

Electric-field control of magnetic states, charge transfer, and patterning of adatoms on graphene: First-principles density functional theory calculations

Yun-Hao Lu,^{1,*} Lei Shi,^{1,2} Chun Zhang,^{1,3,†} and Yuan-Ping Feng¹

¹Department of Physics, National University of Singapore, 2 Science Drive 3, Singapore 117542, Singapore

²Department of Physics and Surface Physics Laboratory, Fudan University, Shanghai 200433, China

³Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore

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We report the first-principles studies aiming at controlling the electronic structure and patterning of adatoms on graphene using an external electric field. We demonstrate that the localized magnetic moment of an Au atom or a NO₂ molecule on graphene can be continuously tuned by the electric field. We also show that the charge transfer between the Au atom and graphene sensitively depends on the direction and strength of the electric field applied. In addition, our calculations suggest that an electric field can be used to control the patterning of adatoms on graphene through the design of underlying electric gate. Our findings may be useful for the future design of graphene-based electronic devices.

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Graphene, a one-atom-thick carbon sheet, has been regarded as one of the most promising candidates for the next generation of electronic materials due to its peculiar electronic properties.^{1,2} A large number of fascinating graphene-based electronic devices have been proposed over the last 10 years.^{3–6} The further development of these devices requires the better control of electronic structure of graphene-based systems. It has been shown by recent studies that adatoms on graphene may be used as an effective tool to tune electronic properties of graphene.^{7–9} For instance, a theoretical study⁹ suggested that graphene nanoribbons (GNRs) can be fabricated without cutting graphene by periodically patterning H atoms on graphene, while several important issues remain challenging for real applications using adatoms on graphene. First, the *p*-type doping of graphene is difficult to achieve by adatoms.^{8,10,11} Second, how to effectively control the localized magnetic states induced by adatoms on graphene which is important for applications of spintronic devices is still a problem.^{12,13} Most importantly, adatoms are normally randomly adsorbed on graphene. The nice control of patterning adatoms is a very challenging issue. Although a scanning tunneling microscope (STM) may be used to position adatoms,¹⁴ it is not practical in future applications which need the large-scale integration of devices. In this Brief Report, we show by first-principles simulation that an external vertical electric field may be helpful in solving all of these issues.

In literature, it has been demonstrated that an external electric field (around 0.2 V/Å) can be used to effectively control the physical and chemical properties of a hybrid system.^{15,16} Quite recently, several groups reported their studies of effects of electric field on adatoms on graphene: Choi *et al.* proposed by density functional theory (DFT) simulation that an electric field parallel to the graphene surface may drive alkali- or alkaline-earth metal atoms adsorbed on a graphene nanoribbon from one side to another;¹⁷ Uchoa suggested by Anderson impurity model that the localized magnetic moment of adatoms on graphene may be tuned by a vertical electric field.¹⁸ In this Brief Report, we focus on the first-principles calculations of effects of an external ver-

tical electric field on Au atoms and NO₂ molecules on graphene. Our theoretical modeling suggests important effects of electric field on atomic and electronic structures of the hybrid graphene system under study and reveals the underlying mechanism of these important effects that are different from those in aforementioned studies.

The electronic structure and nature of bonding of an Au atom adsorbed on graphene under an external electric field (shown in Fig. 1) were studied in this Brief Report with first-principles method under the framework of DFT using PWSCF package.¹⁹ DFT calculations were performed with a plane-wave basis (30 Ry for the kinetic-energy cutoff) and scalar relativistic ultrasoft pseudopotentials.¹⁹ In the calculation, the generalized gradient approximation (GGA) in Perdew-Burke-Ernzerhof (PBE) format²⁰ was included. Our previous studies have demonstrated that DFT+GGA calculations are capable of generating good enough results for Au nanowires and clusters.²¹ The external electric field was simulated by a periodic saw-tooth-like electric-static potential.²² In determining the ground-state structure of the system under study, a supercell that includes 4 × 4 unit cells of graphene in *x*-*y* plane (graphene plane) and 20 Å in the *z* direction, 6 × 6 × 1 *k*-points sampling²³ and a force convergence criteria of 0.0002 Hartree/Bohr were employed.

Without the external electric field, the most stable adsorp-

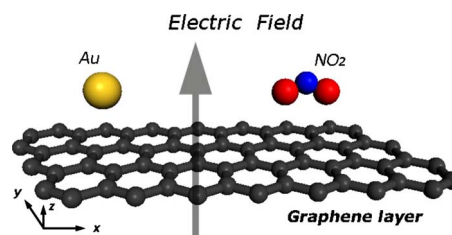


FIG. 1. (Color online) Schematic view of Au and NO₂ adsorbed on graphene with positive electric field indicated by arrow. The black honeycomb structure represents graphene layer, the blue (small dark gray) and red (bigger dark gray) balls are nitrogen and oxygen atoms respectively and the yellow (light gray) ball is Au atom.

