International Journal of Nanoelectronics and Materials
Volume 11, No. 1, Jan 2018 [33-42]

The Electronic Transport Properties of CuO and Zn Doped CuO Nanotubes

L.Muthaiyan[a], S. Sriram[b] and D. Balamurugan[a,b]*

[a]*Functional Nanomaterials Lab, Centre for Nanotechnology and Advanced Biomaterials (CeNTAB), SASTRA University, Tirumalaisamudram, Thanjavur 613401, India*
[b]*School of Electrical and Electronics Engineering, SASTRA University, Tirumalaisamudram, Thanjavur 613401, India*

Received 17 May 2017; Revised 12 June 2017; Accepted 15 Aug 2017

ABSTRACT

The electronic transport properties of cupric oxide (CuO) armchair and Zinc (Zn) doped CuO armchair nanotubes were studied using density functional theory (DFT) based on non-equilibrium Greens function method (NEGF). In addition, the adsorption effect of ammonia (NH_3) molecules of undoped and Zn doped CuO nanotubes were also studied. The electronic transport properties were studied in terms of density of states (DOS) and transmission spectra of the respective structures. From the obtained results, Zn doped CuO showed enhanced transport properties than the undoped CuO nanotubes due to the 'd' orbital overlapping. Similarly, the NH_3 adsorption on the Zn doped CuO has enhanced the current flow through the device and confirms the adsorption process.

Keywords: Nanotubes; DOS; Transmission; HOMO; LUMO.

1. INTRODUCTION

Nano dimensional materials such as one dimensional (1D) materials are basic the building blocks owing to their potential applications in biomedical engineering, sensors and optoelectronics [1]. Among the 1D nano structures, nanotubes are very important and have specific applications. After the invention of carbon nanotubes by Iijima [2], there is a tremendous growth in synthesis and characterization of nanotubes. Apart from the carbon based nanotubes, inorganic nanotubes are distinct because of their physical and electronic structure properties comprise of 1D and 2D nano structure properties [3]. The nanotubes can also be used as a pipeline in nanofluidic systems and sensor devices. In particular, transition metal oxide based nanotubes are very important since they possess both metal and oxide properties in the nano regime. Morphologically controlled transition metal oxide nanostructures attracted researchers in this decade owing to their electrical, catalytic and optical properties [4]. Cupric oxide (CuO) is a promising material and appropriate for waste water treatment[5], photocatalysts[6], gas sensors[7] and charge storage devices[8]. Nanostructures of CuO are synthesized by many methods such as hydrothermal[9], thermal decomposition[10], chemical deposition[11], and sputtering[12]. In particular, CuO nanotubes are experimentally synthesized by an anodic templating[13], hydrothermal method[14], and thermal oxidation[15]. In order to tailor the properties of CuO nanotubes, theoretical methods are necessary to predict the material properties. Using first principle analysis, Paudel et al.[16]

* Corresponding author information: L.Muthaiyan, S. Sriram, D. Balamurugan. Functional Nanomaterials Lab, Centre for Nanotechnology and Advanced Biomaterials (CeNTAB), SASTRA University, Tirumalaisamudram, Thanjavur 613401, India
School of Electrical and Electronics Engineering, SASTRA University, Tirumalaisamudram, Thanjavur 613401, India
Tel.: +91-9790325839. Email address: *balamurugan@eee.sastra.edu*

reported on the magnetic properties of CuO nano tubes. The present work is aimed to study the electronic transport properties of CuO armchair nanotubes using a two probe system. The effect of substitution of zinc (Zn) on copper (Cu) sites on the electronic transport properties is also studied. In addition, the adsorption effect of ammonia (NH_3) molecule on the CuO and Zn substituted CuO nano tubes are constructed, and their effect on the electronic transport properties are studied, and the results are discussed.

2. COMPUTATIONAL METHOD

The computation was performed on the CuO nanotube structures based on plane wave basis set based density functional theory in Quantum Wise Atomistic Tool Kit (ATK) software package [17]. The device and the electrode geometries were optimized individually and in combined form by conjugate gradient (CG) optimization process. The generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) parameterization was used for exchange and correlational energy function. The wave function expansion was implemented with double zeta plus polarization except for gold electrode atoms. For the gold electrode atoms, triple zeta triple polarized (TZTP) basis function was used in these calculations to better explain the surface states. Brillouin Zone sampling was done using a mesh of 1×1×50 with Monkhorst-Pack scheme. For the transport calculations, the device was constructed with three individual parts namely left electrode, right electrode and the device region (scattering region). The average length of the device was set to be 20Å [18] and which was enough to observe the device properties. The transport property of CuO nanotube devices with and without ammonia adsorption was studied using Non-Equilibrium Green's function (NEGF) [19] technique implemented in Atomistic Tool Kit (ATK). In general, the transmission across a nano electronic device may be influenced by the chemical potential due to the electrode atoms. However, the bias voltage applied to the electrode also made significant changes in the transmission spectrum. The current across the device was calculated using Lanunder-Buttiker formula [20].

