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A comparative study of the interaction of nickel, titanium, palladium, and gold metals with single-walled carbon nanotubes: A DFT approach

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ABSTRACT

Interactions between transition metal atoms, nickel, titanium, palladium and gold and (3,3), (4,2), (6,0) and (5,1) carbon nanotubes were studied using first principles calculations. The Fermi energy levels of the carbon nanotubes studied were found to increase during interactions with the transition metal atoms. Amongst the four metals, gold atom was found to have an enhanced interaction with the nanotubes transforming from semiconducting to a conducting tube. Titanium was also found to show similar characteristics to gold only when the atom was placed in the middle of the carbon nanotubes. Nickel and palladium atoms interactions did not affect much the electronic properties of the carbon nanotubes, with some slight changes in the electronic properties at some specific sites of the nanotubes. It is proposed from this study that, the carbon nanotube-metal interactions could be used as a guide to shed light on the electronic properties of such materials which could become promising engineering materials and revolutionize the electronic industry.

Introduction

The ongoing quest to miniaturize electronic devices in an effort to make life simpler has posed the materials science community with newer challenges each and every day. In an attempt to solve the problem of integration of nanoscale components on an integrated circuit, scientists have resorted to Carbon Nanotubes (CNT) [1,2]. These carbon nanotubes have been one of the major materials under consideration in the field of nanoelectronics, attracting a lot of attention due to their unique electrical [3], thermal, physical and mechanical properties. Depending on their chirality and size of diameter, there exists a vast number of distinct carbon nanotubes with different electronic properties [4]. Semiconducting carbon nanotubes with small band gaps can be applied in CNT-based transistors while metallic semiconductors are useful in interconnect systems [5].

Studies on carbon nanotubes do not end with just the pristine models; recent research work carried out shows that carbon nanotubes exhibit even better properties when interacted with metal atoms [6,7]. A myriad of potential applications include catalytic sensors, fabrication of nanostructures, nanoelectronics [8], nano-electro mechanical systems (NEMS) and spintronics [6] have been proposed. It is also reported [9] that, CNT-metal interactions are essential in the formation of nanowires and by continuously coating the sidewalls of these carbon nanotubes with metals atoms, metallic or superconducting [10] nanowires could be obtained.

An in-depth knowledge and understanding of how CNT-metal interactions alter the electronic properties of pristine carbon nanotubes would prove beneficial to the scientific community and the electronics industry [11,12]. For example, different carbon nanotubes each possessing different electronic properties could be engineered to have si-

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Table 1
Properties of pristine CNT data.

Carbon nanotube	Electronic property	Size of diameter (Å)	Number of atoms	Chirality	Bang gap (eV)
(3,3)	Metallic	4.01	48	Armchair	–
(4,2)	Semiconductor	4.15	56	Chiral	0.04
(5,1)	Metallic	4.32	124	Chiral	–
(6,0)	Semiconductor	4.70	72	Zigzag	0.68

Table 2
Adsorption data of CNTs.

Carbon Nanotube	Adsorption concentration (%)	Fermi energy of pristine CNT (eV)	Range of Fermi energies upon adsorption (eV)
(3,3)	2.04	−2.22	−1.53 to −2.11
(4,2)	1.75	−2.29	−1.09 to −2.01
(5,1)	0.8	2.83	2.75 to 2.98
(6,0)	1.37	−2.11	−0.91 to −1.53

milar electronic properties [5]. Also, such knowledge would be useful in the fabrication of optimal CNT-based devices such as CNT-based field effect transistors [7]. Therefore, the aim of this study is to investigate and compare the electronic properties of nickel, palladium, titanium and gold when interacted with single-walled carbon nanotubes, (3,3), (5,1), (6,0) and (4,2) using first principles calculations.

