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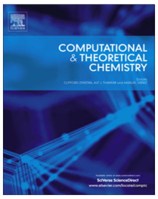

# Surface and size effects on the charge state of NV center in nanodiamonds

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ABSTRACT

Electronic structures and stability of nitrogen–vacancy (NV) centers doped in nanodiamonds (NDs) have been investigated with large-scale density functional theory (DFT) calculations. Spin polarized defect states are not affected by the particle sizes and surface decorations, while the band gap is sensitive to these effects. Induced by the spherical surface electric dipole layer, surface functionalization has a long-ranged impact on the stability of charged NV centers doped in NDs. $NV^-$ center doped in DNs is more favorable for n-type fluorinated diamond, while $NV^0$ is preferred for p-type hydrogenated NDs. Therefore, surface decoration provides a useful way for defect state engineering.

## 1. Introduction

Nanodiamonds (NDs) have high surface areas and tunable surface structures with intriguing mechanical and optical properties [1]. Those NDs containing impurities and defects are also of considerable interest in both fundamental and application aspects. Nitrogen–vacancy (NV) center in diamond has attracted intense experimental and theoretical studies recently due to its outstanding electronic and magnetic properties, including electron spin resonance [2], Rabi Oscillation [3], single-photon source [4,5], two-qubit operation [6,7], quantum communication [8] and computation [9,10].

An NV center is composed of a vacancy with one adjacent carbon atom replaced by a nitrogen atom [11–13], as shown in FIG 1a. Commonly, two various kinds of charge states, neutral $NV^0$ and negative $NV^-$ centers, have been observed experimentally, which can be discriminated by their photoluminescence spectrum and interconvert each other with laser excitation [14]. The $NV^0$ has an unpaired electron and is paramagnetic, while $NV^-$ has an $S = 1$ ground state. In high-purity diamond, the $NV^-$ state dominates. Since different charge states lead to different magnetic properties, it is very desirable to control the charge state of NV centers. Our recent theoretical work [15] has proved that surface functionalization can induce a nondecaying long range effect via a surface dipole layer localized on the diamond surface to control the relative stability of NV centers doped in diamond.

Most recently, NDs hosting the NV centers have been demonstrated experimentally as ultrasensitive magnetometers [16,17]. More interestingly, many experimental studies have shown that the photoluminescence properties of the NV centers are affected by the particle sizes [18–20] and surface decorations [21–24] in NDs. Particle size may also have an effect on the relative stability of NV centers [20]. To understand these experimental observations, a theoretical study on the electronic structures and stability of the NV centers doped in NDs is very desirable.

In the present work, we have investigated electronic properties and stability of the NV centers doped in NDs via first-principles calculations, and found that intrinsic properties of the NV centers are independent of the particle sizes and surface decorations of NDs. Surface functionalization in NDs has a long-rang impact on the stability of charged NV center in diamond. In detail, n-type fluorinated diamond surface is more conducive to form negatively charged $NV^-$ center compared to p-type hydrogenated surface, which relatively favors the neutral $NV^0$ counterpart.

## 2. Theoretical models and methods

It is well known that atomic structures and electronic properties of NDs depend strongly on their particle sizes and surface decorations [25–27]. In this work, different NDs in diameter from 0.5 nm to 2.5 nm are considered (Fig. 1b–d, for example). Initial spherical structures are cleaved from bulk diamond, and then dangling bonds on the surfaces are passivated with hydrogen atoms, denoted as p-type hydrogenated NDs. Several n-type fluorinated NDs [28,29] are also studied. We put the NV centers in the center of NDs in order to facil-

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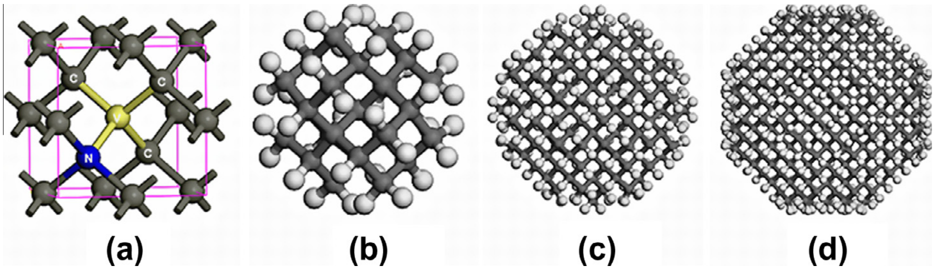

**Fig. 1.** Atomic structures of (a) the NV center in bulk diamond and hydrogenated NDs, (b) $C_{29}H_{36}$, (c) $C_{293}H_{172}$ and (d) $C_{705}H_{300}$. Yellow, white, gray, and blue balls denote vacancy, hydrogen, carbon and nitrogen atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

itate the calculations and comparisons, though they are more stable close to the surface in diamond [15]. In fact, when the NV centers are close to the surface of NDs, the doping depths are also weakly affected their relative stability.

