

The Electric Field Effect on the Chemisorption of Cu Atom on Perfect Graphene

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ARTICLE INFO	ABSTRACT
<p>Keywords Chemisorption on 2D materials, Anderson Model, External field effect.</p>	<p>The influence of an external static electric field on the chemisorption of a single Cu atom on perfect graphene (Cu/graphene) is explored and investigated using magnetic moment and electronic structure calculations based on the Anderson model, which is characterized by various model parameters. The Cu atom on top of a carbon atom site configuration is taken into account in our research. The effects of an electric field on Cu chemisorption on graphene were examined. The changes in charge accumulation on the adatom Cu confirm the potential of altering the magnetic characteristics of Cu/graphene via the perpendicular electric field direction. The magnetic moment on Cu/graphene was measured as a function of the electric field. Metallic state is observed for multiple electric field values on a single Cu adatom/graphene with variable electronic structure. It has been discovered that the bonding between Cu atoms and graphene can be tuned using an electric field. The dependence of adatom/graphene electronic and magnetic properties on the density of states indicates the importance of the microscopic details for graphene functionalization towards spintronics applications. Our findings could be quite interesting since they imply that the magnetic moment and spin dependent electronic structure on the Cu atom site can be modified by the electric field action.</p>

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1. Introduction

Following the discovery of graphene (a single layer of carbon) [1,] monolayer graphene can be considered a gapless semiconductor; its carriers imitate two-dimensional massless Dirac fermions with the speed of light replaced by the Fermi velocity (106 m/s). Because the mass of the Dirac fermion in graphene functions as the energy gap[2]. The concept of Dirac fermions has grown in importance in condensed matter physics[3]. The carriers of graphene in a low excitation regime are governed by a 2D massless Dirac Hamiltonian and display a linear dispersion relation[4]. The graphene conduction and valence bands contact each other in the Dirac points. Because of this unparalleled geometrical structure, a broad diversity of applications in electronics and spintronics were performed for graphene. The transport properties of massless Dirac fermions in graphene reveal many interesting behaviors[3]. Graphene can be also considered as a hopeful nominee for spintronic devices because the electron spin flip length in graphene is very long (of order of 1 μm) at room temperature[5]. Accordingly, monolayer graphene has become favorable material for applications in nanoelectronics such as spintronics due to its intriguing electronic properties[2]. The spintronics applications of graphene [6] has earned a lot of regard because of its high mobility, low spin-orbit coupling, gate tunability and its low hyperfine interactions. The importance of the microscopic specifics of adatom/graphene was highlighted in many theoretical studies [2,7-10]. Calculations that are accomplished by using density functional theory exhibited that the chemisorption process can be determined by two factors. These are, the adatom species and its site of chemisorption on the sheet[10]. Therefore to functionalize graphene for spintronic properties, rigorous control on the atom-scale is an substantial requirement. Both theoretical and experimental studies about the function of adatoms that resulted in the prevalent spin scattering mechanism [10]. Adatoms are unique building blocks (a different atom-by-atom size) inspire a huge field to alter graphene's electronic and spintronic features. The size of adsorbate highlights the microscopic specifics of adatom/graphene interaction. Several studies had been accomplished to understand the structure disintegration of graphene under high electric field [11]. The field evaporation of a random arranged graphite by field ion microscopy method was investigated and found that field evaporation of carbon atom took place at electric field strength of 70×10^8 V/nm [12]. Graphene had been used in the high electric field (beyond 1 V/nm) application such as field electron emission and scanning tunneling microscopy [12]. Experimentally, a direct observation of structure distortion phenomenon of vertical few-layer graphene under high electric field in situ tunneling electron microscopy (TEM) was reported in ref. [12]. The structure deformation of different defect conditions and different crimped layer direction of vertical few-layer graphene (FLG) under high electric field were investigated.



It is well known that, graphene is non-magnetic but it can be produced into a ferromagnetic state by means of the proximity effect. This possession is very serious for application of graphene in spintronic technology.[2]. Charge and spin transport parameters in two-dimensional graphene are hardly affected by actual parameters related to their native environment. In this paper, the role of electric field in tuning the magnetization on the adatom/graphene will be studied and investigated through the local magnetization and the total density of states calculations.

