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First-principles density-functional investigation on the electronic properties and field emission of a hydrogenated nanodiamond

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ABSTRACT

First-principles calculations using quantum-mechanical density functional theory (DFT) are carried out to investigate the geometrical structure and electronic properties for hydrogen terminated nanometer-sized diamonds. The results reveal that the size dependent feature in the electronic structures for nanodiamonds is different from that of Si clusters. The field emission properties for nanodiamonds are also explored, and it is found that under applied electric field Mulliken charges redistribute and accumulate on the emission side. Furthermore, the emission currents from the occupied orbitals for nanodiamond are calculated and it is revealed that the largest emission current comes from the third highest occupied molecular orbital.

1. Introduction

Nanometer-sized diamond has attracted much interest from both experimental and theoretical sides [1–7]. Recently, diamondoids with tens of carbon atoms have been extracted from petroleum and separated into monodisperse samples [8]. Having the same stability and light weight as fullerenes and nanotubes, these carbon nanostructures emerge as promising candidates for building blocks in future nanotechnological devices [9]. Since the size of these isolated clusters changes from 0.5 to 0.9 nm, quantum confinement effect will play an important role in their properties. However, X-ray absorption spectroscopy studies on these clusters show that bulk-related unoccupied states do not exhibit any quantum confinement [10]. Theoretically, nanodiamond with hydrogenated surface has been widely studied by first-principles calculations [11–14]. Raty et al. [12] have performed first-principles calculations to study the quantum confinement in nanodiamond. They have found that the size of diamond must be reduced to at least 2 nm to observe an increase in the optical gap. Investigations on the electronic properties of diamondoids show that the lowest unoccupied molecular orbitals do not exhibit a size dependent feature [13], which is consistent with the experimental results. Lu et al. [14] have performed *ab initio* calculations to study the electronic and vibrational properties of hydrogen terminated nanodiamond systematically and found that most of these properties show size dependent features. However, it is necessary to carry out a further investigation on the properties of hydrogenated nanodiamonds to find out whether these size dependent features are retained for larger clusters.

Nanodiamonds are promising candidates for field emitters, and extensive studies of field electron emission from nanodiamond films have been carried out during the past several years [15–19]. It has been observed experimentally that the electron emission of Si [15] and Mo [16] tip emitters could significantly be enhanced by coating with ultrananocrystalline diamond (UNCD) films. Emission from isolated diamond nanoparticle deposited onto Mo needles has also been measured experimentally [16]. However, the emission mechanism for diamond related materials is still under argument [20–24]. Furthermore, the complex structure and components of nanodiamond films result in multiple emission mechanisms, which depend upon a large number of factors. It is very difficult to know which factor is truly important in the field emission for nanodiamond films. Theoretical investigations on the emission property for a single diamond nanoparticle will be helpful to reveal the emission mechanism for nanodiamond.

In this work, we have performed first-principles density functional theory (DFT) calculations on the structure and electronic properties for hydrogen terminated nanometer-sized diamonds, whose diameters vary from 0.5 nm to 1.3 nm. The unique size dependent feature for hydrogenated nanodiamonds, compared to Si nanoparticles, is presented. Particularly, we have theoretically investigated the field emission properties for nanodiamonds and try to reveal the corresponding field emission mechanism.

2. Theoretical details

In our calculations, eight hydrogenated nanodiamonds with different sizes were selected. These nanoparticles were chosen from the diamondoids with high symmetries, which were similar to what had been reported by Dahl et al. [8]. Details about the structures of these clusters are given in Table 1.

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Table 1
Symmetry, diameter and carbon bonding environment for each nanodiamond.

Cluster	Symmetry	Diameter (nm)	Percentage (%)[a]		
			C − C	C − H	C − H_2
$C_{10}H_{16}$	T_d	0.5	0	40	60
$C_{14}H_{20}$	D_{3d}	0.65	0	57	43
$C_{26}H_{32}$	T_d	0.73	23	31	46
$C_{29}H_{36}$	T_d	0.73	17	41	41
$C_{35}H_{36}$	T_d	0.85	14	69	17
$C_{66}H_{64}$	T_d	0.98	39	24	36
$C_{87}H_{76}$	T_d	1.11	40	32	28
$C_{147}H_{100}$	T_d	1.29	48	35	16

C − C means the carbon atom is bound to four other carbon atoms, C − H the carbon atom is bound to one hydrogen atom, and C − H_2 the carbon atom is bound to two hydrogen atoms.

[a] Percentage of carbon atoms with different bonding environments.

Geometric optimization was performed to make all the structures fully relaxed before the electronic property calculation. Both geometric optimization and electronic property calculation were performed by DMol3 program [25,26] (module from MATERIALS STUDIO software package of Accelrys Inc.). In our DFT calculations, the all-electron Kohn–Sham wavefunctions were expanded in the local atomic orbital basis set represented by the double numerical polarized basis set with an orbital cutoff of 3.7 Å. The generalized gradient approximation with the Perdew–Burke–Ernzerhof [27] correlation gradient correction was used to describe the exchange and correlation energy in all calculations, which had been demonstrated to have a precise calculation on nanodiamond [12,13] and Si cluster [28]. Self-consistent field procedure was done with a convergence criterion of 10^{-6} hartree, and optimization of the structure was done until the change in energy was less than 10^{-5} hartree. These conditions allowed us to find the ground state geometric and electronic structure accurately.