First-principles calculations are based on the density functional theory (DFT) implemented in the SIESTA [30] package. The local spin density approximation (LSDA) [31] is chosen due to its good description of electronic and magnetic properties of the NV centers in diamond [32–34]. Test calculations under the generalized gradient approximation of Perdew, Burke, and Ernzerhof (GGA-PBE) [35] give similar results [32]. All the elements have a double zeta plus polarization orbital basis (DZP) to describe the valence electrons within the framework of a linear combination of numerical atomic orbitals (LCAO) [36]. Atomic coordinates are relaxed using the conjugate gradient (CG) algorithm [37] until the energy and force are less than $10^{-4}$ eV and 0.02 eV/Å, respectively.

As a benchmark, we have checked the electronic and magnetic properties of NV centers doped in bulk diamond (Fig. 2). A large $4 \times 4 \times 4$ supercell with 512 carbon atoms is chosen to make the concentration of NV centers as low as possible. The obtained results are fully agree with previous theoretical calculations [32]. Both $NV^0$ and $NV^-$ centers in diamond are spin-polarized with magnetic moments of 1.0 and 2.0$\mu_B$, respectively. Three carbon atoms and one nitrogen atom around the vacancy center take a tetrahedral configuration, leading to four states, two fully symmetric $a_1$ states (one of them lies deep in the valence band of diamond), and two doubly degenerated $e_x$ and $e_y$ states in the $NV^-$ center. These two degenerate states are split in $NV^0$ due to the Jahn–Teller effect [33].

In order to evaluate the stability of NV center doped in NDs, the formation energy [38–41] is defined as

$$E_{form} = E_{doped} - E_{pure} + 2 * \mu_C - \mu_N + q * \mu_e \tag{1}$$

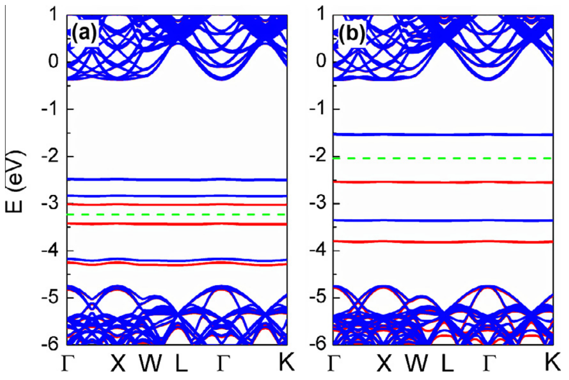

**Fig. 2.** Electronic band structures for (a) $NV^0$ and (b) $NV^-$ centers in bulk diamond in the $4 \times 4 \times 4$ supercell. The red and blue color lines represent spin-up and spin-down states, respectively. The Fermi level is denoted by green dotted lines. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

where $E_{pure}$ and $E_{doped}$ represent the diamond total energy before and after the doping of an NV center with a charge state $q$, respectively. $\mu_C$ and $\mu_N$ represent the chemical potential of carbon and nitrogen, which are determined by bulk diamond and nitrogen molecule, respectively [42,43]. $\mu_e$ represents the electron chemical potential of diamond hosting NV centers, which mainly depends on the chemical environment in experiments [40]. In this study, it is aligned with the degenerated $NV^-$ energy level ($e_x$ or $e_y$) in the spin-up channel, because the $NV^-$ defect is stable when $\mu_e$ is above this defect level [40].

## 3. Results and discussion

First, we check atomic structures and electronic properties of different NDs. The results (Fig. 3) show that the HOMO–LUMO band gaps (the highest occupied molecular orbital energy minus the lowest unoccupied molecular orbital energy) are decreased when increasing the diameter in both hydrogenated and fluorinated NDs, agreeing well with previous experimental and theoretical studies in NDs [44–48]. Our calculated band gap of bulk diamond is 4.33 eV, which is smaller than experimental value of 5.47 eV [49], due to the underestimate originated from DFT calculations [50]. Due to the outer surface effects [48], the band gaps of hydrogenated and fluorinated NDs are decreased to smaller than that of bulk diamond when their diameters are increased to larger than 2.5 and 2.2 nm, respectively. Additionally, band gaps of NDs are also decreased when modifying chemical surface terminations from hydrogen (p-type) to fluorine (n-type). It is worth mentioning that parts of fluorinated NDs are unstable and tend to reconstruct with C═C double bonds and carbon dangling bonds, showing high chemical activity on the surfaces, which are not considered in this work.