2. Theoretical Background

The structure (adatom/graphene) can be described by the following Hamiltonian using second quantization form [13-15]:

$$H = \sum_{k\sigma} \varepsilon_k^\sigma n_k^\sigma + \sum_{\sigma} \varepsilon_a^\sigma n_a^\sigma + U n_a^\sigma n_a^{-\sigma} + \sum_{k\sigma} (V_{ak}^\sigma C_a^{\sigma+} C_k^\sigma + V_{ka}^\sigma C_k^{\sigma+} C_a^\sigma) \quad \dots(1)$$

where, ε_k^σ and (n_k^σ) are the graphene energy band levels and the conforming occupation number respectively, for a set of quantum numbers k and spin σ , ε_a^σ ($\varepsilon_a^{-\sigma}$) is the spin up (down) adsorbed atom energy and n_a^σ ($n_a^{-\sigma}$) is the conforming number of occupation. Considering the image, correlation and electric field effects will modify the adatom energy level to be:

$$\varepsilon_a^{\pm\sigma}(z) = \varepsilon_a^0 + \Delta\varepsilon(z) + U_{eff} n_a^{\mp\sigma} + \Delta E_f \quad [16].$$

ε_a^0 equals to $(\Phi_0 - V_i)$. Z is the (normal) adatom-sheet distance. Φ_0 is the graphene sheet work function, V_i is ionization level for the atom and ΔE_f is the shift due the electric field. The Coulomb correlation is calculated by using the following well known relation $U_{eff}(Z) = V_i - V_A - 2\Delta\varepsilon(Z)$.

$\Delta\varepsilon(Z) (= \frac{e^2}{4(Z+Z_0)})$ represents the (image) shift due to the adatom-sheet electrons interaction (at certain value of Z), Z_0 represents the closest approach. The occupation number n_a^σ of spin σ (*i. e.* ε_a^σ) is written as:

$$n_a^\sigma = \int_{u_\sigma}^{\phi_0} f(\varepsilon, T) \rho_{ad}^\sigma(\varepsilon) d\varepsilon \quad \dots\dots (2)$$

u_σ is the energy band bottom. ρ_{ad}^σ is the localized DOS on adatom site and $f(\varepsilon, T) (= \frac{1}{1+e^{(\varepsilon/k_B T)}}$) is the electron Fermi distribution in Graphene. T is the temperature and k_B is Boltzman constant. By considering the broadening ($\Delta(\varepsilon)$) and the quantum shift ($\Lambda(\varepsilon)$), the onsite DOS is a (Lorentzian) distribution function centered at ε_a^σ ($\varepsilon_a^{-\sigma}$) [14]:

$$\rho_{ad}^\sigma(\varepsilon) = \frac{1}{\pi} \frac{\Delta(\varepsilon)}{[\varepsilon - \varepsilon_a^\sigma - \Lambda(\varepsilon)]^2 + [\Delta(\varepsilon)]^2} \quad \dots\dots(3)$$

Where, $\Delta(\varepsilon) = \pi |V_o|^2 \rho_G(\varepsilon)$ and $\Lambda(\varepsilon) = \frac{1}{\pi} P \int d\varepsilon' \frac{\Delta(\varepsilon')}{\varepsilon - \varepsilon'} \rho_G(\varepsilon')$ is the graphene sheet DOS, and V_o is the coupling interaction strength. The broadening and the (quantum) shift are calculated by utilizing the DOS for idealistic graphene. The bond shaped between any adatom and a sheet can be straggled

into an ionic and metallic parts. The metallic contribution can be expressed by[16], $\varepsilon_m(Z) = \sum_{\sigma} \int_{u_0}^{\varphi} \varepsilon f(\varepsilon, T) \rho_{ad}^{\sigma}(\varepsilon) d\varepsilon - U_{eff} n_a^{\sigma} n_a^{-\sigma}$