Model system

In this paper, four different carbon nanotubes, (3,3), (5,1), (6,0) and (4,2) were built using the Virtual NanoLab (VNL 2017.1) software [13]. These carbon nanotubes were chosen because their theoretical diameters are in the range of 4 Å [14]. Details are provided in Table 1 below. A total of sixteen (16) carbon nanotubes were built for each of the 4 different configurations of the carbon nanotubes in which the transition metal atoms; nickel, titanium, palladium and gold, were interacting with each of the carbon nanotube at different adsorption sites on the carbon nanotube hexagonal ring to obtain 64 different CNT-metal atom models. The transition metal atoms interacted with the single walled carbon nanotubes via adsorption and doping. Adsorption onto the carbon nanotube was done, with no replacement of the carbon atoms, at three different sites. The first site was at the top left corner of the carbon nanotube hexagonal ring, the second adsorption site was at the bottom right corner of the hexagonal ring and the last site was in the middle of the carbon nanotube as illustrated in Fig. 1.

Computational methods

The ab initio calculations of the carbon nanotube-metal interactions were performed using Density Functional Theory (DFT) method, with the Local Density Approximation (LDA) as the exchange-correlation functional (XC). The plane-wave pseudopotential method and the ultrasoft pseudopotential were employed in the calculations using the Quantum Espresso software version 5.3 [15]. The ultrasoft datasets (Au.pbe-nd-rrkjus, C.pz-n-rrkjus_psl.0.1, Ni.pz-n-rrkjus_psl.0.1, Pd.pz-n-rrkjus_psl.0.2.2 and Ti.pz-spn-rrkjus_psl.1.0.0) used were obtained from the Quantum Espresso library [13]. The pseudopotential used for the gold had a valence electron configuration of $5d^{10}6s^{1}$. That of titanium and palladium were $3s^{2}3p^{6}3d^{2}4s^{2}$ and $5s^{0.5}4d^{9.5}$ respectively. Also, the valence electron configuration for nickel and carbon potentials were $4s^{2}3d^{8}$ and $2s^{2}2p^{2}$ respectively. The plane-wave cut-off energy was set to 130 Rydberg and a Monkhorst-Pack k-point mesh of $1 \times 1 \times 15$ was chosen for self-consistent field calculations (SCF) and band structure calculations. For non-self-consistent field calculations (NSCF), density of states (DOS) and projected density of states calculations (PDOS), a Monkhorst-Pack k-point grid of $2 \times 2 \times 30$ was used. The charge density of the carbon nanotube-metal models was also calculated using the Xcrysden software, version 1.5.60. [16].

Results and discussions

Electronic properties

Adsorption studies

Four 3d transition metals, Au, Pd, Ti and Ni were considered to be adsorbed onto each of the carbon nanotubes, (3,3), (4,2), (5,1) and (6,0) at three different sites as shown in Fig. 1. The C-Au bond length was determined to be ~2.20 Å. For Pd adsorption, the C—Pd bond length was determined as ~2.15 Å while those of C—Ti and C—Ni bond lengths were calculated as ~2.13 Å and ~1.97 Å, respectively. Table 2

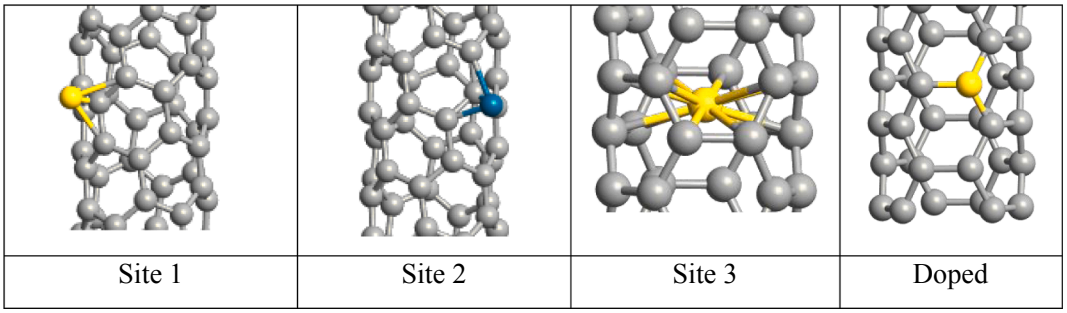

Fig. 1. Different interaction sites for Gold (yellow) and Palladium (blue) metal atoms on a (5,1) CNT and (3,3) CNT. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