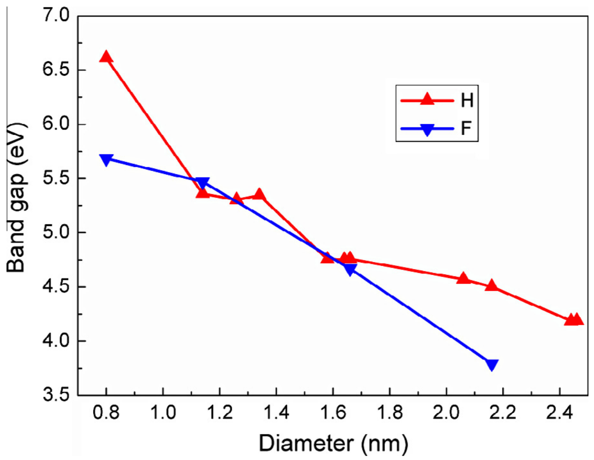

**Fig. 3.** The HOMO–LUMO band gap change when increasing the diameter sizes and modifying chemical surface terminations from hydrogen (H) to fluorine (F) atoms in NDs.

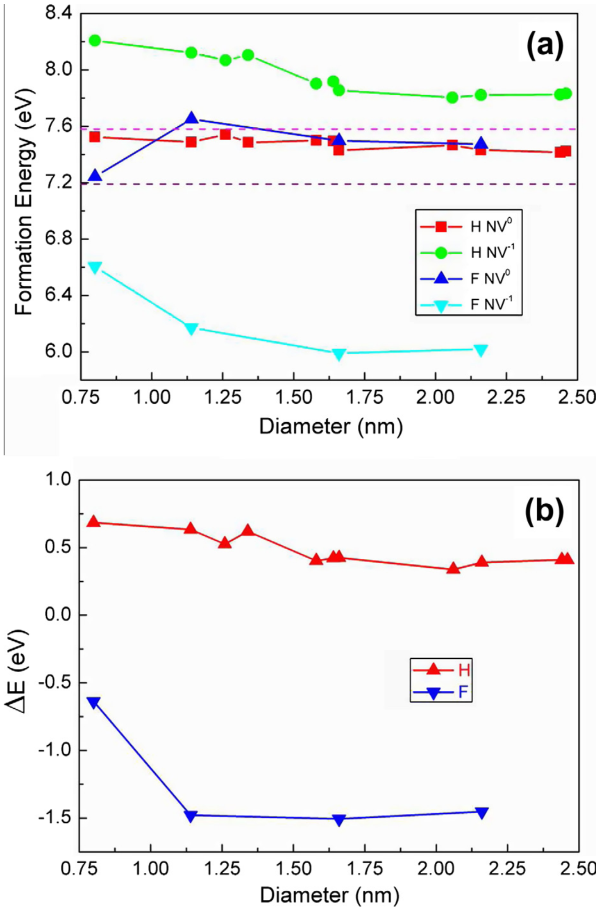

**Fig. 4.** (a) Formation energy $E_{form}$ for NV$^0$ and NV$^-$ centers in hydrogenated (H) and fluorinated (F) NDs. (b) Formation energy difference $\triangle E$ between NV$^0$ and NV$^-$. $E_{form}$ of NV centers doped in bulk diamond is marked by horizontal dashed lines ($E_{form}$(NV$^0$) = 7.58 eV and $E_{form}$(NV$^-$) = 7.19 eV).

Then, electronic and magnetic properties of the NV centers doped in NDs are studied. The NV centers doped in NDs are spin-polarized with magnetic moments of $1\mu B$ and $2\mu B$ for NV$^0$ and NV$^-$, respectively, which are in good agreement with our calculated electronic band structures and previous theoretical studies on NV centers doped in bulk diamond [13,32]. Furthermore, intrinsic properties (local defect states) of the NV centers doped in NDs are independent of their particle sizes and surface decorations, which is consistent with experimental measurements [18,23].

More interesting, Fig. 4 shows that the formation energy of the NV$^-$ center doped in NDs can be decreased when increasing the diameter sizes or changing the surface terminations from hydrogen to fluorine atoms, but both of which have no effects on the stability of its NV$^0$ counterpart. The ratio of the concentration of NV$^-$ and NV$^0$ depends on the formation energy difference ($\triangle E = E_{form}$(NV$^-$) − $E_{form}$(NV$^0$)), according to the following relationship:

$$\frac{[NV^-]}{[NV^0]} \propto exp\left(-\frac{\triangle E}{kT}\right) \qquad (2)$$

where $k$ is the Boltzmann constant and $T$ is the temperature. For hydrogenated NDs, $\triangle E > 0$, but in case of fluorinated ones, $\triangle E < 0$. Therefore, the n-type fluorinated diamond surface is more conducive for NV$^-$ formation in NDs. On the contrary, the p-type hydrogenated surface is favorable to form NV$^0$ centers. That is why a $[NV^-]/[NV^0]$ ratio inversion can be observed experimentally when modifying the surface terminations from p-type to n-type [22].

