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Investigate the electron structure and magnetic properties of carbon doped zinc oxide nanosheet: DFT

دراسة الخصائص الإلكترونية والمغناطيسية لطبقة نانو من أوكسيد الزنك (ZnO nanosheet) بعد أشابته بالكاربون : DFT

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Abstract

In the present work the Density functional theory (DFT) calculations were performed on the electron structure and magnetic properties of Carbon-doped ZnO nanosheet. The predicted for carbon doping modifies the electronic structure of ZnO nanosheet. Through optimized the C_n-ZnO (n=1-7) compounds, we found that compounds are stable. Also calculated binding energy and ionization potential of carbon exohedral doping ZnO nanosheet. The compounds have been found to be more chemically reactive. Mullikan charge analysis shows the presence of the magnetic moment in these systems.

Keywords: ZnO; anaosheet; ab initio calculations; Exohedral doping; electronic structure; magnetic moment

الخلاصة

في هذه الدراسة استخدم نظرية دالة الكثافة لحساب الخصائص الكترونية والمغناطيسية لطبقة من أوكسيد الزنك (ZnO anosheet) المشوب بالكاربون بطريقة (exohedral). حيث ان الكاربون يعمل على تغير في ترتيب الكتروني لأوكسيد الزنك. من خلال إيجاد الشكل الأمثل للمركب اوكسد الزنك بعد اشابته بعدد من ذرات الكاربون (1- 7ذرة) ، وجدنا ان المركبات جميعها في حالة مستقرة. وتم حساب طاقة ربط الاصرة وجهد التاين والوفرة الاكترونية وطاقة الفجوة، وجد ان المركبات تكون اكثر فعالية كيميائيا. ومن خلال شحنة مليكان (Mullikan charge) يظهر وجود لعزم مغناطيسي في مركب أكسيد الزنكnanosheet بعد الاشابة.

Introduction

Zinc oxide nanosheet is a monolayer layer of atoms in honeycomb structure, exhibits various interesting physical properties [1], which could lead to important applications in various fields. Normally, two dimensional (2D) , has been n-type character, in the absence of intentional doping and its electrons and holes behave like a massless Dirac fermion. One interesting aspect of industrial compounds is Zinc oxide nanosheet, it was one of semiconductor metal oxide, which indicates the quantum confinement effects in the experimentally accessible size [2], This observation is the material of choice because it is so far the most common material in commercial manufacturing and research due to its low cost and widespread availability. It is useful both for direct application or preparation of other compounds [3,4]. Doping is a popular and fruitful method of modifying and tailoring the properties of many materials the electrical properties [5]. Generally, there have two interactions between metal with ZnO nanosheet, substitutional and exohedral doping. The substitutional doping is represented, that the dopant atom is included in the ZnO nanosheet. while the exohedral doping in this case the dopant is outside or between ZnO nanosheet [6]. Various studies on ZnO have been reported both theoretically and experimentally. Version hexagonal two dimensional ZnO nanosheets were successfully synthesized using zinc acetate and urea based on a facile microwave hydrothermal method. The structure, morphology and size of the ZnO nanosheets were investigated by X-ray diffraction (X-ray), field emission scanning electron microscopy (FESEM), showed that the obtained ZnO nanosheets are crystalline corresponding to

the pure ZnO phase with an average particle size of 12 nm. Optical properties of ZnO nanosheets were investigated [7]. In another theoretical study using first-principles calculations based on density-functional theory, to investigate the mechanical properties, including high order elastic constants, of the graphene-like hexagonal zinc oxide monolayer (g-ZnO), It is observed that g-ZnO exhibits a nonlinear elastic deformation up to an ultimate strain [3]. Investigated the characteristics and structures of ZnO clusters with hexagonal prism configurations using ab initio calculations based on pseudopotentials scheme. The size of compound dependent on ground state energies and electronic structures of ZnO nanosheet. [8].