$$I(V_b) = G_0 \int_{\mu_R}^{\mu_L} T(E, V_b) dE \quad (1)$$

where G_0 is the quantum conductance of the value $G_0=2e^2/h$ and $T(E,V_b)$ is the probability of transmission under the biased condition, V_b. Transmission energies and the current through the device was calculated using TBTRANS[21] utility in the SIESTA package.

3. RESULTS AND DISCUSSION

3.1 Structures of CuO nano tube devices

Structures of CuO nanotube devices, with Zn substitution and NH_3 adsorption, were shown in Fig. 1 and Fig. 2. The CuO nanotube consists of 94 atoms with an unequal stoichiometry of Cu and oxygen (O) atoms. To study the effect of Zn substitution in CuO nanotube, Zn atoms were placed in Cu atomic positions in the order of 2, 4, 6, 8 and 10. In order to study the effect of NH_3 adsorption on CuO and Zn substituted CuO, nanotubes nitrogen atom in the NH_3 molecule was attached with Cu and Zn atoms in the CuO and Zn substituted CuO nanotubes respectively. The CuO nano tube device was constructed along the (1 0 0) direction attached with gold electrodes on both ends. For the calculation purpose, 27 gold atoms were considered in the electrode region on both sides of the device. The golden electrodes were connected through a sulfur atom with the scattering region on both sides. This was for balancing the potentials of the electrodes and the scattering region atoms since sulfur has high affinity with gold and

scattering region atoms. For the transport calculation, the bias voltage was varied from 0 to 2 in term of 0.2V.