Moreover, when the diameter sizes of NDs are increased, $\triangle E$ of the NV centers doped in hydrogenated NDs trends to decrease slowly. Thus, the $[NV^-]/[NV^0]$ ratio could slightly increase with the diameter sizes, which are good agreement with experimental results [23]. But, when the diameter sizes are increased to larger than 1.5 $nm$, the $\triangle E$ remains unchanged, which indicates that the different behavior of NV$^-$ compared to NV$^0$ is caused by a surface-decoration sensitive long-range effect. By long-range, we mean that this effect does not decay theoretically [15].

The long range effect can be understood in terms of a simple model based on surface electric dipole layers induced by the partially ionic bonds on the surfaces [51], which can generate an electric potential

$$\phi(\vec{r}) = -\frac{p}{4\pi\varepsilon}\int_S \frac{\vec{r}' - \vec{r}}{|\vec{r}' - \vec{r}|^3}\cdot n\, dS' \qquad (3)$$

where $p$ and $\varepsilon$ represent the electric dipole moment per unit area on the surfaces and the dielectric constant of diamond, respectively. Other integration parameters are plotted in Fig. 5a clearly. In this work, we adopt spherical surface electric dipole layer. The electric field is zero inside spherical surface, where the electric potential

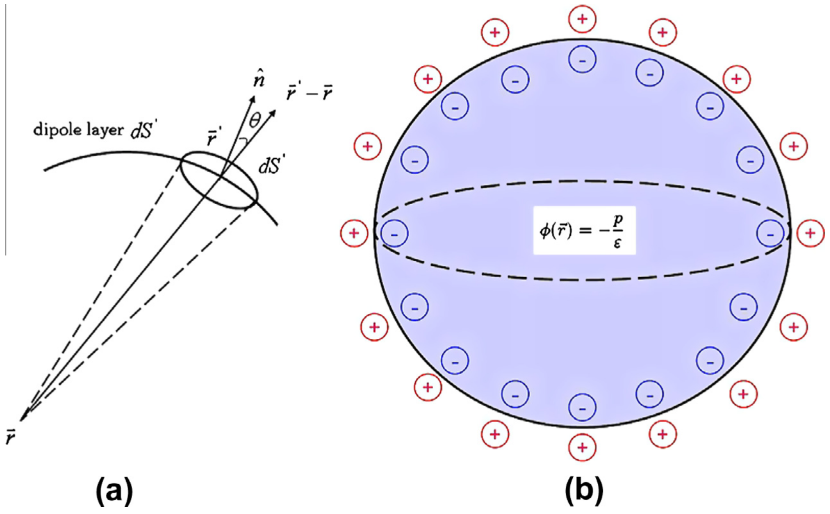

**Fig. 5.** Electric potential jump produced by (a) a surface electric dipole layer and (b) spherical surface electric dipole layer.

is unchanged. Seen from Fig. 5b, the electric potential shift inside spherical NDs can be calculated as

$$\phi(\vec{r}) = -\frac{p}{\varepsilon} \tag{4}$$

Therefore, spherical surface dipole layer is ready to provide a long-range effect on the stability of charged defects, which is independent of the diameter sizes in NDs and only depends on the electric dipole moment on the surfaces. That is why the formation energy of the $NV^-$ center doped in NDs is affected by surface decorations. In addition, the stability of the $NV^0$ center doped in NDs is found to be almost independent of surface decorations in NDs due to its zero-charge feature. It must be pointed out that the ND diameters actually have a weak impact on the formation energy of the NV centers doped in NDs, especially the $NV^-$ center doped in hydrogenated NDs, because effective electric dipole moment on the surfaces is decreased slightly if increasing the diameter sizes of NDs when the diameter is small [20].

## 4. Summary and conclusions

In summary, we have investigated electronic structures and stability of NV centers doped in diamondoids by first-principles DFT calculations, and found that the intrinsic nature of the NV centers doped in NDs is independent of their diameter sizes and surface decorations, but which seriously affect band gaps of NDs. Interestingly, surface functionalization can be used to control the stability of charged NV centers doped in NDs in a nondecaying long-range way. This investigation makes an important contribution to the development of promising applications of NV centers for potential diamond-based electronic devices.

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