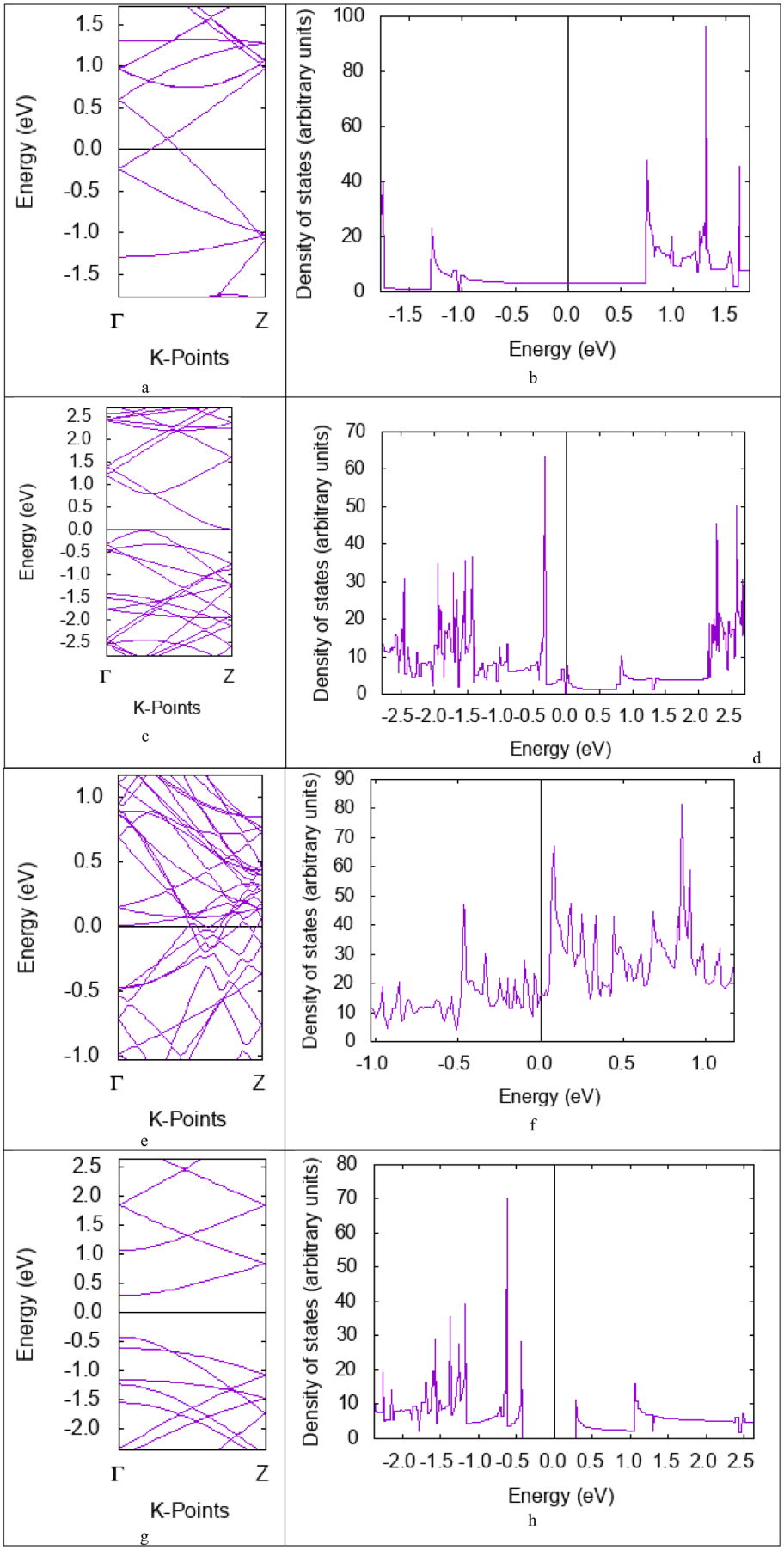

Fig. 2. a- Band structure of a pristine (3,3) CNT, b- DOS of a pristine (3,3) CNT, c- Band structure of a pristine (4,2) CNT, d- DOS of a pristine (4,2) CNT, e- Band structure of a pristine (5,1) CNT, f- DOS of a pristine (5,1) CNT, g- Band structure of a pristine (6,0) CNT, h- DOS of a pristine (6,0) CNT.