Computational details:

Atomic structure of matter at the nanoscale, can be quite varied from a quantitative understanding of the experiments has been also often difficult. The computer simulations were used to understand the properties of materials at the nanoscale, under controlled conditions. We performed DFT-GGA pseudopotential calculations by using an efficient computer code, known as SIESTA, [9-11]. Where the Kohn–Sham density functional approach has an advantage, it's made it easier for one needs to solve Hartree-like equations. Despite that various methods exist to solve the Kohn–Sham equation which is based on the standard Kohn–Sham self-consistent density functional theory (DFT) [12]. Standard norm-conserving pseudopotentials are constructed using a Trouiller–Martins scheme [13] to describe the interaction of valence electrons with the atomic cores. The exchange-correlation potential of Perdew–Burkle–Ernzerhof (PBE) for generalized gradient approximation (GGA) corrections are adopted [14,15]. The atomic orbital set employed throughout was a double-zeta polarization DZP function [16], therrepresents a complete basis set and calculations can be implemented for molecules of matter in nanoscale. We have successfully described the structural, electronic and magnetic properties of charge transfer from the metal (M) into the unoccupied carbon cage orbitals, which is fostered by the high electron affinity of the fullerenes, raises expectations for M_n-ZnO, (M=C) to exhibit metallic properties C-doped exoohedral ZnO nanosheet, which validates the applicability of our calculation on complex ZnO and C based system. The binding energy of the complexes is calculated from energy difference between reactants (ZnO nanosheet atoms and the relevant number of carbon atoms) and the complex product species. The binding energy is calculated using.

$$E_B = E_{Mn\text{-}ZnO} - E_{ZnO} - nE_M/n \quad \ldots\ldots\ldots (1)$$

Where E_B is the total energy of the ZnO nanosheet with n carbon dopant atoms. E_{ZnO} is the total energy of pure ZnO nanosheet and E_{Mn} is the total energy of one carbon atom. The optimized ZnO nanosheet structure was used for carbon interaction. we assign initial coordinates to carbon atom and ZnO atoms of nanosheet molecule and allow the system to relax with respect to all degrees of freedom without additional constraints .The structures investigated include C atoms varying from the lowest energy structures of C_n-ZnO (n =1-7) is shown in figure(1).

Results and discussion

In the present study, initial structures were obtained by exohedral doping of carbon atoms for ZnO nanosheet .The structural and electronic properties of the ZnO have been determined to thoroughly investigate the modification of the ZnO upon the doping of carbon atom. Before presenting results for ZnO nanosheet and C-doped ZnO nanosheet, energy convergence tests with respect to the lattice constant, kinetic energy cut off, and special k-points were performed, the order to analyze the stability and size-dependent properties of exohedral ZnO nanosheet, In addition to this, the Occupancies local electron is also fundamental importance to knowledge the characteristics of the global of a system. In cases, where there is a redistribution of valence electrons and charge transfer. The occupations analysis in each one of the orbitals involved in the bonding can provide us also with relevant information concerning the energetic and local electronic structure.

We have further performed calculations which involve various steps on C exohedral doped ZnO nanosheet to investigate electronic properties. The binding energy per/ atom, ionization potential, electron affinity, HOMO-LUMO gap and magnetic momentum with a number of dopant were calculated. The question how does the exohedral dopant of element atoms modify electronic structure and reactivity of ZnO nanosheet?

Through our study we show the optimized structure pure ZnO and ZnO-C_n (n=1-7) are presented in (fig. 1). The variation of binding energy per dopant atom has been plotted in (fig.2). Initially, B. E. increased with increasing number of C dopants atoms, the result explains stability the compound, because the values of binding energy are closed form value -4.1048 eV, which represent the binding energy for pour ZnO nanosheet [8].

