Density Functional Theory Study of Influence of Hydrogen Adsorption on the Field Emission Properties of Open-Ended Carbon Nanotubes

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Abstract The field emission properties of hydrogen-adsorbed carbon nanotubes (CNTs) are studied using first-principles density functional theory. Open-ended (5,5) single-walled carbon nanotubes models with different numbers of hydrogen molecules adsorbed are built, and the adsorption energy, highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) band gap, the induced dipole moment of the model with and without applied electric field are calculated and analyzed. The calculation results reveal that the structure of carbon nanotubes with hydrogen molecules is stable under field-emission conditions, HOMO-LUMO band gap becomes narrower, the local density of states at the Fermi level increases with the adsorption of hydrogen molecules, and electrons emit more easily.

Key words optoelectronics; carbon nanotube; density functional theory; field emission; hydrogen adsorption

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氢吸附开口碳纳米管场发射密度泛函研究

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摘要 利用第一性原理密度泛函的方法对氢分子吸附开口碳纳米管的场发射性质进行了综合研究,建立了(5,5)开口碳纳米管吸附不同氢分子数量的吸附模型,并对加电场和未加电场下的模型进行了吸附能、最高占有分子轨道-最低未占分子轨道(HOMO-LUMO)带隙及诱导偶极矩的计算和分析。计算结果表明吸附能随着电场的增加而变大,吸附稳定性增强。吸附氢分子的碳纳米管在施加外电场后,HOMO-LUMO 带隙明显减小,费米能级附近的局域态密度随着氢分子的吸附而增加。氢分子对碳纳米管的吸附可以在其尖端表面产生诱导偶极矩,导致电荷由碳纳米管向氢分子大量转移,从而驱使电子由碳纳米管尖端发射到真空中,提高了碳纳米管的场发射性能。

关键词 光电子学;场发射;碳纳米管;密度泛函;氢吸附

OCIS codes 250.0250; 200.0200;160.0160

1 Introduction

Carbon nanotubes (CNTs) have outstanding advantages for electron field emission because of their unique structure and properties[1~3]. We deposited CNTs films by microwave plasma chemical vapor deposition (MPCVD) method directly on the stainless steel substrate. The source gas for growing the CNTs was a mixture of H_2 and CH_4, in which the hydrogen gas serves as both etching reagent for the formation of catalyst nanoparticles issued from the substrate and diluting gas. In the CNT films′ field emission test, the emission current at second time test is smaller than that at first time obviously, and the slope of Nordheim-Fowler (F-N) plot increases[4~7]. This is mainly because hydrogen atom′s desorption on the surface of CNTs films causes the superficial work function to increase. Supposing the above view was correct, we may then extrapolate that the CNT films after the field emission test would adsorb hydrogen to form the C－H bond, and so CNT′s superficial work function will reduce again, namely the F-N plot′s slope reduces and the emission current increases correspondingly. In order to test and verify the above-mentioned, we study the influence of hydrogen molecule adsorption on the field emission properties of open-ended CNTs.

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2 Computational details

All calculations were carried out using first-principles density functional theory (DFT) code provided by DMol[3] code[8]. The local density approximation (LDA) was employed to optimize the geometrical structures of CNTs during self-consistent iterations, with the Perdew-Wang (PWC)[9] parameterization of the local exchange-correlation energy. The generalized gradient approximation (GGA) was adopted to calculate the total energy and various properties of CNTs with the Perdew-Burke-Ernzerhof (PBE)[10] correlation gradient correction. The all-electron Kohn-Sham wave functions were expanded in the local atomic orbital basis set. The atomic orbital was represented by the double numerical polarized (DNP) basis set. A finite basis set cutoff of 0.55 nm was used to guarantee computational accuracy.

In our study, we compared the electronic structures of six types of CNTs, i.e. (5, 5) CNT, (5, 5) CNT with one hydrogen molecule, and (5, 5) CNTs with 3～6 hydrogen molecules, as shown in Fig.1.

