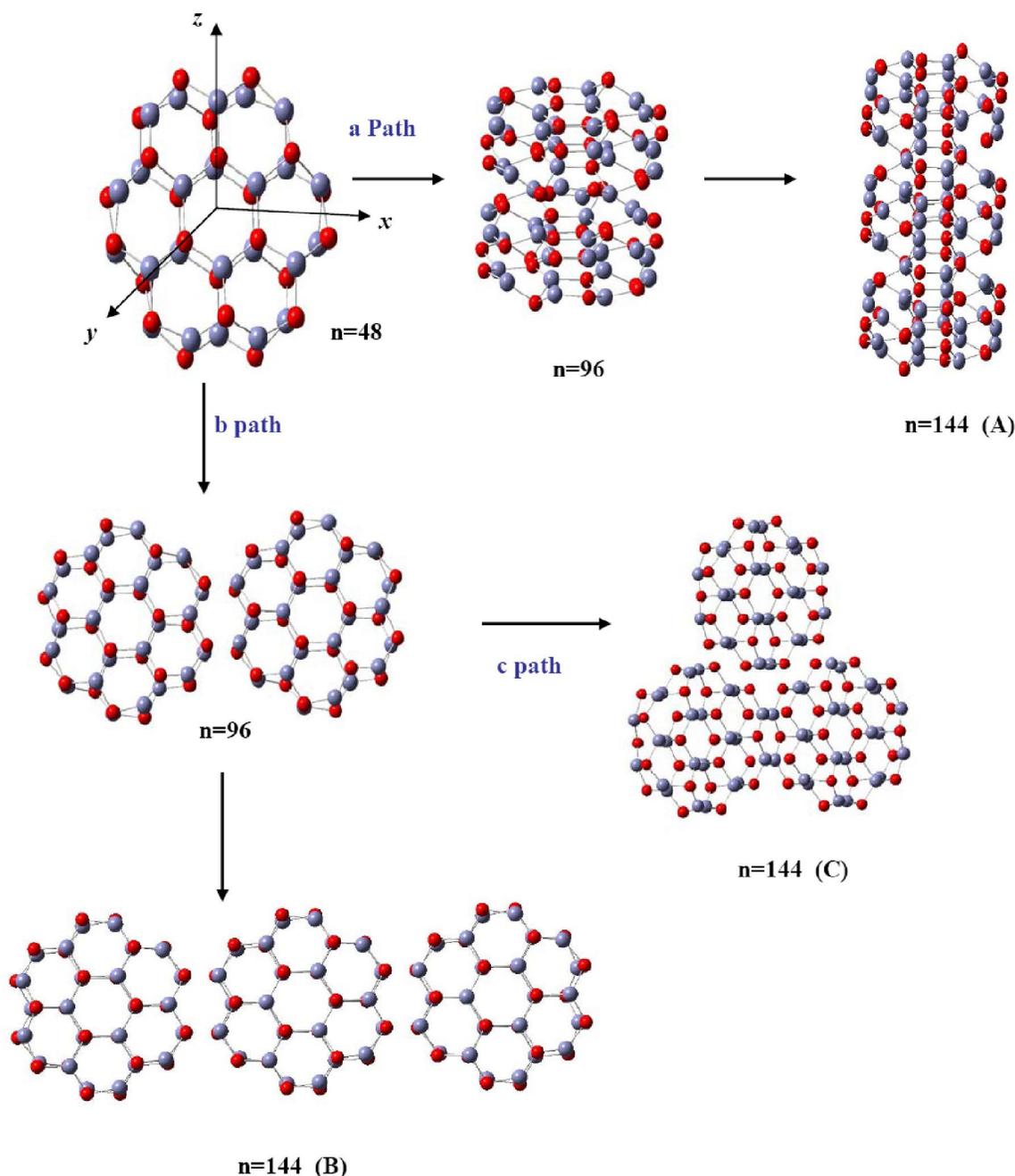


Figure 3 : The optimized structures of different nanostructures of ZnO with 144 atoms from three paths.

TABLE 1 : Stability energy between different nanostructures of ZnO from A, B and C paths.

ΔE (Kcal/mol)	A path	B path	C path
$\Delta E = E_{(n=96)} - 2E_{(n=48)}$	21.65	7.23	
$\Delta E = E_{(n=144)} - 3E_{(n=48)}$	43.72	15.21	23.70

terpoise method.

Both systems 1 and 2 render exothermic adsorption energies and the corresponding values are: -46.30 and -47.75 kCal/mol, respectively. Now the binding

energies differ by only 1.45 kCal/mol.

The result of NBO charge calculation of ZnO nanowire with 48 atoms shows the local average charges on Zn and O atoms is +0.65 and -0.65 respectively. Also the analysis of NBO charge distributions indicates a charge transfer from Cu to surface, with similar values of charge transfer for both types of interactions, -0.265 and -0.232 for system 1 and 2 respectively. This excess of charge is mainly gathered by Zn atoms of surface. This result is consistent with the Muliken analysis

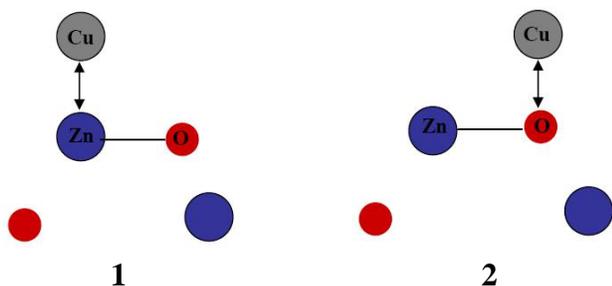


Figure 4 : Schematic view of the two models for simulating the adsorption of Cu on the ZnO surface. Model1, Cu on Zn center and model 2, Cu on O atom of ZnO surface.

previously reported^[34].

COCLUSION

In contrast to the large body of the experimental work in recent years on the different ZnO nanostructures, little attention has been paid to the theoretical investigation of this important field in nanotechnology. In this study an ab initio density functional theory method was employed to study the non polar ZnO nanowires and nanotubes. The results of present calculations show that, for 1D ZnO structures ($d \approx 36$ atoms), the SWZONT is energetically more favorable than nanowire form, but as the wire grows larger, the nanowires will have lower energy than the SWNT. For the large size of nanostructure until 144 atoms the growth of nanowires in the Z direction to form seven parallel nanotubes is about 20-28 Kcal/mol more stable than the other nanostructures. Also full coverage of Cu atom on O positions, system 2, is slightly more energetically favorable than the full coverage over Zn atoms, system 1, of the ZnO surface, and the charge transfer process from Cu atoms to the ZnO surface is centered on the Zn atoms.

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