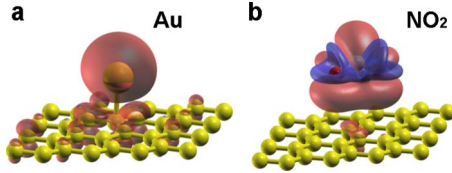


FIG. 2. (Color online) The isosurface of spin density of Au (a) and NO₂ (b) adsorbed on graphene without electric field. The spin density is defined as the difference between spin-up and spin-down electron densities, $\rho_{\uparrow} - \rho_{\downarrow}$. Positive spin densities are in red and negative ones in blue (dark gray).

tion site of the Au atom is on top of carbon with a binding energy 0.12 eV which is in good agreement with previous studies.^{24,25} The Au-carbon bond length ($d_{\text{Au-C}}$) is calculated to be 3.35 Å. In vacuum, a single Au atom is magnetic with a magnetic moment 1 μB due to an unpaired 6s electron. When adsorbed on graphene, according to our calculations, this magnetic moment survives but becomes a bit smaller, 0.84 μB , due to the charge transfer from graphene to Au. The isosurface of the spin density of electrons is given in Fig. 2(a) from where we can see that the magnetic moment is mainly localized on the Au atom.

When an external electric field is applied, the charge redistribution driven by the field changes the charge transfer between the graphene and the adsorbate. As a result, the unbalanced occupation of spin-up and spin-down orbitals that is the origin of the magnetic moment of the adsorbate is affected, which makes the localized magnetic state of the adsorbate depending on the external electric field. We want to emphasize here that these subtle effects of the electric field can only be understood by first-principles studies. In Fig. 3(a), the magnetic moment of the Au atom as a function of electric field is shown (note that the “positive” direction of the field refers to the direction pointing from graphene to Au as shown in Fig. 1). When the electric field varies from -0.3 to 0.3 V/Å, the magnetic moment changes from 0.7 μB to above 0.95 μB . Within this region, the magnetic moment linearly depends on the field. If we further increase the field, the magnetic moment reaches 1 μB around 0.5 V/Å and then undergoes a drop to 0.95 μB at 0.6 V/Å.

An important new direction in the research of nanospintronics is to achieve high tunneling magnetoresistance (TMR) using nonmagnetic leads connected by an atomic/molecular-scale magnetic center.²⁶ Therefore, a magnetic center with controllable magnetic moment is highly desired. Comparing with a previous proposal¹⁷ that using an electric field parallel to the plane of graphene to control the localized magnetic moment of adatoms by tuning the adsorption sites of those atoms, an obvious advantage of the method we proposed in this Brief Report is that the magnetic moment of adatoms on graphene can be continuously tuned by the electric field as we see in Fig. 3(a). Underlying this continuous behavior of magnetic moment is the continuous response of the charge transfer between graphene and adatoms to the electric field.

The change of charge transfer as a function of the electric field is given in Fig. 3(b). In the figure, the change in the charge transfer, ΔQ , is defined to be the difference between

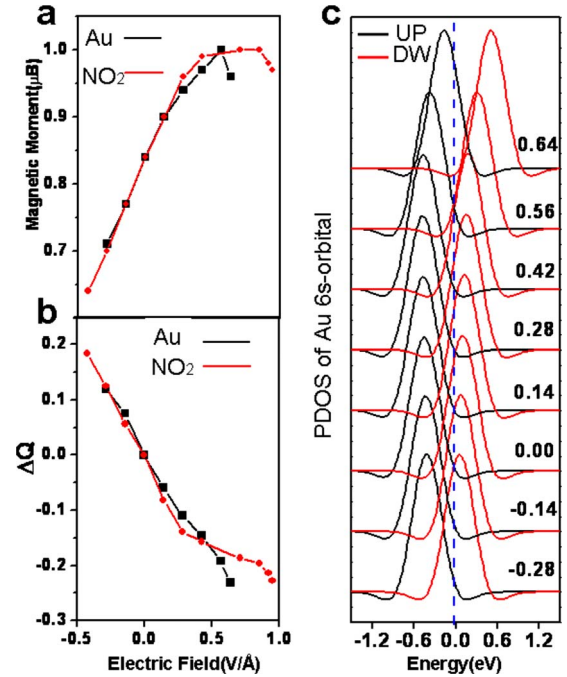


FIG. 3. (Color online) (a) Magnetic moments of Au at graphene (black squares) and NO₂ at graphene (red circles) as functions of electric field. (b) Change of charge transfer of Au at graphene (black squares) and NO₂ at graphene (red circles) as functions of electric field. (c) Spin-polarized PDOS of Au 6s orbital under different electronic fields. The strength of electric fields (black number in the figure) are in the unit of V/Å. The Fermi level (blue dash line) is set to zero.