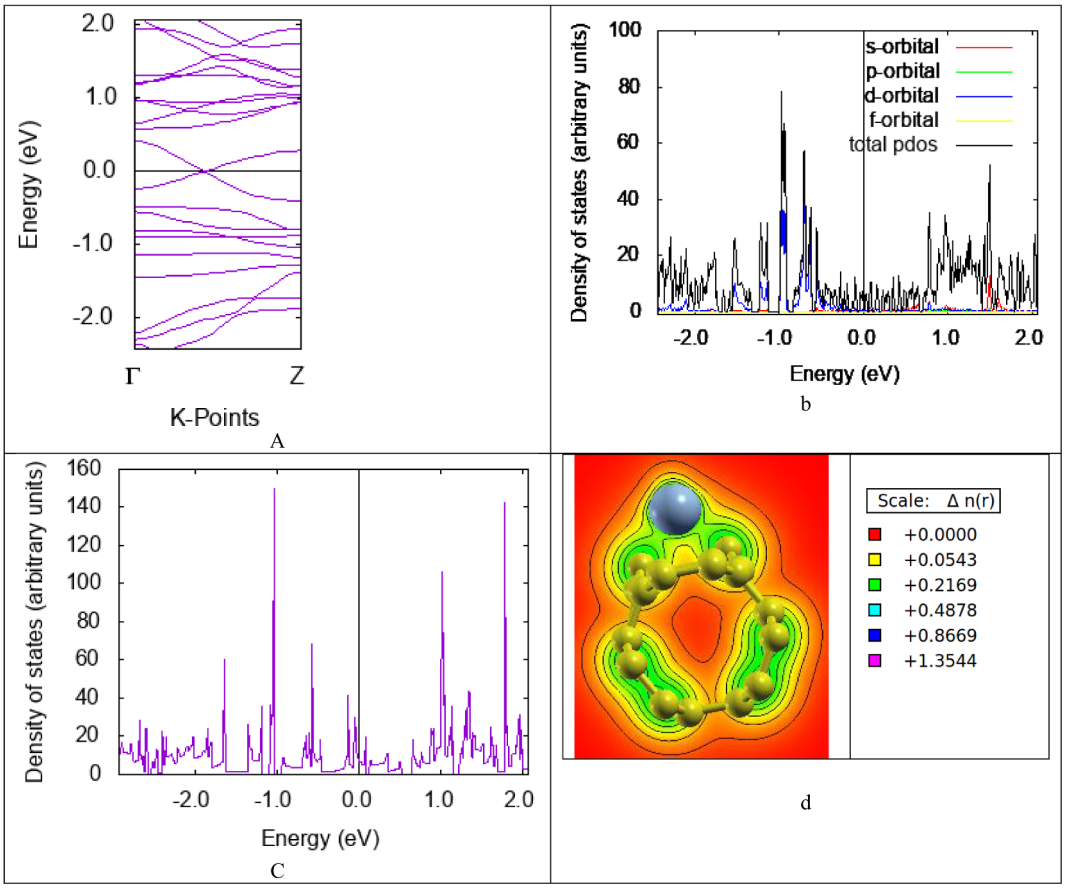

Fig. 3. Where a- Band structure of a (3,3) CNT with Ni adsorbed at Site 2, b- PDOS of a (3,3) CNT with Ni adsorbed at Site 2, c- DOS of a (3,3) CNT with Ni adsorbed at Site 2, d- Charge density plot for a (3,3) CNT with Ni adsorbed at Site 2.

below shows the adsorption data of the carbon nanotubes. From the data below, it can be seen that the Fermi energies increased upon metal adsorption implying that more states were added to the valence region of the carbon nanotubes.

The electronic band structures, DOS, PDOS and charge densities of the different carbon nanotube models at zero pressure and temperature, along high symmetry path of the Brillouin zone are presented in Figs. 3–5, in order to understand the electronic properties of the metal atom interacting with the nanotubes. Fig. 2 provides the band structure and DOS for pristine carbon nanotubes, (3,3), (4,2), (5,1) and (6,0) respectively. From Figs. 3a, 4a and 5a with high symmetry $\Gamma \rightarrow Z$, it was observed that the minimum conduction band and the maximum valence band intersected indicating that the carbon nanotube possessed metallic properties. The pristine carbon nanotubes (4,2) and (6,0) are semiconducting CNT as shown in Table 1. However, when they were interacting with Ti, and Au respectively, their properties changed from semiconducting to conducting.