At initial state ($Z = \infty$), the atom and sheet can be separated, so it reads;

$$\varepsilon_m(\infty) = \sum_{\sigma} \int_{u_0}^{\varphi} \varepsilon f(\varepsilon, T) \delta(\varepsilon - \varepsilon_a^{\sigma}) d\varepsilon \quad \text{and} \quad \varepsilon_m(\infty) = \varepsilon_a^{\sigma} f(\varepsilon_a^{\sigma}, T) = (\varphi - V_i) \theta(V_i - \varphi)$$

With θ is unit step function. The ionic part of the chemisorption energy $W(Z)$ must be also considered; $\varepsilon_{ch}(Z) = \varepsilon_m(Z) + W(Z)$. The final state can be described as adsorbing adatom on the sheet separated by closest approach Z_0 , accordingly the bonding energy is written as:

$$\varepsilon_{bond} = \varepsilon_{ch}(Z_0) - (\varphi - V_i) \theta(V_i - \varphi) \quad \dots (4)$$

3. Results and discussions

The calculations are achieved by solving the equations, that concerning the occupation numbers n_a^{σ} and the corresponding energy levels ε_a^{σ} , self-consistently. Since, all the functions that characterize the physical adsorption of atom on the sheet are solved self-consistently. The sheet work function used in our calculations is approximated to 5.0 eV[17]. The values of the adatom energy level shift due to electric field used in our calculation are $-1.0 \text{ eV} \leq \Delta E_f \leq 1.0 \text{ eV}$, with a negative value for the direction from Cu atom to Graphene and a positive value for the direction from Graphene to Cu atom [8,18]. All the system electronic properties interested parameters considered in our study are presented in Table1, while T is fixed at 300K. The Cu atom is placed at Z_0 ($=2.03 \text{ \AA}$) on top site normal to the graphene plane. Our calculations are accomplished for each value of ΔE_f at Z_0 (the adjacent approach). The results that invert the most significant physical advantages are abstracted in Table 2. Our calculations for the change of the occupation as a function of (normal) distance show the accepted solution at equilibrium, since n_a^{σ} is greater than $n_a^{-\sigma}$ for all values of ΔE_f . This solution is consistent with the physical feature that ε_a^{σ} is lying lower than $\varepsilon_a^{-\sigma}$. The direction of the applied electric field has an interesting physical feature especially at the closet approach, since the self-consistent solution for the occupation numbers shows nonmagnetic solution for the direction of the electric field from graphene to Cu atom ($\Delta E_f \geq 0.05 \text{ eV}$), while for the opposite direction i.e. from Cu atom to graphene the solution is magnetic (see Table 2). This means that the type of the physical self-consistent solution can be tuned by the direction of electric field. The self-consistent magnetic solution is enhanced by increasing the electric field (in the direction from Cu atom to Graphene), since all values of ε_a^{σ} ($\varepsilon_a^{-\sigma}$) are lying below (above) Fermi level. To explore the magnetic manner on copper/graphene system, one must calculate the magnetization ($M = n_a^{\sigma} - n_a^{-\sigma}$) for all normal distance values. The magnetization is predominant for all distances as shown in Fig. 1 except for $\Delta E_f \geq 0.05 \text{ eV}$ at the closest approach distance. The magnetization is decreasing with increasing the