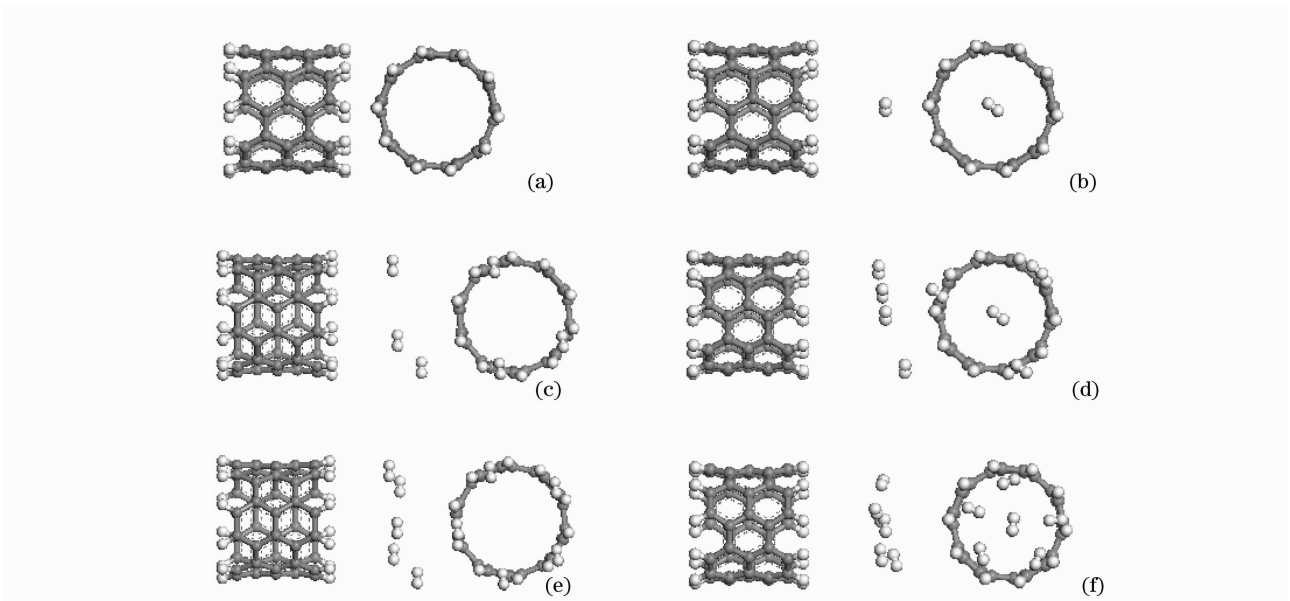

Fig.1 Side views and top views of the optimized geometrical structures of (a) clean CNT, (b) CNT with one hydrogen molecule, and (c)～(f) CNTs with 3～6 hydrogen molecules

3 Results and discussion

Before calculating the field emission performance of CNTs film with hydrogen molecules adsorbed, it is necessary to choose a steadily adsorbing CNT. Therefore, we calculated the adsorptive energy of open-ended CNTs with hydrogen molecules adsorbed at one end in two kinds of situations with and without an applied electric field. The adsorptive energy may be obtained by

$$E_{\mathrm{A}} = E_{\mathrm{nanotube}} + E_{\mathrm{adsorbate}} - E_{\mathrm{nanotube+adsorbate}}, \tag{1}$$

where E_{nanotube}, $E_{\mathrm{adsorbate}}$ and $E_{\mathrm{nanotube+adsorbate}}$ represent separately the total energies corresponding to their subscript structure. The definition of adsorptive energy has already been used widely.

We have calculated the adsorptive energy of the structures in Figs.1(b)～(f) in two kinds of situations with and without electric field. The calculated adsorptive energy relative to each hydrogen molecule is listed in Table 1.

It is shown in Table 1 that the adsorptive power of all adsorbing CNT is positive, and it means that such adsorptive structure is stable. The adsorptive energy of all adsorbing CNTs is bigger in the situation with an applied electric field than that one without an applied electric field. This indicates that in the electric field the hydrogen molecule′s condition has changed, and transforms from the physisorption into the chemisorption, so that the CNT′s adsorption structure becomes more stable. In the situation with or without an applied electric field, the adsorptive energy increases as the adsorption molecule number increases.

Table 1 Calculated adsorption energies per hydrogen molecule, induced dipole moments and HOMO-LUMO energy gaps of CNTs as shown in Fig. 1 with and without the applied electric field

System	Adsorption energy /eV		Induced dipole moment /D		LUMO-HOMO /eV	
	$E=0$	$E=0.1$ eV·nm	$E=0$	$E=0.1$ eV·nm	$E=0$	$E=0.1$ eV·nm
Clean CNT	—	—	—	—	1.19	1.16
One-hydrogen CNT	0.07	0.13	0.01	2.73	1.19	0.81
Three-hydrogen CNT	0.20	0.53	0.04	9.48	1.19	0.57
Four-hydrogen CNT	0.31	0.63	0.07	11.81	1.19	0.54
Five-hydrogen CNT	0.33	0.84	0.10	16.81	1.2	0.54
Six-hydrogen CNT	0.63	0.95	0.14	21.81	1.19	0.54

$1\mathrm{D}=3.338\times10^{-30}$ C·m.