The ionization potential is a measure of the strength of correlation of electrons, and as a function of exohedral doping ZnO nanothsset by C dopant atoms, as it shown in (fig.3), the ionization potential for carbon dope increasing with increase the number of carbon atoms up to n=2 doped exohedral ZnO, thereafter the plot shows odd-even alternative behavior. The even number of s-valence electron have larger values of the ionization potential compared th their immediate neighbors. The electron affinity varies as a function of the number of doped carbon atoms exohedral ZnO nanothsset. In (fig. 4) shows odd-even alternative behavior also when the number of dopant atoms n=1 upto n=4, While the electron affinity decreasing with increase the number of carbon atoms form n=5 upto n=7.

The concepts of the highest occupied molecular orbital (HOMO), and lowest unoccupied molecular orbital (LUMO) are of fundamental crucial importance in understanding the charge transfer, stability and reactivity of many organic molecules. Fermi level and HOMO-LUMO gap varies with the number of carbon atoms doped ZnO nanosheet are representing in table (1), shows the Fermi level odd-even alternative behavior with increase the number of carbon. The HOMO and LUMO energy is clear that decreasing with increase the number of carbon upto n=4, that is prove the behavior of compounds It will be a high-connectivity compared with the value ofpour ZnO nanosheet is 0.2798 [8], While the HOMO-LUMO gap is growing with increase the number of carbon atoms form n=5 upto n=7 as calculated by a SIESTA.

We also refer to the (fig.5) shows the magnetic variation as a function of the number of exohedral carbon doped ZnO nanothsset. Majority of substances show magnetic moment, from Mullikan charge analysis we find that there is magnetic moment in the system with specific number of dopant atoms nature. These are either paramagnetic or diamagnetic. A diamagnetic substance is one repelled by a magnetic field, while diamagnetic behavior is due to the presence of paired electrons in the atomic orbitals. Thus the energy gap is dependent on the the bonding and anti-bonding carbon states. The transitions between these states have been identified as 2s and 2p states (these refer to the angular momentum character of the final states). The plot shows generally magnetic moment increases with increasing number of C dopants atoms.

Conclusions and prospects

Exohedral ZnO nanothsset is particularly interesting, because electron transfer from the metal atom to the ZnO nanothsset has been known to occur and this change dramatically at electronic and magnetic properties of nanosheet. In this work, density function theory, calculations were conducted to study some effects of carbon doping ZnO nanothsset. The characteristic bands of ZnO nanothsset are shifted slightly toward higher frequencies. The charge is increased as a result of carbon doping, and consequently the total dipole moment is also increased. The magnetic properties of exohedral ZnO nanothsset has not been fully understood because of the limited amount of cleaner materials, which are usually available for these measurements.

However, magnetic measurements on some of the ZnOnanosheet have been performed.From the proposed theoretical models, one can readily observe that ZnOnanosheet showed the ability to increase its electrical and or magnetic properties as a result of doping, even when ZnOnanosheet is doped with a 2 electron atom element (carbon). Finally, The pseudopotentials are constructed using

a Trouiller–Martins scheme, to describe the interaction of valence electrons with the atomic core methods show that one is able to produce accurate spectroscopic and physical data in a very reasonable computation time. We conclude that carbon doped exohedral ZnO nanosheet is stable compared with undoped ZnO nanosheet. One can dope to a maximum of 7 atoms of carbon exohedral ZnO nanosheet with distance 2.2A between carbon atoms without distorting the ZnO nanosheet. Electron affinity, ionization potential and HOMO-LUMO gap are modified and make ZnO nanosheet more reactive. Carbon doped ZnO nanosheet have also shown the presence of magnetic moment, which is earlier observed in substitutional doping.