A nickel atom adsorbed at site 2 on a (3,3) carbon nanotube maintained its conducting nature as seen in the band structure diagram in Fig. 3a. There was however an increase in the states in the valence band as shown in the PDOS and DOS graphs in Fig. 3b and Fig. 3c, respectively. The low density of states at the Fermi level also indicated that the carbon nanotube has a weak metallicity. Furthermore, it can be seen that the d-orbital of the nickel atom provided most of the contribution to the overall density of states. The charge density plot (Fig. 3d) shows a homogenous charge distribution between the nickel atom and carbon atom signifying that a significant bonding took place.

When a titanium atom interacted with a (4,2) CNT in the middle, it was observed that the electronic properties of the carbon nanotube changed from semiconducting to metallic as shown in the band structure in Fig. 4a. The PDOS graph in Fig. 4b, indicates that the d-orbital of titanium contributed significantly to the total density of states. The reason for this can be deduced from the charge density plot in Fig. 4d. The plot shows a higher density of charges around the carbon atoms

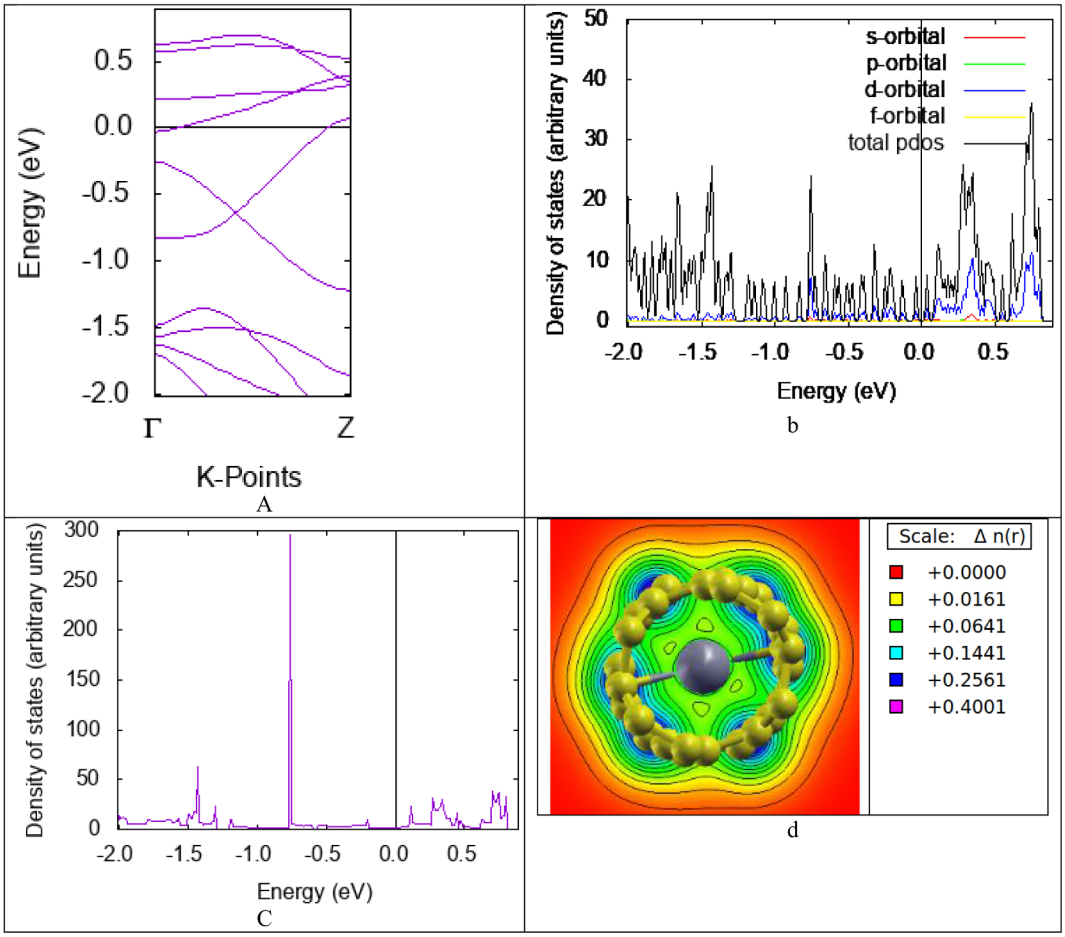

Fig. 4. Where a- Band structure of (4,2) CNT with Ti interacting at site 3, b- PDOS of (4,2) CNT with Ti interacting at Site 3, c- DOS of (4,2) CNT with Ti interacting at Site 3, d- Charge density of (4,2) CNT with Ti interacting at Site 3.