the total charge accumulated on Au atom under an electric field and that under the zero field. The total charge on Au atom is calculated by integrating the charge density above the plane cutting through the mid point of Au-C bond. When the field varies from -0.3 to 0.3 V/Å, ΔQ changes from 0.12 to -0.15 electrons continuously. Considering that there is only one Au atom in the system under study, this change in ΔQ is quite significant. Note that when the direction of the field changes, the sign of ΔQ changes also. The sensitivity of the charge transfer to both the direction and strength of external electric field is important for the future design of graphene-based electronic devices. Our findings provide a possible way for the control and tuning of both *p*-type and *n*-type doping of graphene. It is worth noting here that the continuous change of magnetic moment as electric field varies we predicted does not depend on the quantitative method we used for charge transfer.

To further understand the field dependence of the magnetic moment and the charge transfer, we show the partial density of states (PDOS) of Au 6s orbital for both spin channels under different electric fields in Fig. 3(c). When the field is zero, the spin-down 6s orbital is partially occupied as shown in the figure which leads to a magnetic moment of 0.84 μB . When a positive field is applied, the peak of spin-down PDOS moves rightward crossing the Fermi energy, representing a charge transfer from Au 6s spin-down orbital to graphene. This charge transfer enhances the unbalanced occupation of two spin orbitals, thus increases the magnetic

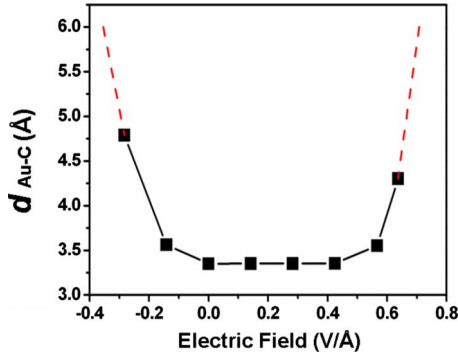


FIG. 4. (Color online) The bond length ($d_{\text{Au-C}}$) between Au and graphene layer as a function of electric field.

moment. When the positive electric field is strong enough so that the Au $6s$ spin-down orbital is completely depleted, the electron on spin-up orbital starts to populate to graphene which decreases the magnetic moment. When the field is reversed, the direction of the charge transfer is reversed too. In this case, electrons on graphene populate onto Au $6s$ spin-down orbital, which moves the peak of PDOS of this orbital leftward and decreases the magnetic moment.

We examine next the effects of the electric field on the bond length between Au and graphene. In Fig. 4(a), we show the bond length $d_{\text{Au-C}}$ as a function of electric field. When the field varies from -0.2 to 0.5 $\text{V}/\text{\AA}$, $d_{\text{Au-C}}$ almost remains the same and only changes a little from 3.35 to about 3.5 \AA at -0.2 and 0.5 $\text{V}/\text{\AA}$. Interesting things happen when the field is stronger than 0.5 $\text{V}/\text{\AA}$ in positive direction or 0.2 $\text{V}/\text{\AA}$ in negative direction. Beyond these critical strong fields, $d_{\text{Au-C}}$ suddenly increases. When the field reaches 0.3 $\text{V}/\text{\AA}$ in negative direction or 0.7 $\text{V}/\text{\AA}$ in positive direction, the Au atom is essentially dissociated from graphene. These sudden changes in $d_{\text{Au-C}}$ are caused by the competition between the electric field and the Au-graphene bonding. The external electric field always tries to separate positively charged centers from negatively charged ones, while the bond (either covalent or ionic) maintains the distance between them. When adsorbed on graphene, the Au atom becomes slightly negatively charged due to the charge transfer from graphene to Au, and a bond between Au and graphene forms. When a negative electric field is applied, this charge transfer is enhanced so that the Au atom is more negatively charged, and the field will try to separate the negatively charged Au and locally positively charged graphene. If the field is strong enough (>0.3 $\text{V}/\text{\AA}$) so that the force trying to separate them dominates, the bond is broken. Similarly, a strong positive field (>0.7 $\text{V}/\text{\AA}$) will break the bond also. A positive field much stronger than 0.3 $\text{V}/\text{\AA}$ is needed to do so because originally (when the field is zero) the Au atom is negatively charged, and the positive field has to be strong enough to reverse the charge transfer to make the Au atom positively charged and then break the bond. The same field-induced bond-breaking process is also observed for the case of two Au atoms in a 6×6 supercell. It is worthy mentioning that a field of >0.3 $\text{V}/\text{\AA}$ can be easily achieved in experiment.²⁷ The sudden bond breaking under a field of -0.3 or 0.7 $\text{V}/\text{\AA}$ implies a nice controllable patterning of adatoms on graphene using an external electric field.