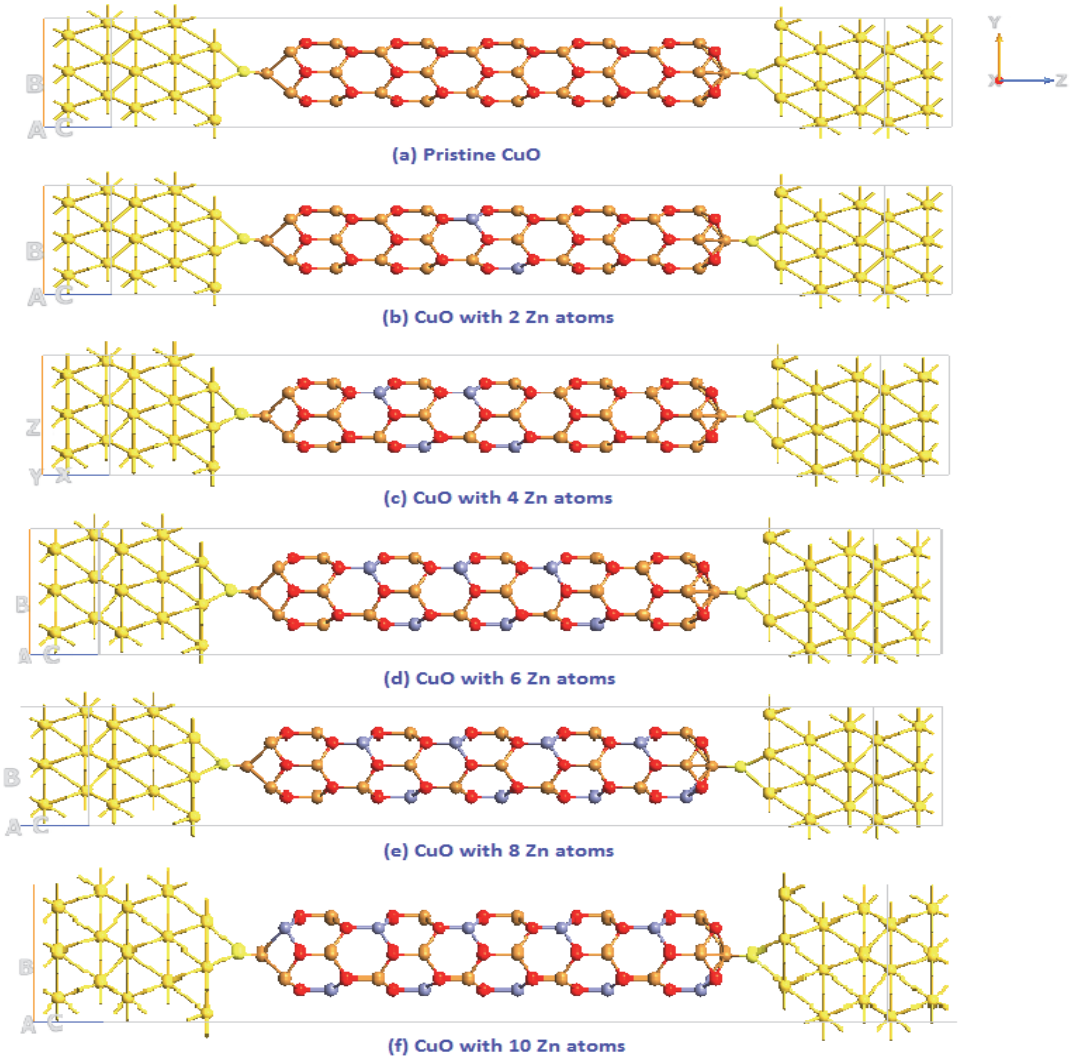

Figure 1. Structures of CuO nano tube devices with Zn substitution

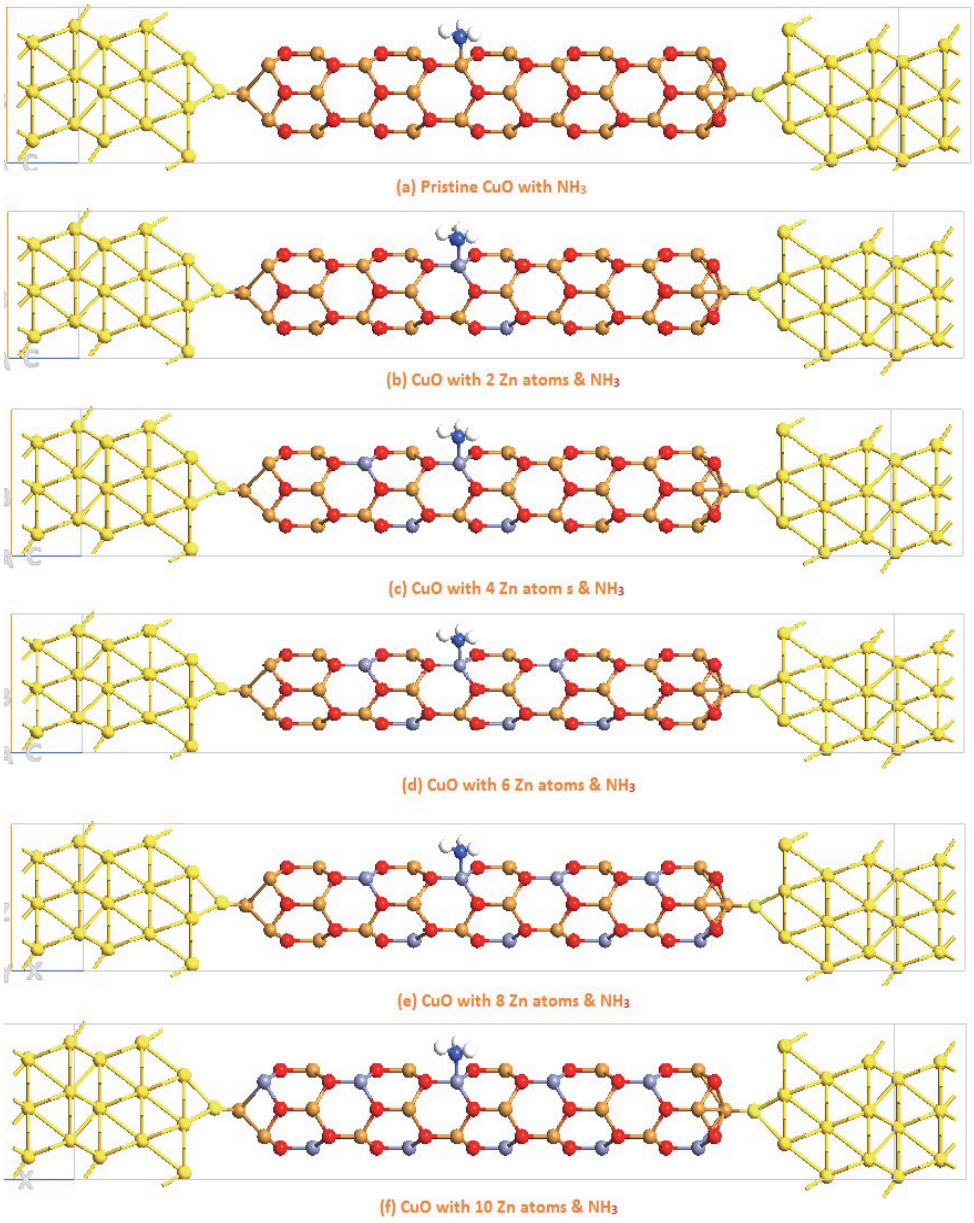

Figure 2. Structures of CuO nano tube devices with Zn substitution and ammonia adsorption

3.2 Electronic Properties of CuO nano tube devices

The electronic properties of the CuO nano tube devices in its pristine form, Zn substituted forms, and NH_3 adsorbed forms were studied in term of its HOMO (Highest Occupied Molecular orbit) and LUMO (Lowest unoccupied molecular orbit) configurations. Usually, the HOMO and LUMO values correspond to the valence and conduction bands. The visualization of HOMO and LUMO of CuO and NH_3 adsorbed CuO nano tube devices were shown in Figure 3.