than the titanium atom. This is apparently due to carbon being more electronegative than titanium. As a result, the carbon atoms drew more electrons to themselves.

In the case of the (5,1) CNT, when interacted with a palladium atom at Site 1, the metallic properties of the carbon nanotube were maintained as seen in the band structure (Fig. 5a) and DOS (Fig. 5c). Although the carbon nanotube displays conduction properties, there appears to be very little contribution from the palladium orbitals to the total density of states as observed in Fig. 5b. This is as a result of very weak coupling between the d- and s- orbitals of the palladium metal and that of the nanotube respectively. In terms of charge distribution, there is a uniform sharing between the palladium and carbon atoms as seen in Fig. 5d.

Doping studies

The four different carbon nanotubes were each doped with nickel, palladium, titanium and gold as shown in Fig. 1. Table 3 displays the doped CNT data. This was done in order to understand whether there is a site specific interaction that will give an optimal energy. Once again, more states were added to the valence region resulting in the increase of the Fermi energy.

A (6,0) CNT doped with a gold atom modified the electronic properties to conducting as seen in the band structure diagram in Fig. 6a. The DOS graph (Fig. 6c) also indicated high densities of states in the valence band near the band gap and in the conduction band. A study of the PDOS in Fig. 6b showed that the high density of state in the valence region was as a result of some contribution from the p and d orbitals of the gold atom whereas the s and p orbitals contributed to the high-density states in the conduction bands. The charge density plot in Fig. 6d also showed an excellent distribution between the gold and carbon atoms because of their very similar electronegativities.

Conclusion

Employing density functional theory within the local density approximation exchange-correlation functional, the electronic properties