electric field (Table 2). At the graphene sheet, the effective charge number on the adatom ($Z_{eff}(Z_o) = 1 - n_a^\sigma(Z_o) - n_a^{-\sigma}(Z_o)$) is around zero, this gives significant information about the manner of bonding at the sheet. This emphasized that the ionic contribution is vanished and the metallic contribution is the prevalent one for all Z . As the energy splitting between ε_a^σ and $\varepsilon_a^{-\sigma}$ due to electric field increases (at negative values), the metallic energy (contribution) increases, while as the positive values of the electric field decreases, the metallic energy contribution decreases. The relationship between the electric field and the bonding energies is linear. The bonding energy increases as the electric field increases toward the positive values, i.e. for the direction of electric field from graphene to Cu atom. The role of electric field effect in the adsorbate (ADOS) and the imperfect graphene density of states (GDOS) is also investigated. The DOS on the adatom site, which inserted the adatom level broadening due to hybridization with electrons in the sheet at the closest approach ($Z=Z_o$), is shown in Fig.2. This figure shows that $\rho_{ad}^\sigma(\varepsilon) \neq \rho_{ad}^{-\sigma}(\varepsilon)$ for all values of ΔE_f , this indicates that the self-consistent solution is magnetic (i.e. $n_a^\sigma \neq n_a^{-\sigma}$). But, we have $\rho_{ad}^\sigma(\varepsilon) = \rho_{ad}^{-\sigma}(\varepsilon)$ for $\Delta E_f \geq 0.5$ eV. The most significant physical feature in our results can be deduced by using the calculated DOS. Since, the energy conforming to the maximum value of DOS for spin up (spin down) $E_{\rho m, \sigma}$ ($E_{\rho m, -\sigma}$) is shifted down (up) as $|\Delta E_f|$ increases for all negative values of ΔE_f . While for positive values of ΔE_f , as ΔE_f increases then $E_{\rho m, \sigma} \cong E_{\rho m, -\sigma}$ which means that the spin accumulation on Cu atom is zero. Our results can be experimentally employed to estimate the energy splitting due to field effect and then the electric field strength.

Table1: The parameters of the copper/graphene system.

Atom	V_i (eV)	$\emptyset - V_i$ (eV)	V_A (eV)	V_0 (eV)	Z_0 (Å)
Cu	7.72	-2.72	1.235	2.655	2.03

Table2: The adatom energy levels E_a^σ , magnetization M, metallic chemisorption energy E_m , energy bonding E_{bond} , and $(E_{\rho m, \sigma}, E_{\rho m, -\sigma})$ for the Cu/graphene system for different values of ΔE_f .

ΔE_F (eV)	E_a^σ (eV)	$E_a^{-\sigma}$ (eV)	M	E_m (eV)	E_{bond} (eV)	$E_{\rho m, \sigma}$ (eV)	$E_{\rho m, -\sigma}$ (eV)
-1.0	-1.62889	0.80877	0.8296	-2.7129	-0.00666	-0.68	0.935
-0.5	-1.17091	1.25153	0.82441	-2.19117	-0.52873	-0.38	1.24
-0.1	-0.79518	1.5642	0.80295	-1.7987	-0.92127	-0.135	1.455
-0.05	-0.74598	1.57538	0.79001	-1.75175	-0.9682	-0.1	1.465
-0.03	-0.72528	1.56557	0.77963	-1.73329	-0.98662	-0.09	1.46
-0.01	-0.70318	1.5366	0.76225	-1.71528	-1.00458	-0.075	1.445
0	-0.69117	1.50907	0.7488	-1.70659	-1.01322	-0.07	1.43
0.01	-0.67794	1.46579	0.72956	-1.69831	-1.02141	-0.06	1.41
0.03	-0.63983	1.23631	0.638	-1.68598	-1.03312	-0.045	1.35
0.04	-0.65352	0.12702	0.62982	-1.99374	-0.72599	-0.035	1.305
0.05	-0.36971	-0.36651	5.1E-4	-1.77866	-0.92936	-0.03	1.24
0.08	-0.34769	-0.34769	0	-1.76405	-0.94373	0.005	0.93
0.1	-0.33312	-0.33312	0	-1.754	-0.95363	0.03	0.68
0.2	-0.25623	-0.25622	0	-1.70412	-1.00285	0.175	0.24
0.3	-0.17606	-0.17606	0	-1.65582	-1.04998	0.26	0.275
0.4	-0.09422	-0.09422	0	-1.60946	-1.04176	0.325	0.33
0.5	-0.01112	-0.01112	0	-1.56503	-1.08349	0.38	0.385
0.6	0.07307	0.07307	0	-1.52243	-1.09529	0.44	0.44