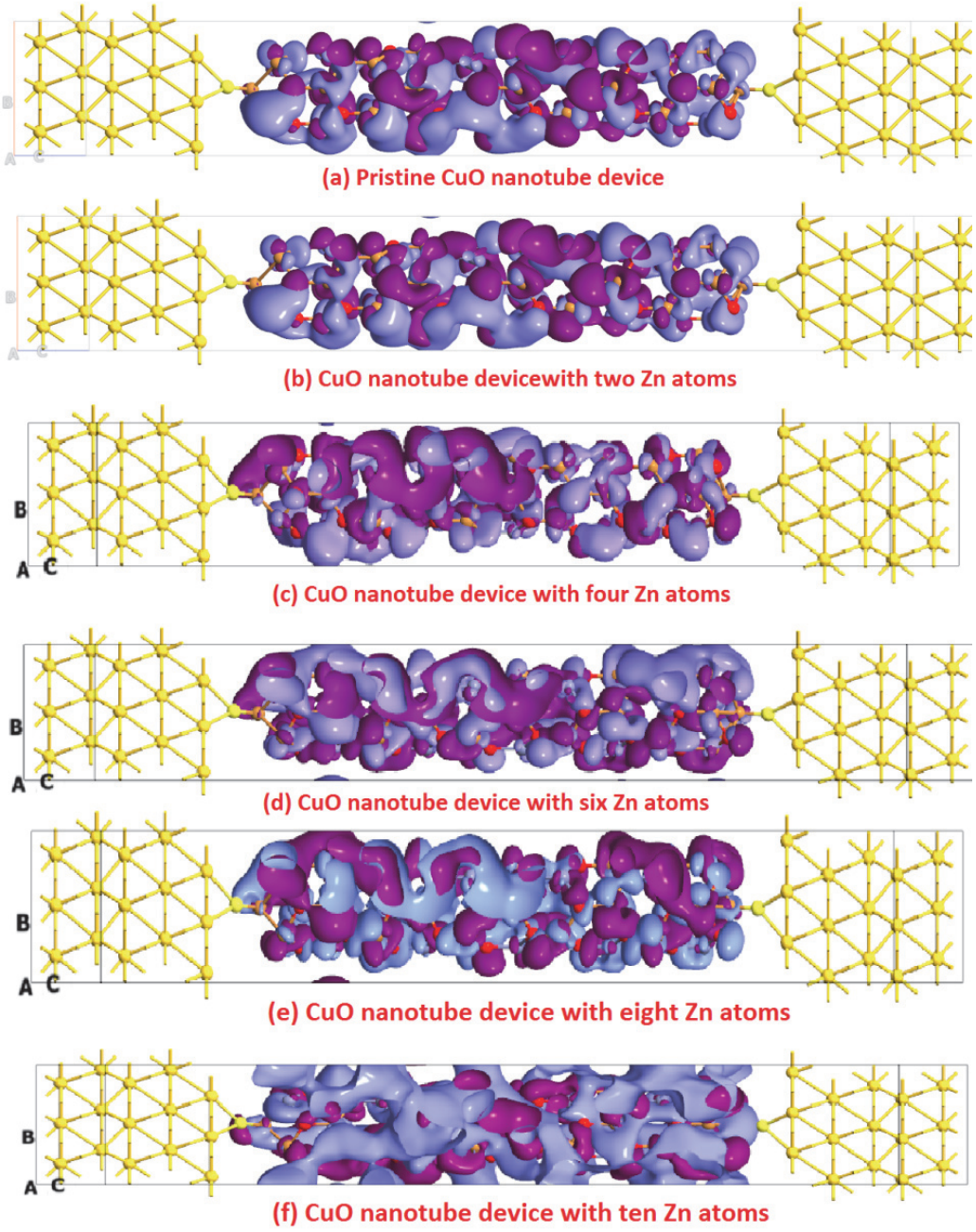

Figure 3. HOMO and LUMO visualization of CuO nano tube devices

In CuO nanotube devices, the HOMO LUMO composed of the valence bands of Cu atom 3d orbital and O atom 2p orbital states. From Fig. 3, it was observed that the HOMO LUMO densities were equally spread throughout the device up to the Zn atom count equal to 8. When the Zn atom count was increased to 10, the total electron density was almost contributed by the HOMO orbitals. This may be due to the substitution of Zn atom 3d orbitals, which appreciably contributes in the molecular orbital of the CuO nanotube. The contribution of 3d orbitals of Zn atoms overlaps with CuO molecular orbit and increases the number of density of states around the Fermi level. This enables easy flow of electrons from the valence band (HOMO) to the conduction band (LUMO).

3.3 Zero bias transport properties of CuO and NH_3adsorbed CuO nanotubes with and without Zn substitutions.

Zero bias transmission spectrums of CuO and Zn substituted nanotubes with and without NH_3 adsorption were shown in Fig. 4. From the transmission spectrum of CuO nanotube devices, the contribution of transmission was fully due to the valence bands of the atoms of the Cu, O and Zn atoms. However, when the number of Zn atom increased above 2, there is a strong peak observed near the Fermi level which fully enables the transmission through the device. In addition, it was noticed that in Fig. 4, the transmission peak intensity near the Fermi level increased when Zn concentration increased. Usually, at zero bias or in an equilibrium condition, the transport was mainly contributed by the chemical potential of the electrodes. However, besides the electrode potential, the influence of the scattering region atoms were in the equilibrium condition. This is strongly due to the influence of the Zn atom 3d orbitals mixed with the molecular orbital of Cu and O atoms.

In the case of NH_3 adsorbed CuO nanotube device, the transmission spectrum possesses the same trend as the CuO nanotube. However, the adsorption of ammonia on the CuO nanotube devices raises the number of peaks below the Fermi level. This confirms the adsorption of NH_3 molecule on the device. Upon the substitution of Zn atoms in the CuO nano tube device, the transmission peak near the Fermi level increases. This enables strong transmission across the device.