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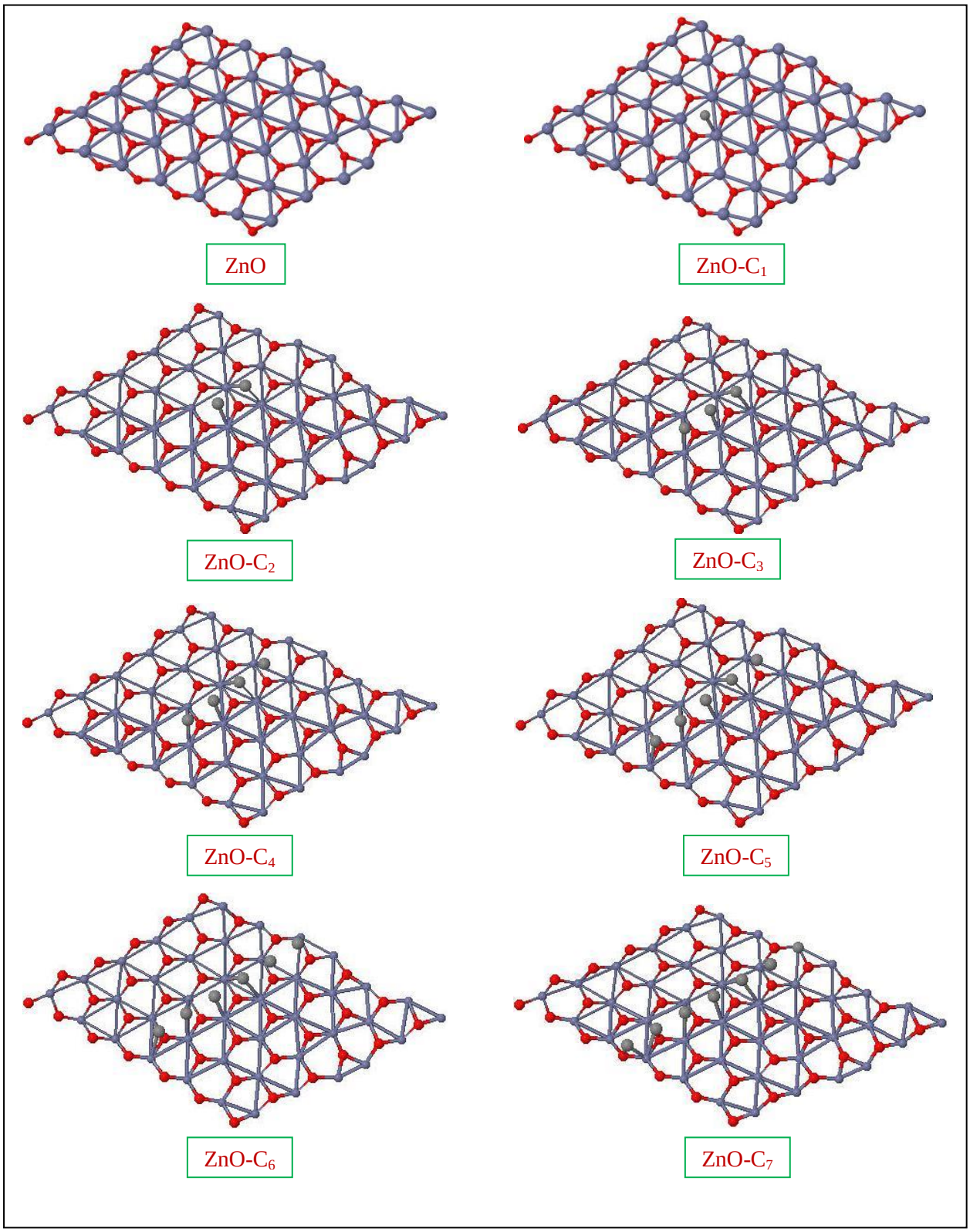

Figure 1. Optimized Structure of C_n- ZnO anosheet (n=1-7)