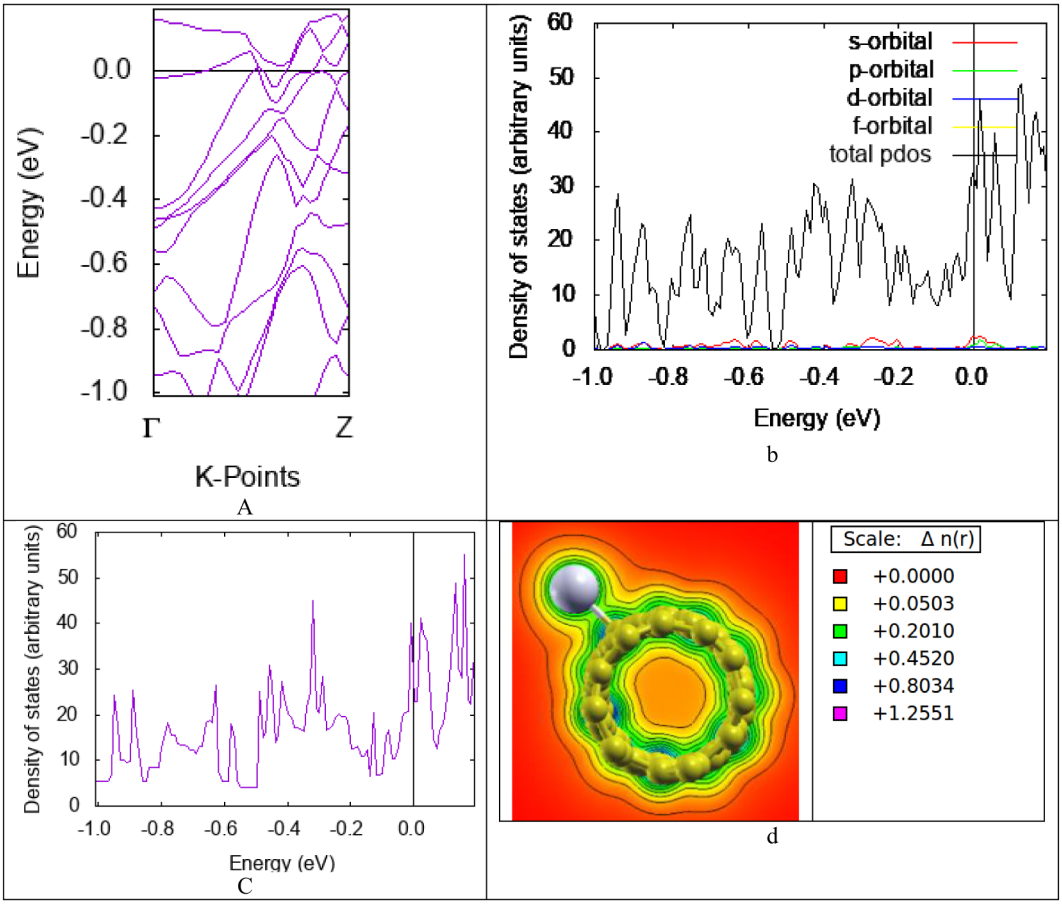

Fig. 5. Where a- Band structure of (5,1) CNT with Pd adsorbed at Site 1, b- Projected DOS of (5,1) CNT with Pd adsorbed at Site 1, c- DOS of (5,1) CNT with Pd adsorbed at Site 1, d- Charge density of (5,1) CNT with Pd adsorbed at Site 1.

Table 3
Doped CNT data.

Carbon Nanotube	Doping concentrations (%)	Fermi energy of pristine CNT (eV)	Range of Fermi energies after doping (eV)
(3,3)	2.08	−2.22	−1.88 to −2.23
(4,2)	1.79	−2.29	−1.80 to −2.01
(5,1)	0.81	2.83	2.76 to 2.82
(6,0)	1.39	−2.11	−1.09 to −1.30

of four small diameter carbon nanotubes and their interactions with four transition metal atoms, Ni, Ti, Pd and Au, were extensively studied. It was found that, nickel, palladium, titanium and gold atoms, changed the electrical properties of the carbon nanotubes when interacting at specific sites. Gold, however, proved to be the best metal for carbon nanotube adsorption since it changed the semiconducting carbon nanotubes to conducting irrespective of the interaction site. The titanium atom showed similar effects only when interacted in the middle of the carbon nanotube. The electrical properties of the (5,1) carbon nanotube was not affected by any of the atom interactions due to a low adsorption and doping concentration.

The projected density of state plot indicated that the d-orbital of the metal atoms was generally the highest contributor to increasing the density of states in the carbon nanotubes except in the (5,1) carbon nanotube where there was generally no contribution from the metal atoms.

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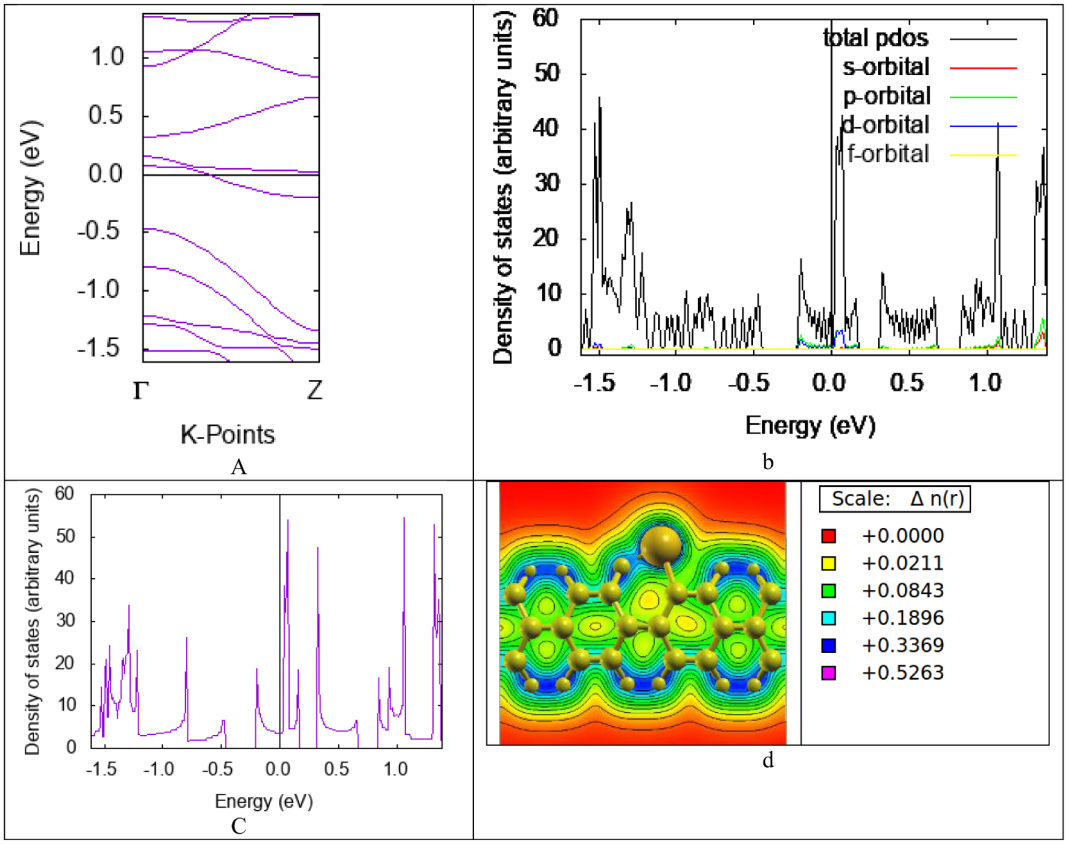

