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Theoretical study of chromium and nickel-related luminescence centers in molecular-sized nanodiamonds

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ABSTRACT

The present work is focused on explanation and description of recently discovered chromium and nickel-related luminescence centers in molecular-sized nanodiamond (ND) particles. Chromium and silicon–nickel luminescence centers can be leading candidates for future quantum devices thanks to their room temperature operation, photostability, narrow bandwidth and short lifetime. On the other hand such nanoparticles can be used for biolabeling. Here, we used Density Functional Theory (DFT) and time-dependent DFT (TD-DFT) techniques to investigate the defects' geometrical parameters, absorption spectra, charge and spin density distribution — we show connections between chemical and optical properties of investigated defects in nanodiamond particles. By fundamental interpretation of chromium and silicon–nickel nanodiamond luminescence centers specificities we suggest appropriate technological steps towards nanodiamond future applications.

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1. Introduction

Among the wide range of carbon allotropes, diamond is by itself a unique material which, due to its outstanding properties can be used in the fields of electronics and biotechnology [1–10]. Diamond is usually recognized by its peculiar exceptional physical and chemical properties such as: high hardness, exceptional thermal conductivity, excellent optical properties, electrochemical inertness and biocompatibility [10–12]. In addition, from the point of view of bioapplications, available with variable sizes in nanoscale (diamond nanoparticles (NDs)) [13] diamond surfaces provide a convenient platform for bioconjugation. Recent investigations demonstrate nanodiamond particles as promising platform for in vivo bio-labeling [14,15].

One of the unique interesting physical features of specifically modified nanodiamonds is their ability of extremely intense single-photon fluorescence [16–18]. Inherent photoluminescence is emanated from structural defects and impurities. Nowadays, alternative centers with narrow emission lines, which can be operated even at room temperature, suitable for microcavity integration, are required. Luminescent centers based on the metal atoms (Ni, Cr) implanted into the nanodiamond particles have been studied as reasonable candidates.

Transition metals, especially nickel, are common impurities in synthetic high pressure high temperature (HPHT) diamonds [19–21]. Specific nickel–nitrogen centers NE8 [22] can play role of single photon emitter, due to its short lifetime (2 ns) and sharp luminescent peak observed at room temperature. Recently discovered centers containing both Ni and Si [19] possess a strong luminescence with a narrow bandwidth which makes them highly prospective for many applications.

Chromium-based single-photon emitters were initially discovered by growing nanodiamond crystals on a sapphire substrate [23]. Chromium is a regular impurity in sapphire, which can be integrated into a nanodiamond crystal during the chemical vapor deposition (CVD) growth. Chromium originated luminescence centers are attractive due to their room temperature narrow bandwidth emission. It has been shown that Cr emitters can be successfully fabricated by ion implantation of chromium with oxygen, sulfur or boron atoms [23,24]. Cr-containing luminescence centers have very short emission lifetimes — from 1 to 4 ns, whereas NV centers have emission lifetimes an order of magnitude longer: NV^0 — 29 ns, NV^- — 13 ns [25].

In the present work we focused on explanation and description of recently discovered chromium and nickel related ND centers optical properties. Many attributes of Ni- and Cr-containing luminescence ND defects (e.g. atom positions, chemical interactions, charge, spin multiplicities) remain to be uncertain, thus here we report the step towards an understanding such complex systems by means of quantum chemical modeling.

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Based on previous results and experiences [2,5,26,27] we have used the Density Functional Theory (DFT) to model main parameters influencing the Ni- and Cr-related ND luminescence center properties: structure, lowest-lying excitation energy, charge distribution, density of states, components of the main orbitals involved in the excitation processes. It has to be noted that similarly to the well-known Si diamond defects Cr and Ni atoms due to their size tend to be in a semi-divacancy state between two carbon vacancies [28]. The aim of the present research is the modeling of influence of metal defects on optical properties by computationally demanding TD-DFT technique. Such luminescent defects have shown local character [5] and therefore calculations on model clusters can help in understanding of optical properties and suggest steps towards practical applications.

2. Materials and methods

TD-DFT technique was previously used for the analysis of optical properties of approximately 100 atoms containing ND particles with neutral and negatively charged vacancy-related ND point defects (N_2V^0, N_2V^-, and N_3V^0) by A. S. Zyubin et al. [29] and for the study of nitrogen-vacancy and silicon carbide divacancy defects in diamond having 147 host crystal atoms [30]. TD-DFT method was also used to calculate Stokes-shift for NV center in 1.1–1.3-nm nanodiamonds [14]. In the present work the quantum chemical calculations of the geometric structures and several low-lying excited states have been performed on clusters having about 100 carbon atoms (more than 170 atoms altogether).

The electronic structures of nanodiamond particles containing various luminescent centers have been modeled using finite clusters of different sizes, terminations and charge states. The ND particles surfaces were terminated by hydrogen. As far as the lattice defects are concerned, we studied in detail the incorporation of Cr, Ni, O, S, B and Si atoms and nitrogen-vacancy embedded into a ND particle. All of the clusters were fully optimized by the DFT procedure.