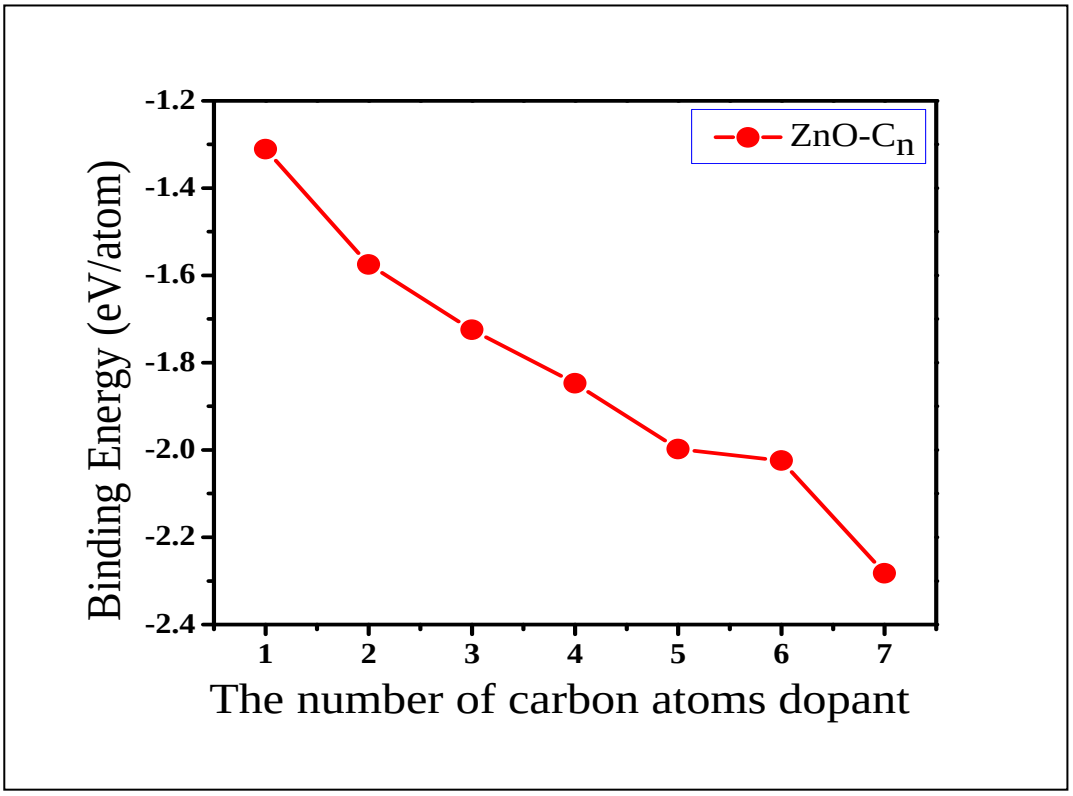

Figure 2. The variation binding energy per atom for C_n- ZnO anosheet (n=1-7).