Fig. 6. Where a- Band structure of (6,0) CNT doped with Au atom, b- PDOS of (6,0) CNT doped with Au atom, d- Charge density of (6,0) CNT doped with Au atom.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.rinp.2019.02.062.

References

[1] Coiffic J, et al. An application of carbon nanotubes for integrated circuit interconnects. Carbon nanotubes and associated devices. International Society for Optics and Photonics; 2008.

[2] Ali A, Parveen H. Carbon nanotube interconnects for IC chips. Institute of Technology Massachusetts; 2006.

[3] Ebbesen T, et al. Electrical conductivity of individual carbon nanotubes. Nature 1996;382(6586):54.

[4] Odom TW, Huang JL, Lieber CM. Single-walled carbon nanotubes. Ann N Y Acad Sci 2002;960(1):203–15.

[5] Fuchs F, et al. Interaction between carbon nanotubes and metals: Electronic properties, stability, and sensing. Microelectron Eng 2015;137:124–9.

[6] Zhuang H, Zheng G, Soh A. Interactions between transition metals and defective carbon nanotubes. Comput Mater Sci 2008;43(4):823–8.

[7] Kim H-S, et al. Controllable modification of transport properties of single-walled carbon nanotube field effect transistors with in situ Al decoration. Appl Phys Lett 2007;91(15):153113.

[8] Wu X, Zeng XC. Adsorption of transition-metal atoms on boron nitride nanotube: A density-functional study. J Chem Phys 2006;125(4):044711.

[9] Zhang Y, et al. Metal coating on suspended carbon nanotubes and its implication to metal–tube interaction. Chem Phys Lett 2000;331(1):35–41.

[10] Bezryadin A, Lau C, Tinkham M. Quantum suppression of superconductivity in ultrathin nanowires. Nature 2000;404(6781):971.

[11] Mananghaya MR, Santos GN, Yu D. Nitrogen substitution and vacancy mediated scandium metal adsorption on carbon nanotubes. Adsorption 2017;23(6):789–97.

[12] Mananghaya M, et al. Theoretical investigation on single-wall carbon nanotubes doped with nitrogen, pyridine-like nitrogen defects, and transition metal atoms. J Nanomater 2012;2012:62.

[13] Quantum Espresso. 2018 [cited 2018; Available from: https://www.quantum-espresso.org/pseudopotentials/fhi-pp-from-abinit-web-site.

[14] Nanot S. et al. Springer handbook of nanomaterials; 2013. p. 105–46.

[15] Giannozzi P, et al. QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. J Phys: Condens Matter 2009;21(39):395502.

[16] Kokalj A. Computer graphics and graphical user interfaces as tools in simulations of matter at the atomic scale. Comp Mater Sci 2003;28:155–68.