0.7	0.15822	0.15822	0	-1.48158	-1.13276	0.495	0.495
0.8	0.24424	0.24424	0	-1.44238	-1.1104	0.55	0.555
0.9	0.33105	0.33105	0	-1.40474	-1.14298	0.61	0.61
1.0	0.41858	0.41858	0	-1.36859	-1.14551	0.67	0.67
1.1	0.50677	0.50677	0	-1.33386	-1.11771	0.73	0.73



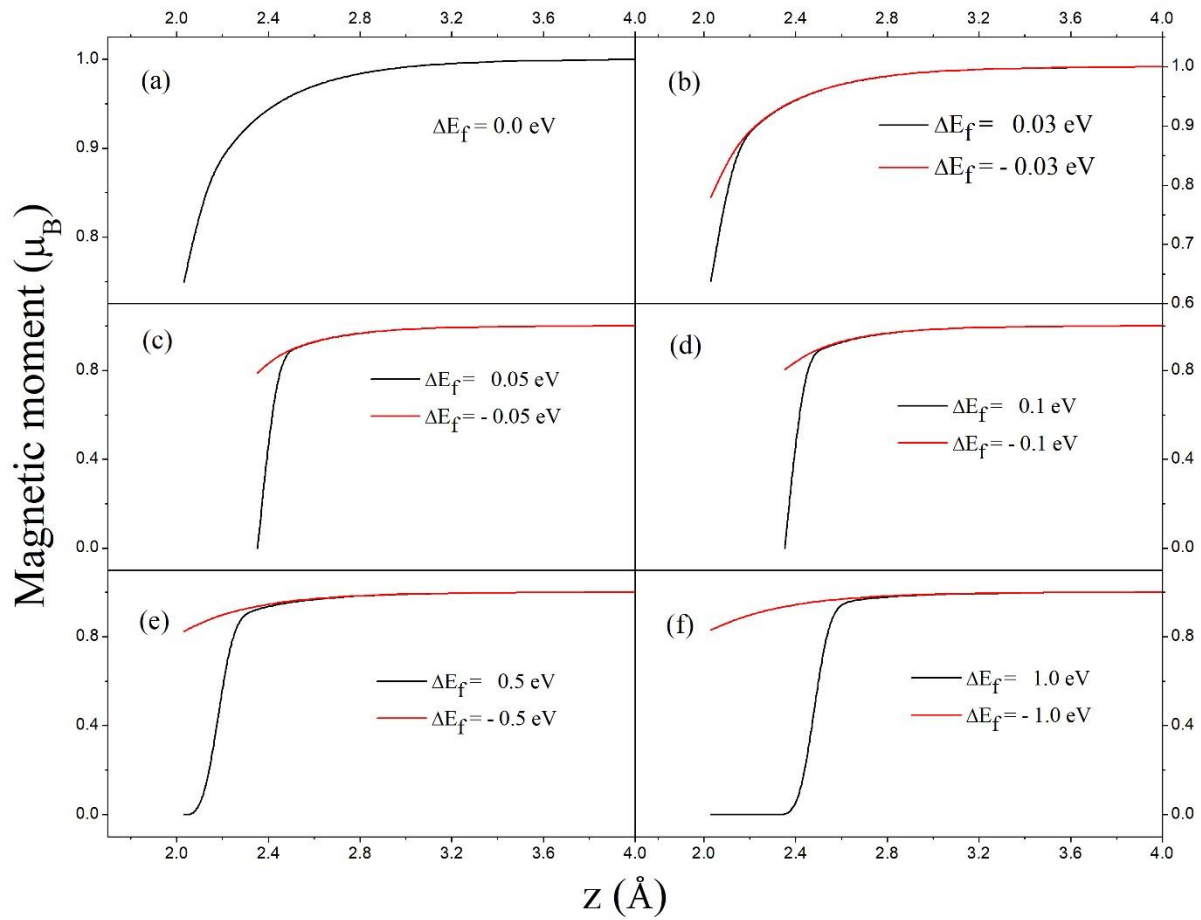


Figure1: The magnetic moment of the adatom site for the Cu/graphene system for different values of ΔE_f .