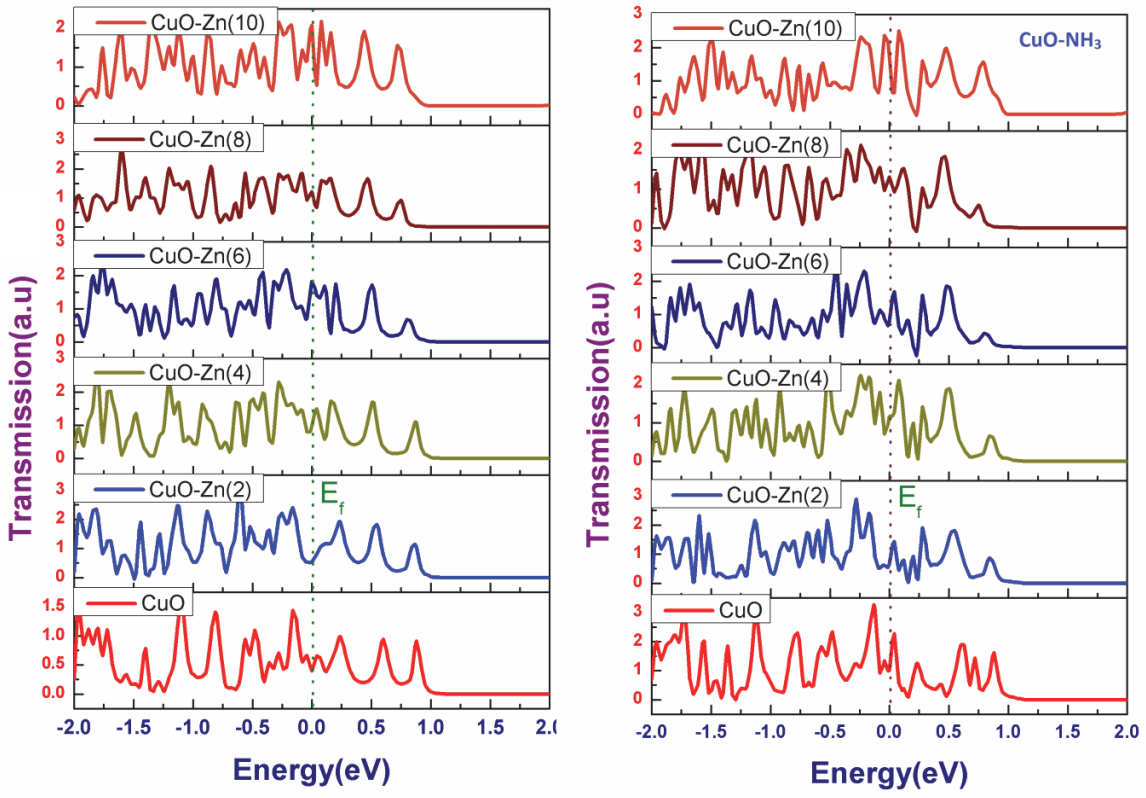

Figure 4. Zero Bias Transmission spectrums of CuO and NH_3 adsorbed CuO nanotube devices

The projected density of states of CuO nano tube devices with and without NH_3 adsorption was shown in Fig. 5. From the figure, it was clear that the number of states originated in the valence band side (below the Fermi level) was more than that of conduction band side due to quasi-bound states formed by the molecular overlapping of Cu and O atoms. However, near the Fermi level, the transmission increased appreciably when the Zn atom substituted on CuO

nanotube device. This is due to the overlapping of Zn 3d orbits with Cu and O orbits. On the other hand, when the NH_3 adsorbed on the CuO nanotube, the valence band states increased. This confirms the adsorption of the NH_3 molecule on the device similar to the work reported [22]. The same trend was observed in the CuO nanotube without NH_3 molecule for Zn atom substitutions. Henceforth, some strong peaks raised above the Fermi level (conduction band) side due to the NH_3 adsorption. The PDOS spectra confirmed the flow of electrons when the Zn atom number was increased as in the transmission spectrum.