In order to explain the interaction between the hydrogen molecules and the CNT, as well as the effects of hydrogen molecules on the field-emission properties, we calculated the dipole moment p_A at the surface induced by the adsorption of hydrogen molecules, which is defined as

$$p_A = p_{\text{nanotube+adsorbate}}[E=E_{FE}] - p_{\text{nanotube}}[E=E_{FE}] - p_{\text{adsorbate}}[E=E_{FE}], \quad (2)$$

where $p_{\text{nanotube+adsorbate}}$, p_{nanotube} and $p_{\text{adsorbate}}$ represent the dipole moments of corresponding structures. The calculated induced dipole moments are listed in Table 1 for the adsorbing CNTs with and without the applied electric field. The positive dipole moment is defined to be along the CNT axis and pointing from the CNT tip to the CNT body, which is parallel to the direction of the applied electric field. It can be seen that all the dipole moments induced by the adsorption of the hydrogen molecules are positive, and they become larger when the electric field is applied. The induced dipole moment is mainly due to the electrostatic interaction between hydrogen molecules and the CNT, leading to induced polarization of the CNT and charge transfer from the CNT to hydrogen molecules. The positive induced dipole moment can drive the electrons on the CNT tip to emit to the vacuum and enhance the electron field emission.

In two kinds of situations with and without an applied electric field, the highestoccupied molecular orbital-lowest unoccupied molecular orbital HOMO-LUMO band gaps of clean CNT and all adsorptive CNTs are also listed in Table 1. Without an applied electric field, the clean CNT′s band gap is 1.19 eV. As the adsorbed hydrogen molecule number increases, the band gap is nearly invariable. This explains that the adsorption of hydrogen molecule is physisorption, the weak physisorption cannot reduce the band gap width and CNT′s surface work function. After exerting an electric field, all adsorbing CNT′s band gaps obviously reduce. This explains that the adsorption of hydrogen molecule may effectively change the electronic structure and electronic occupied state nearby Fermi surface, thus influencing CNT′s band gap width and superficial work function. These results elucidate that the field-emission properties of CNTs can be enhanced by the adsorption of hydrogen molecules, and are consistent with the experimental results[4].

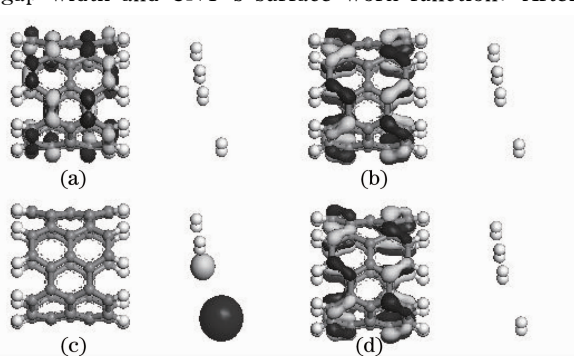

Fig. 2 Side views of the local charge densities of the CNT with four hydrogen molecules. (a) HOMO and (b) LUMO without the applied electric field; (c) HOMO and (d) LUMO under the applied electric field

Figure 2 shows the local charge densities of the HOMO and LUMO of the CNT with four hydrogen molecules with and without the applied electric field. The HOMO and LUMO of other five types of CNTs are similar to those of the CNT with five hydrogen molecules, and are not plotted here. Figure 2 means that the adsorption of hydrogen molecules causes no significant difference for the HOMO and LUMO. We find an interesting phenomenon that without the electric field both HOMO and LUMO are localized at the sidewall of the CNT, and with an applied electric field the HOMO is localized at the hydrogen molecules, and the LUMO is localized at the lower sidewall of the CNT. These states are localized states, which play an important role in the field-emission process. From our calculations, the degenerated energy orbital approximately owns the largest emission current which is mainly distributed on the top of the CNT.

The calculation results could explain the experimental phenomena that hydrogen adsorption on the surface sp^2-

bonded carbon film lowered its work function and then improved the field emission current. Meantime, the reason for the observed initial current degradation behavior and the increasing slope of F-N plot could be explained as the desorption of hydrogen from film surface, which resulted in the increase of the work function of the film according to the calculation results.

4 Conclusion

In summary, the work function changes of CNT films due to hydrogen adsorption on its surface are calculated by using DFT. The calculation results reveal that the work function of CNT films is obviously lowered due to hydrogen adsorption.

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