The electronic structures of all the systems examined were calculated by DFT methods using the Gaussian 09 [31] program package. A hybrid Becke's three-parameter hybrid functional B3LYP [31,32] containing a mixture of exchange-correlation with Hartree–Fock exchange which provides a reasonable description of spectral properties of similar systems [5] was used. Open shell systems were treated by the unrestricted Kohn–Sham (UKS) procedure. The geometry optimizations and spectral calculations were carried out without any symmetry restriction. The bandgap value using the B3LYP exchange correlation functional for abovementioned clusters was about 7.4 eV, which correlated to the previously reported results for the same computational method [34]. The bandgap widening is associated with the quantum dimensional effect [35].

For geometry optimization and spectral calculations, 6–31G(d) Pople split-valence polarized double-ζ basis including core electrons was used. The bond orders were characterized by the Wiberg bond indexes [36]. Bond orders between atoms in luminescent centers defined by Wiberg indices simply mean bond multiplicity — the number of bonds between atoms. In our models, we have introduced perturbation close to the center of the particles so that neither vacancy nor Ni (Cr) was on the particle surface.

Electronic excitations were calculated by time-dependent DFT (TD-DFT) at optimized geometries. TD-DFT is an extension of DFT determined to investigate the excited states and non-equilibrium properties of many-body systems in the presence of time-dependent potentials. This method enables the analysis of the character and localization of individual excited states [37,38] (Tamm–Dancoff approximation (invoked in Gaussian09 by keyword TDA) was not used). Geometry optimizations have been performed for several charge states and multiplicities of given system in order to find the lowest energy structures. The following convergence criteria were set: The maximum force of 0.00045 atomic units (a.u.) for geometry convergence and the energy difference of 10^{-8} a.u. for convergence of the SCF iterations. The most energetically favorable states, which possess strong transition at particular region, are presented. DFT methods have also been used for calculations of the optical gap, absorption spectrum and luminescence of small Si nanocrystals, with hydrogen and oxygen at the surface [33,39]. The effect of the size of clusters up to $C_{696}H_{300}N_1$ was modeled in [39] and we found that their electronic properties are very close to clusters containing around hundred carbon atoms. UV–vis spectra were simulated using Gaussian (3000 cm^{-1} fwhm) functions.

3. Results and discussion

First step of the present research was the investigation of the structure of Cr-related luminescent centers in nanodiamond particles. It was experimentally [20,21] shown that the presence of nitrogen is crucial condition for creating chromium-based luminescent centers. Increment in the emitters' number and the best intrinsic luminescence properties of optical chromium related centers in nanodiamond was achieved by implantation of Cr ions followed by implantation oxygen, sulfur, boron or nitrogen. Subsequent annealing increases the probability of luminescent center formation [20,21]. Owing to relatively low energies of ion implantation (order of 10's keV), irradiated atoms imbedded close to the surface and atoms or groups from the surface can be captured during implantation forming a large variety of defects in the close vicinity to the chromium-related centers. It has been reported [20] that presence of both oxygen and sulfur increase the yield of optically active Cr centers. Since sulfur and oxygen have similar electron configurations, they are expected to behave similarly when introduced into the diamond lattice. Sulfur defects in nanodiamond have been investigated as potential donors. We were looking for the best conditions for luminescence and modeling the influence of nanodiamond perturbation on the excitation spectra. The occurrence of the allowed excitation in a proper energy area is the necessary condition for luminescence in the visible region. Due to the size of the systems studied there we didn't optimize structures of all excited states and estimate the rate of internal conversion to lower excited states and therefore the estimation of the perturbation effects on emission is only qualitative.

If oxygen, sulfur or boron ions are positioned (implanted) in the immediate vicinity to chromium or nitrogen the total emission was enhanced [24,40]. In [5] we presented models of triply positively charged $C_{98}H_{72}Cr_1N_1$ clusters for ^1A, ^3A and ^5A states. It was shown that calculations on +3 charged nanodiamond provided good results for systems containing Cr and NV^0/NV^- centers [5]. Here we extend our previous work and modeled Cr containing centers with O, S or B atoms added (Fig. 1). Geometry optimizations indicate ^3A as the most stable state for all studied Cr containing clusters. Triplet states are located below the singlet states, the triplet–singlet separations are of 2.18, 0.31 and 0.99 eV for O, S or B perturbations, respectively.

Oxygen and sulfur containing ND were found to be triply charged, ND containing boron was doubly charged. For all types of defects Cr atom has total Wiberg index between 3.65 and 4 i.e. Cr is placed in the double vacancy cavity. Spin density for $C_{98}H_{72}Cr_1N_1O_1$ (Fig. 2) shows that unpaired electrons are localized at the metal center and its closest vicinity — Cr containing ND center should be paramagnetic. Similar picture was found in the case of clusters containing the Cr–N–S and Cr–N–B centers.

Optimized geometrical parameters for Cr–N–O and Cr–N–S ND ($C_{98}H_{72}Cr_1N_1O_1$ and $C_{98}H_{72}Cr_1N_1S_1$ clusters) are listed in Table S1. Bond lengths between triply charged Cr and neighboring C atoms are in the range from 1.91 to 2.11 Å (Wiberg indexes between 0.72 and 0.52). The Cr–N bond is relatively weak but next Cr–C3 bond is even weaker (Table S1). Cr–S bond is stronger than Cr–O bond indicating that Cr–N–S center is more stable than the Cr–N–O center. In ND with Cr–N–O and Cr–N–S, the Cr^{3+} is strongly bonded to three adjacent carbons while the other bonds are weak which can cause lower interaction

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