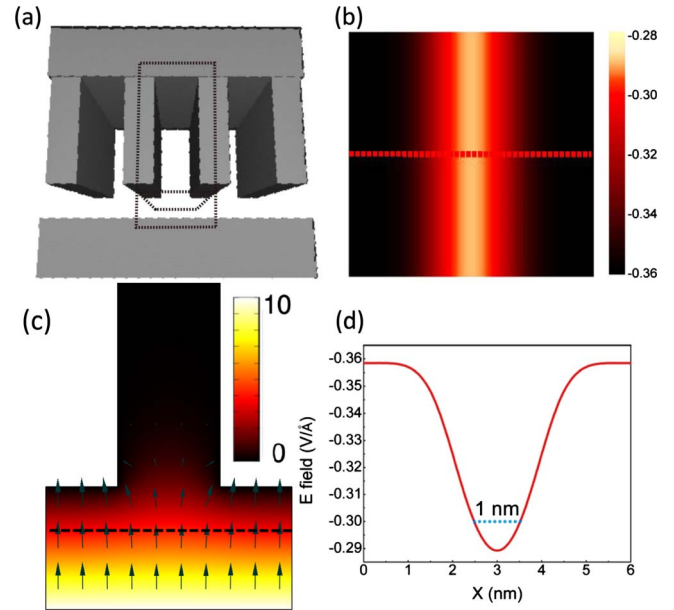


FIG. 5. (Color online) (a) The one-dimensional nanostructured metal gate. The upper gate consists of periodic metal walls (2 nm wide and 10 nm high) on a metal substrate. Two adjacent walls are separated by 4 nm. The counter gate is 3 nm away from the top of walls. The graphene surface is parallel to negative gate, and 1 nm below metal walls. (b) Calculated electric-field distribution on graphene surface under a gate voltage of 1 V. (c) Side view of electric-field distribution in one unit cell. The dashed line denotes the position of graphene surface. Arrows show the direction of electric field. (d) The field distribution on graphene surface along the direction perpendicular to metal walls.

The key point here is to generate a desired pattern of electric-field distribution on graphene which in turn can be used to control the adsorption of Au atoms. This can be done through the design of underlying metal gate. In Fig. 5(a), we show a one-dimensional nanostructured metal gate consisting of periodic metal walls on a metal substrate whose width and height are 2 and 10 nm, respectively. Two adjacent metal walls are separated by 4 nm. The size of the system is chosen in this way for the efficiency of simulating electric field, and due to the scaling law of Maxwell equations, the electric-field distribution of larger systems can be derived. The counter gate is 3 nm away from the top of metal walls. With a gate voltage of 1 V, the electric-field distribution in real space is then calculated by solving Maxwell equations via finite element method using COMSOL package.²⁸ The electric-field distribution on graphene surface [see Fig. 5(a)] is plotted in Fig. 5(b). The one-dimensional distribution of the field can be clearly seen from this figure. In Fig. 5(c), we show the side view of electric-field distribution, where we can see that on the graphene surface (dashed line), the field is indeed perpendicular to the surface, therefore, our electronic structure calculations can be applied in this case. In Fig. 5(d), we plotted the field on the graphene surface along the dashed line as shown in Fig. 5(b). We can see that only within a small region around 1 nm in the middle, the electric-field strength is below -0.3 $\text{V}/\text{\AA}$ which suggests that Au atoms will be adsorbed only in this region under the gate voltage of

1 V according to aforementioned field dependence of Au-graphene bond length. In practical, nano structures as small as 20 nm can be fabricated,²⁹ which enables us to control the adsorption of Au atoms around 10 nm. We also simulated the electric-field distribution of two-dimensional nanostructured metal gates, for example, periodically patterned metal rods (not shown in this Brief Report), and concluded that in this case, Au atoms will be adsorbed in a two-dimensional array of circles on graphene. Since Au adatoms are important for applications of graphene-based devices due to the fact they can generate *p*-type doping in graphene,⁸ the method we proposed here that enables us to control the patterning of Au atoms on graphene at nanoscale provides us a powerful tool for future design of electronic devices.

Beside Au atom, we also investigated the effects of electric field on atomic and electronic structures of NO₂ molecule on graphene, and similar phenomena were observed. In Fig. 2(b), we showed the isosurface of spin density of NO₂

on graphene without electric field. The field dependence of magnetic moment and change in charge transfer are shown in Figs. 3(a) and 3(b), respectively.

In summary, with first-principles DFT calculations, we have demonstrated that the magnetic moment of Au atoms on graphene can be continuously tuned by an external electric field normal to the plane of graphene. Underlying the continuous behavior of localized magnetic moment is the continuous response of charge transfer to the electric field. We also proposed that the adsorption of adatoms on graphene can be nicely controlled via the design of underlying electric gate.

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*phylyh@nus.edu.sg

†phyz@nus.edu.sg

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