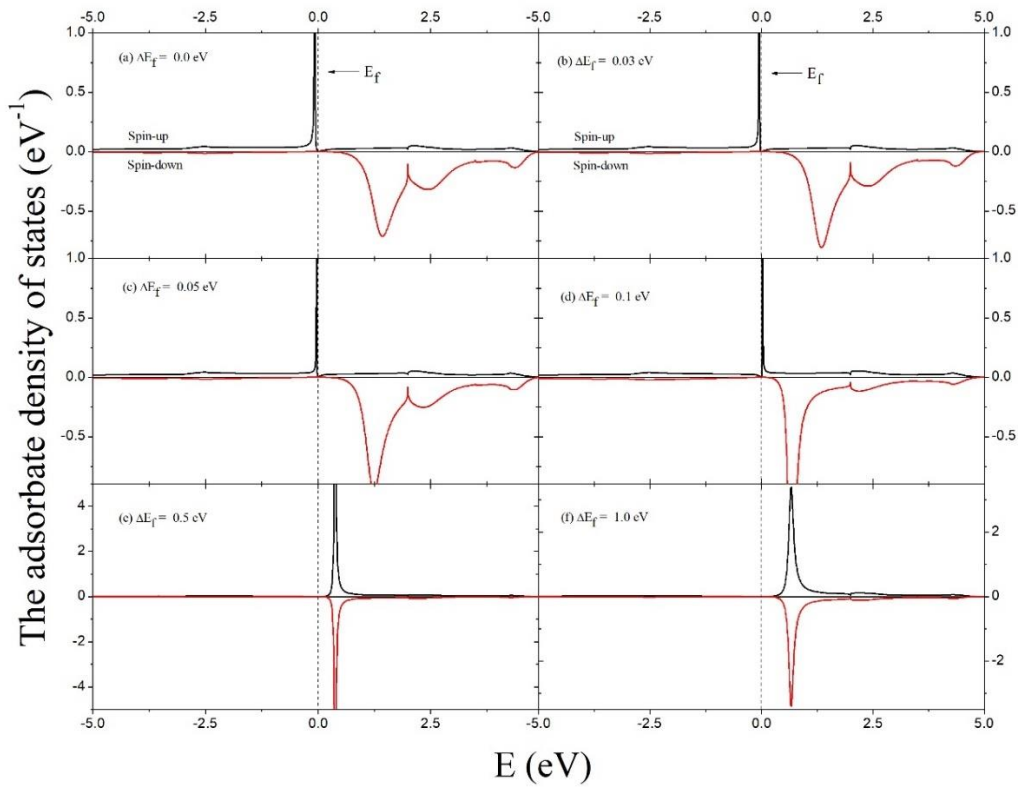
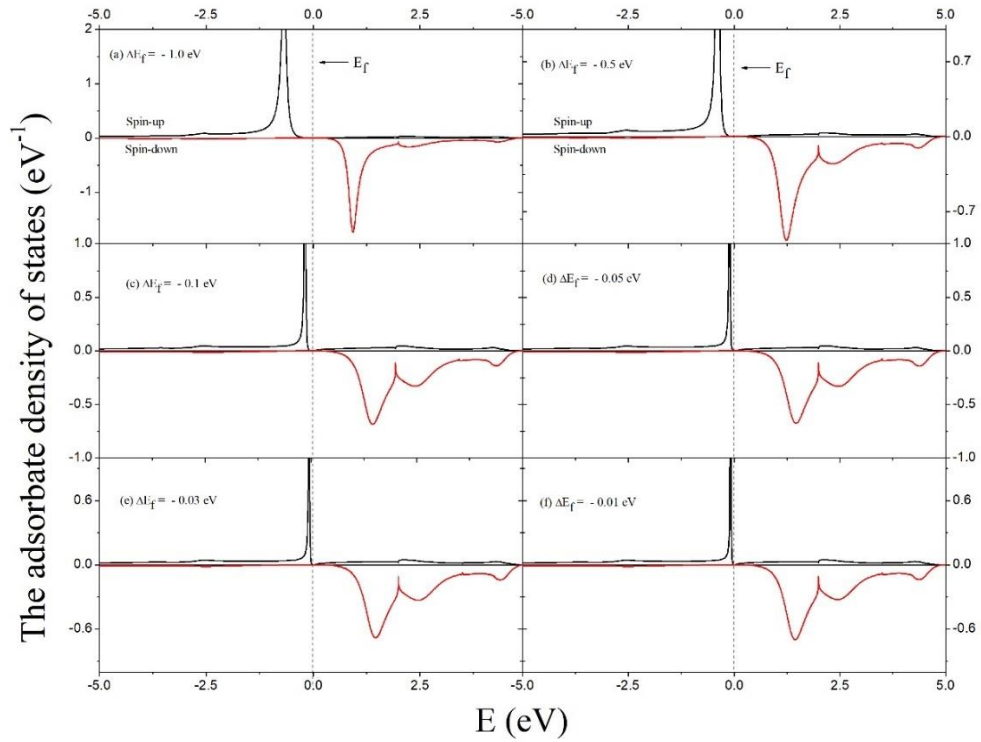