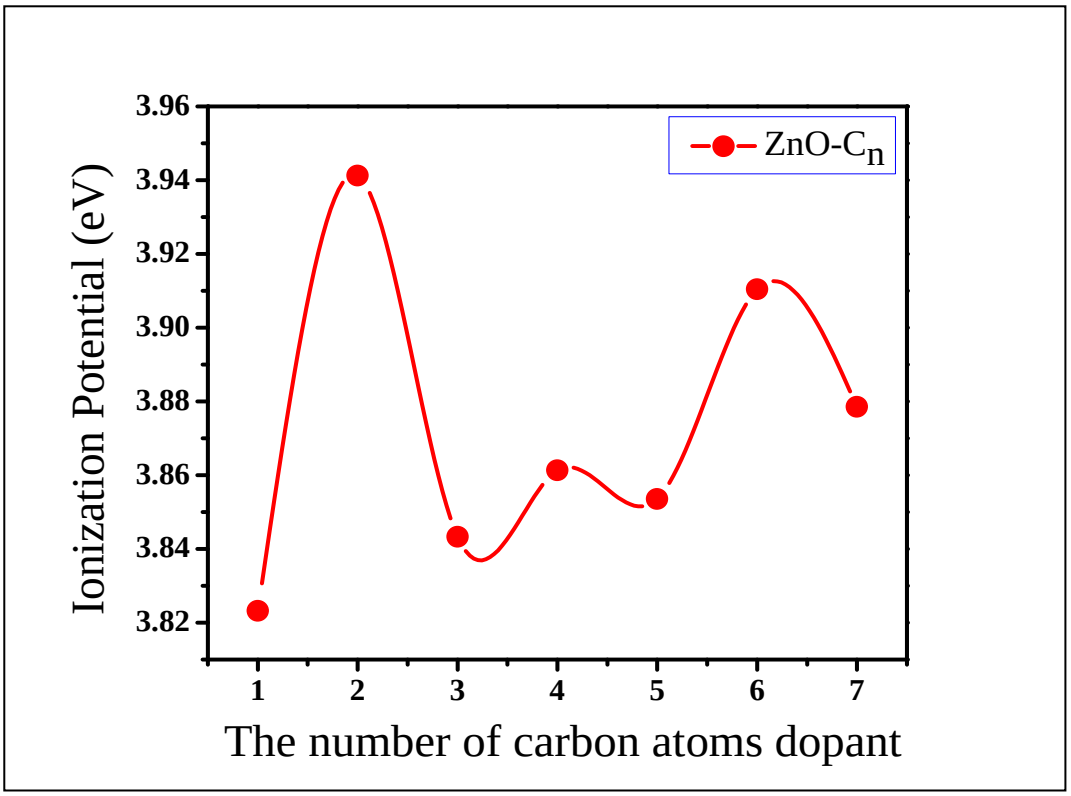

Figure 3. The ionization potential as a function of the number of C_n- ZnO anosheet (n=1-7).

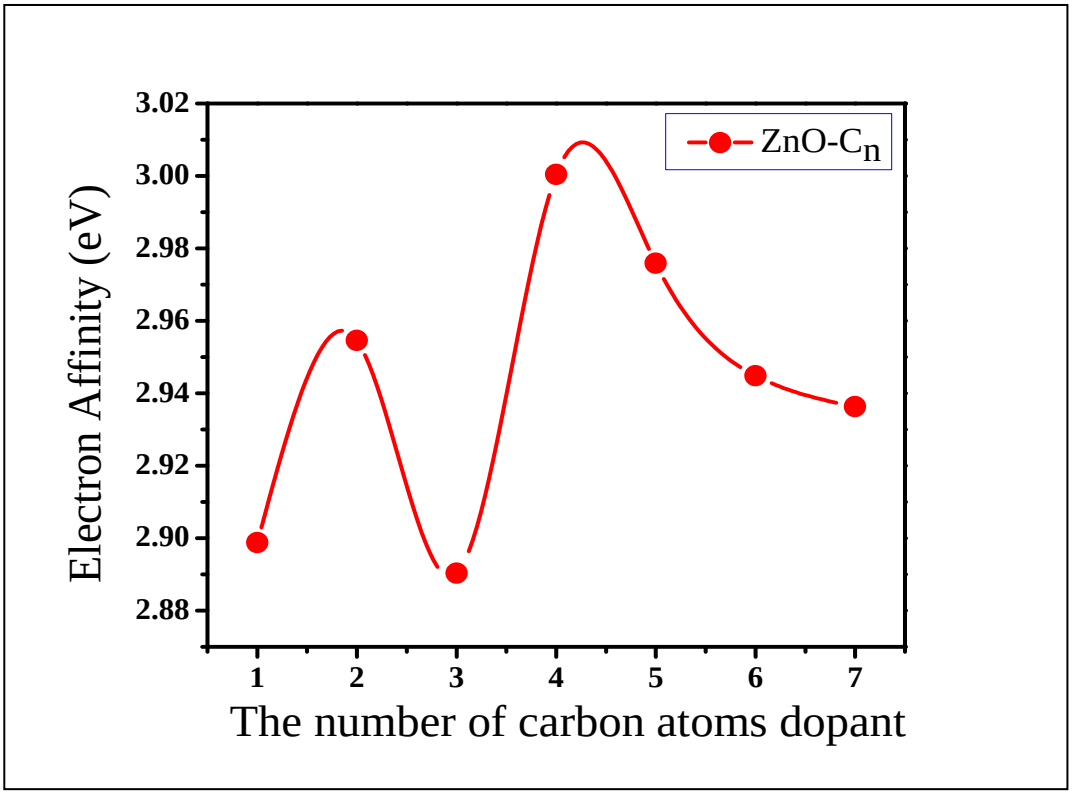

Figure 4. The electron affinity as a function of the number of C_n- ZnO anosheet (n=1-7).