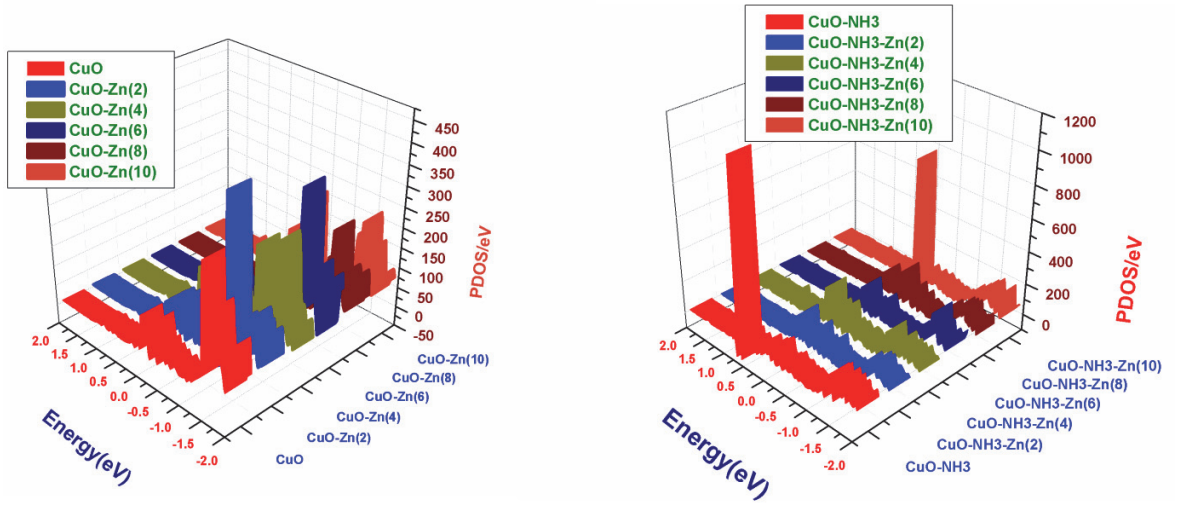

Figure 5. PDOS spectrum of CuO nano tube devices at Zero Bias

3.4 V-I characteristics

Fig. 6 shows that for CuO and Zn substituted CuO devices; the current value increased with the increase in voltage. High peak current was obtained for CuO nano device at 0.8 V. However, when Zn was substituted instead of Cu atom in the device, the current value drastically decreased irrespective of a number of Zn atoms. Tsai et al. [23] reported that the current value of CuO nanotube increased when the Zn content increased. The results in present study contradict the results observed by theoretical calculations. This may be due to the single oxidation state of Zn atom which increases the band gap of CuO nanotube. Referring to Fig. 6, the current value dropped to near zero after the applied bias was 0.8 V. This shows that the coupling between the electrodes and the scattering region was broken. In the case of NH_3 adsorbed CuO and Zn substituted CuO nanotube devices, the magnitude of the current was high compared to CuO and Zn substituted nano tube devices. The reason for the increase in the current was due to the adsorption of NH_3 molecule. Since NH_3 molecule act as a donor, it supplies electron to the CuO nanotubes. Thus, the current through the device was increased. Usually in an adsorption process, when a molecule was adsorbed, if the adsorbent molecule gives the charge to the base material it refers the endothermic process and if the adsorbent molecule acquires the charge from the base material refers to an exothermic process. In this current case, the charge was transferred from the adsorbent molecule to the base material. Therefore, the current increases through the device.

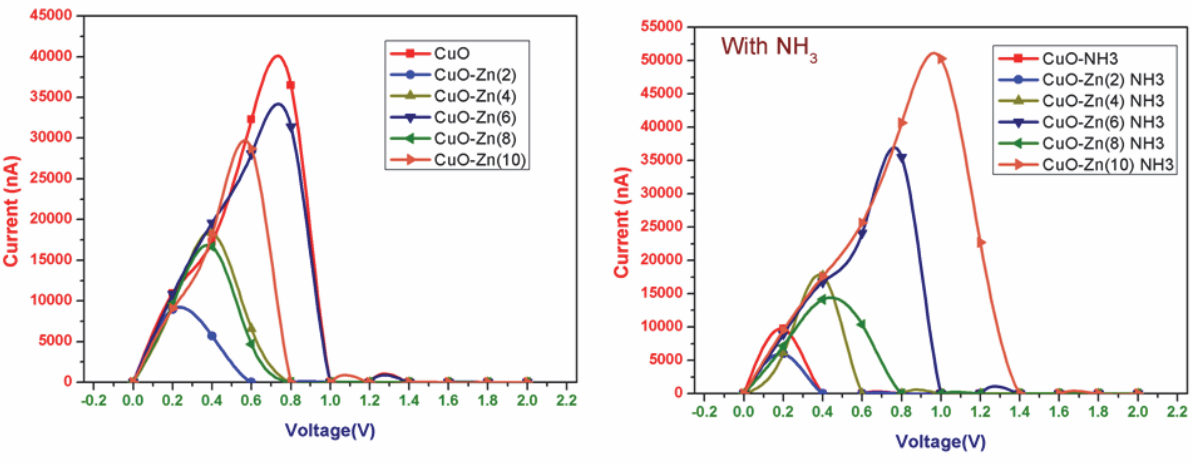

Figure 6. V-I characteristics of CuO and CuO with NH_3 nanotube devices

4. CONCLUSION

Electronic transport properties of CuO nanotube devices were studied using DFT+NEGF formalism. The obtained results show that upon substitution of Zn atom the current and transmission values are decreased. This is regarded as singlet state excitation of Zn atom in the molecule. However, when NH_3 molecule is adsorbed on CuO nanotube devices, the magnitude of transmission and the current values are increased. Moreover, this increase in the current value is identified as the supply of the charge by the adsorbent molecules NH_3 to the base CuO nanotube device. The increased in current confirms the adsorption of the NH_3 molecule on CuO nanotube devices.

ACKNOWLEDGEMENT

The authors acknowledged the management of SASTRA University for providing the cluster computational facility to perform the computational work.

REFERENCES

[1] Qing Yang, Zhiang Guo, Xiaohong Zhou, Juntao Zou, Shuhua Liang.: Ultrathin CuO nanowires grown by thermal oxidation of copper powders in air. Materials Letters.**153**, 128–131(2015)

[2] Sumiolijima, Helicial microtubules of graphitic carbon. Letters to nature.**35**4, 54-58 (1991)

[3] Joshua Goldberger, Rong fan, Peidongyang, Inorganic Nanotubes: A Novel Platform for Nanofluidics. Accounts of Chemical Research.**39**, 239-248(2006)

[4] Q Ahsanulhaq, Jin-Hwan Kim, Yoon-Bong Hahn, Controlled selective growth of ZnO nanorod arrays and their field emission properties. Nanotechnology.18485307, 1-6 (2007)