In order to study the field emission properties for a hydrogenated nanodiamond, a uniform electric field was applied perpendicular to the (111) surface of the nanodiamond, and then the electronic properties under electric field were computed. Similar theoretical investigation on the emission properties of carbon nanotubes [29,30] had been successfully carried out. Recently, the emission properties of water adsorbed [31] and nitrogen doped [32] carbon nanotubes had also successfully been studied using the same theoretical method.

The emission current of a hydrogenated nanodiamond was calculated using the method presented by Khazaei et al. [33], which was based on the first-principles results. This calculation had been successfully performed to study the emission current of carbon nanotubes [34,35]. In this method, currents along individual grid lines were calculated according to the DFT results, and then the total current was obtained by summing the currents along these grid lines. The details of this calculation can be found in Ref. [33].

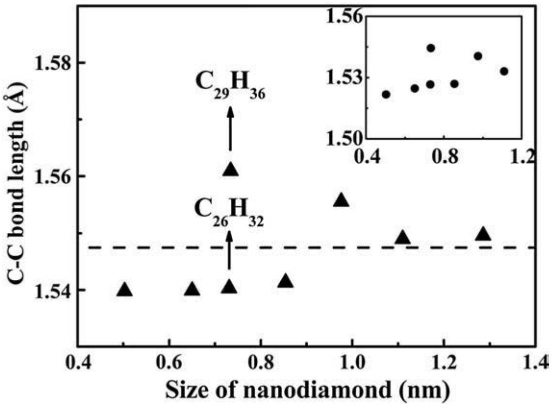

Fig. 1. Average length of C − C bond as a function of the diameter for nanodiamond. The dashed line denotes the value of C − C bond length for diamond. The inset shows the results calculated with local density approximation.

3. Results and discussion

3.1. Properties of isolated hydrogenated nanodiamond

Eight hydrogenated nanodiamonds are relaxed without constraint, and the average lengths of C − C bonds of these clusters are calculated. According to the previous results reported by Lu et al. [14], the average lengths of C − C and C − H bonds increase slightly with increasing cluster size. However, their work only focuses on the isomers of diamondoids with small sizes. For comparison, clusters ($C_{10}H_{16}$, $C_{14}H_{20}$, $C_{26}H_{32}$ and $C_{35}H_{36}$) with small sizes are also investigated in our study. The average lengths of C − C bonds for these clusters are all about 1.54 Å according to our calculation. When the size of the cluster increases, a slightly increase in average bond length is found, which is consistent with Lu et al.'s results [14]. However, other clusters with large sizes we have studied do not show such a feature. For these larger clusters, their average bond lengths are about 1.58 Å, which is about 2% longer than that of bulk diamond. In particular, the cluster $C_{29}H_{36}$ exhibits the longest average C − C bond length according to our calculation, which is much longer than that for the cluster $C_{26}H_{32}$, although both clusters have similar sizes of about 0.73 nm (Fig. 1). In order to check the reliability of our present calculation, we have relaxed these clusters using DFT software package ATK [36–38] with self-consistent pseudopotential method and double-ζ polarized basis set. The local density approximation (LDA) is employed in this calculation, and the calculated average C − C bond lengths for diamond clusters are shown in Fig. 1 (inset). Although a different method is used, the same trend in the average bond lengths is found, which shows the reliability of our calculation. This result implies that

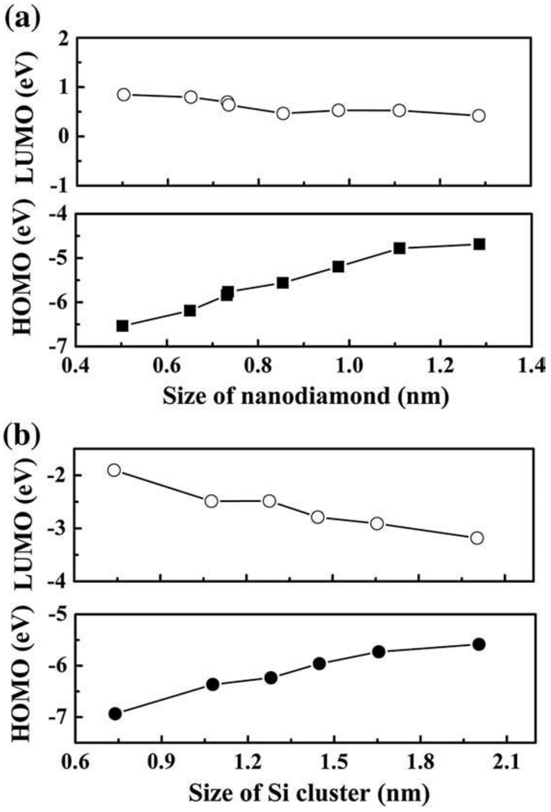

Fig. 2. Energy levels of HOMO and LUMO for nanodiamond (a) and Si cluster (b) versus the diameter of the nanoparticles. The zero point in the energy axis is fixed to the vacuum level.