Table1. The Fermi level, and Energy Gap, for C exohedral doped ZnO anosheet (n=1-7).

Complexes	Fermi levels (eV)	Energy Gap (eV)
ZnO-C_1	-3.3884	0.2082
ZnO-C_2	-3.4127	0.1600
ZnO-C_3	-3.3938	0.1318
ZnO-C_4	-3.4402	0.0900
ZnO-C_5	-3.4324	0.1229
ZnO-C_6	-3.4391	0.2549
ZnO-C_7	-3.4150	0.1604

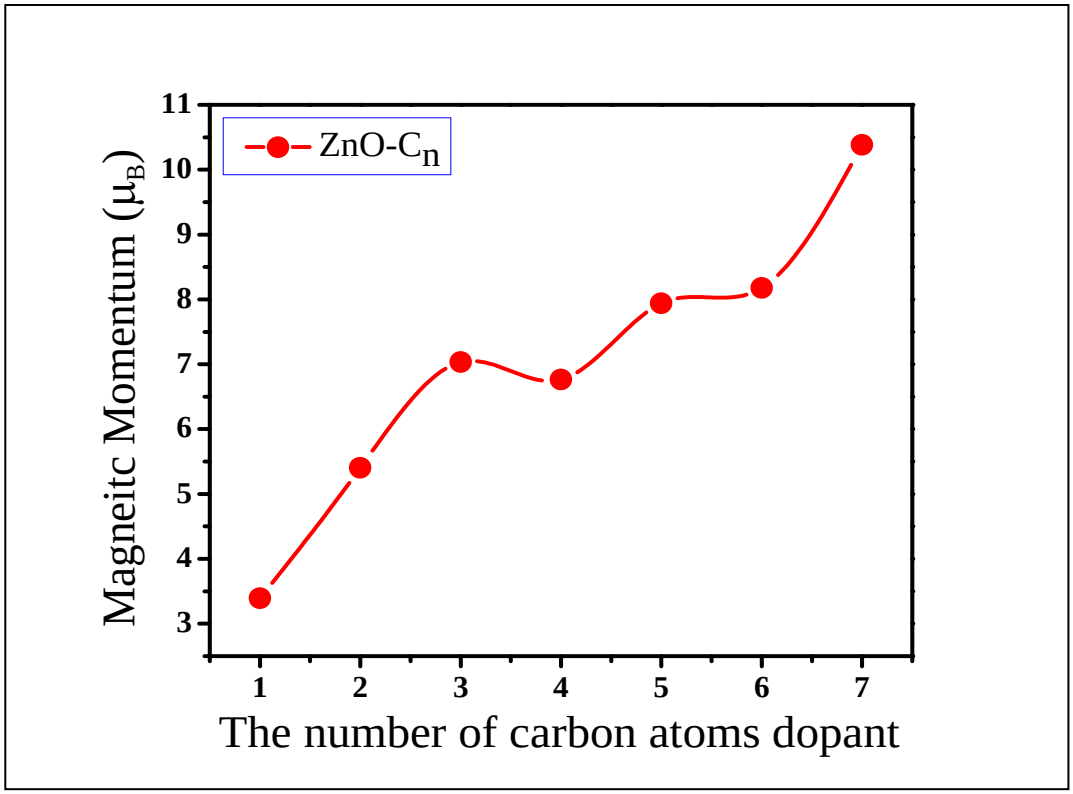

Figure 5. The variation magnetic momentum as a function of the number of C exohedral doped ZnO nanosheet.