[5] Vinod Kumar Gupta, Ramesh Chandra, Inderjeet Tyagi, Monu Verma, Removal of hexavalent chromium ions using CuO nanoparticles for water purification applications. Journal of Colloid and Interface Science. **478**, 54–62 (2016)

[6] M. Umadevi, A. Jegatha Christy, Synthesis, characterization and photocatalytic activity of CuONanoflowers. SpectrochimicaActa Part A: Molecular and Biomolecular Spectroscopy. **109**, 133–137 (2013)

[7] S. Bhuvaneshwari, N. Gopalakrishnan, Hydrothermally synthesized Copper Oxide (CuO) superstructures for ammonia sensing. Journal of Colloid and Interface Science. **480**,76–84(2016)
[8] V. Senthilkumar, Yong Soo Kim, S. Chandrasekaran, Balasubramaniyan Rajagopalan, Eui Jung Kim, Jin Suk Chung, Comparative super capacitance performance of CuO nanostructures for energy storage device applications. RSC Advance. 20545-20553(2015)
[9] Tuğbaİpeksaça,b, FigenKaya a, CengizKaya.: Template-free hydrothermal method for the synthesis of multi-walled CuO nanotubes.Materials Letters.**130**, 68–70(2014)
[10] Ping Cui, An-Juan Wang, Synthesis of CNTs/CuO and its catalytic performance on the thermal decomposition of ammonium perchlorate.Journal of Saudi Chemical Society. **20**, 343–348 (2016)
[11] V. Ramya, K. Neyvasagam, R. Chandramohan, S. Valanarasu, A. Milton Franklin Benial, Studies on chemical bath deposited CuO thin films for solar cells Application. Mater Electron. **26**, 8489–8496(2015)
[12] P Samarasekara, N T R N Kumara, N U S Yapa, Sputtered copper oxide (CuO) thin films for gas sensor devices. Journal of Physics: Condensed Matter.**18**, 2417–2420(2006)
[13] Yu Liu, XiaoyuCai, Weidong Shi, Free-standing graphene/carbon nanotubes/CuO aerogel paper anode for lithium ion batteries. Materials Letters.**172**, 72–75 (2016)
[14] Tuğbaİpeksaç ,Figen Kaya, Cengiz Kaya, Template-free hydrothermal method for the synthesis of multi-walled CuO nanotubes. Materials Letters.**130**, 68–70 (2014)
[15] J. T. Chena, F. Zhang, J. Wanga, G. A. Zhang , B. B. Miaoa, X. Y. Fan, D. Yana, P. X. Yan, CuO nanowires synthesized by thermal oxidation route. Journal of Alloys and Compounds. **454**, 268–273(2008)
[16] Sushmita Dandeliya, Rajneesh Chaurasiya, Anurag Srivastava, Magnetism in Zigzag and Armchair CuONanotubes: Ab-Initio Study.Journal of Magnetism and Magnetic. **406**, 8-14(2015)
[17] For all calculations we use Atomistix Toolkit-16.1, QuantumWise A/S (*www.quantumwise.com*)
[18] S.Sriram, V. Nagarajan, R. Chandiramouli.: H2S and NH3 adsorption characteristics on CoO nanowire molecular device – A first-principles study. Chemical Physics Letters. 636, 51–57 (2015)
[19] Neophytos Neophytou, Shaikh Ahmed, Gerhard Klimeck, Non-equilibrium Green's function (NEGF) simulation of metallic carbon nanotubes including vacancy defects. J Comput Electron. **6**, 317–320 (2007)
[20] M. Büttiker, Y. Imry, R. Landauer, S. Pinhas, Generalized many-channel conductance formula with application to small rings. Physical Review B. **31**, 6207(1985)
[21] Pabitra Narayan Samanta, Kalyan Kumar Das, Electronic-Transport Properties of Single-Walled Zigzag SiGeNanotubes. The Journal of Physical Chemistry C, **118**, 18153–18159 (2014)
[22] V. Nagarajan, R. Chandiramouli, First-Principles Investigation on Interaction of NH_3 Gas on a Silicene Nanosheet Molecular Device. IEEE Transactions on Nanotechnology. **16**, 445 – 452 (2017)
[23] Tsung-Ying Tsai, Cheng-Liang Hsu, Shoou-Jinn Chang, Szu-I. Chen, Han-Ting Hsueh, Ting-Jen Hsueh, Enhanced Field Electron Emission FromZinc-Doped CuO Nanowires. IEEE Electron Device Letters. **33**, 887-889(2012)