Figure2: The spin dependent adsorbate density of states $\rho_{ad}^{\sigma}(E)$ and $\rho_{ad}^{-\sigma}(E)$ for the Cu/graphene system at $Z=Z_0$ for different values of ΔE_f .

4. Conclusions

The influence of external electric field on Cu atom adsorbed on graphene is studied by using Anderson-Newns model. Apparent description to the type of formative bonding with the sheet is demonstrated. Our results are interesting for spintronics applications, since lowering the bonding energy enhances the magnetic state on the site of the Cu atom. These facilitated and extensive calculations give explicit features about the adsorption of copper on 2D sheet. In conclusion, it is demonstrated that the calculated spintronic properties of Cu/Graphene can be tuned by applying a perpendicular electric field in the direction from Cu atom to graphene. This means that, perpendicular electric field can be used for specific functionalization of adatom/ single layered nanostructures.

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تأثير المجال الكهربائي على الالتصاق الكيميائي لذرة نحاس على الكرافين التام

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المستخلص

تمت دراسة وفحص تأثير المجال الكهربائي الخارجي الساكن في الالتصاق الكيميائي لذرة نحاس مفردة على الكرافين التام (نحاس/الكرافين) ومن خلال فحص العزم المغناطيسي وحساب التركيب الإلكتروني بناءً على إنموذج اندرسون الذي يتميز بمعاملات مختلفة. في دراستنا، تم اعتبار توزيع ذرة النحاس بموقع أعلى ذرة الكربون. تم فحص التغيرات في الالتصاق الكيميائي للنحاس على الكرافين بسبب المجال الكهربائي. تؤكد التغييرات في تراكم الشحنة على ذرة النحاس الملتصقة على إمكانية معالجة الخواص المغناطيسية للنحاس/الكرافين من خلال اتجاه المجال الكهربائي العمودي. تم كشف العزم المغناطيسي على النحاس/الكرافين كدالة للمجال الكهربائي. تم تحديد الحالة المعدنية على ذرة نحاس ملتصقة/الكرافين بتركيب إلكتروني مختلف كما تم الكشف عنها لقيم المجال الكهربائي المختلفة. وجد أن التآصر بين ذرة النحاس والكرافين يمكن ضبطه بالمجال الكهربائي المطبق. يشير اعتماد الخواص الإلكترونية والمغناطيسية للذرة الملتصقة/الكرافين على كثافة الحالات إلى أهمية التفاصيل المجهرية لتوظيف الكرافين باتجاه تطبيقات الإلكترونيات البرمية. إن نتائجنا ذات أهمية كبيرة لأنها تشير إلى أنه يمكن التحكم في العزم المغناطيسي والتركيب الإلكتروني المعتمد على البرم على موقع ذرة النحاس وذلك من خلال التحكم بتأثير المجال الكهربائي.

