First principles study of silicon carbide nanocrystals

Thesis Booklet

Bálint Somogyi

Supervisor: Dr. Adam Gali

Budapest University of Technology and Economics

Department of Atomic Physics

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Introduction

A very promising biological application for novel nanomaterials is fluorescent biological imaging. In fluorescent biological imaging, one or more biomolecules (such as antibodies, peptides, oligonucleotides or viruses) are chemically attached to molecule-sized fluorescent particles (biomarkers), and these bioconjugated nanoparticles can be tracked by the detection of their photoluminescence utilizing appropriate illumination sources and imaging systems. The biological imaging applications of fluorescent biomarkers can be naturally grouped into two distinct categories: *i) in vivo* applications, where the biomarkers are introduced into a biological sample which is studied under laboratory conditions (usually by the means of fluorescent microscopy), and *ii) in vivo* applications, where the biomarkers are introduced into a living organism. Compared to the more conventional imaging methods such as magnetic resonance imaging, positron emission tomography or X-ray computed tomography, *in vivo* fluorescent imaging offers a cost-effective alternative which can potentially substitute or complement the aforementioned approaches. Each biological application has its stringent set of criteria for the biomarker, creating a considerable challenge in the design and fabrication of fluorescent biomarkers. This is especially true for *in vivo* applications, where biomarkers should be non-toxic, chemically stable, and possess bright and stable fluorescence in the biological window. This biological window is the spectral region where the absorption of the blood and tissue is minimal, and the autofluorescence and Rayleigh-scattering of the body is relatively weak. This window falls into the near-infrared (NIR) region, and it is often divided into the first (650-950 nm) and second (1000-1350 nm) biological window with a recently proposed third window (1550-1870 nm) [Hemmer et al., 2016]. Originally organic dyes were utilized as fluorescent biomarkers with the Green Fluorescent Protein being the most recognized example. However, organic molecules are prone to photobleaching, i.e. they lose their fluorescent property if they are illuminated for a longer period of time, and the light induced chemical transformation often results in toxic by-products. Because of the aforementioned shortcomings of organic biomarkers, semiconductor nanocrystals (often referred as Quantum Dots) became the frontrunners for the realization of *in vivo* fluorescent agents. Compound semiconductor nanocrystals made from Group II-VI or III-V elements have exceptional photostability and very strong photoluminescent emission. The as-made nanocrystals are hydrophobic, thus their surface has to be coated by appropriate ligands in order to make them soluble. Unfortunately, none of the existing biomarkers made of compound semiconductors passes the two most important requirements for biological applications: while it is possible to fabricate quantum dots whose emission falls into the NIR region (InAs, PbSe QDs) [Michalet et al., 2005], the potential emission of toxic ions raises concerns about their *in vivo* applicability. The severity of the toxic side

effects of these compound nanocrystals is still highly debated as the outcomes of the QD toxicity assessments depend on the size and surface coating of the nanoparticles as well as the varying tolerance of different cells to QD related toxicity [Wang et al., 2013]. All in all, currently there exists no such fluorescent biomarker which would enable the safe and efficient optical tracking of biomolecules in the human body. This is the reason that while labeling cells, intracellular molecules or nuclear antigens can be considered as routine under *in vitro* conditions, the *in vivo* applications are still in the experimental stage and yet to make their ways into the medicine.

While the efforts to alleviate the toxicity of Group II-VI and III-V semiconductor nanoparticles continue, it is worthwhile to consider alternative, non-toxic materials for the fabrication of fluorescent biomarkers. Silicon carbide (SiC) is a wide band gap semiconductor, which is already widely utilized in various biological medical application due to its excellent biological compatibility [Saddow, 2016]. Few nanometer sized SiC nanoparticles can be produced by the wet chemical etching method, and the SiC nanocrystals showed excellent biocompatibility [Fan et al., 2008]. Unfortunately, optical properties of as-produced SiC nanocrystals are far from ideal for *in vivo* applications as they emit in the visible spectral region and they have poor fluorescence quantum yield ($\lesssim 1\%$). By modifying the optical properties of SiC nanocrystals, these shortcomings can be potentially overcome, resulting in ideal marking agents for *in vivo* applications.

Objectives

The primary goal of my PhD studies was to find and explore the possible ways of making the optical properties of SiC nanocrystals more suitable for *in vivo* biological imaging, without compromising their excellent biological compatibility and optical stability. To achieve this, I performed atomistic simulations which can be considered as a cost-effective complementer for the experimental research.

The introduction of certain color centers is a promising approach, where the nanocrystal serves only as a host to the point defect which is the source of the luminescence. I investigated Si-vacancy, divacancy and certain transition-metal related point defects, as the experiments performed in bulk SiC indicated their potential for NIR emission. While the introduction of the aforementioned color centers into the SiC nanocrystals remains a difficult challenge for material science, the combination of the biological compatibility of SiC nanocrystals and the strong NIR emission of the color centers has a lot of potential.

Another way to achieve NIR emission could be the introduction of donor-acceptor pairs. My goal was to investigate the effect of Al-N and B-N co-doping of SiC nanocrystals. While donor-acceptor pairs may not have as great potential for biological imaging as the

color-centers that create deep defect levels in the gap, the doping of SiC nanocrystals with B,N and Al is expected to be 3comparatively easier as large ($\sim$ 1%) concentration levels were reached in bulk samples [Muranaka et al., 2008].

My secondary goal was to investigate the effect of the nanocrystal's surface on its optical properties, focusing once again on the luminescence. While NIR emission may not be achievable just by the modification of the surface chemistry of the SiC nanocrystals, it is important to understand structure and role of the surface. This work was carried out in collaboration with the experimentalists of our research group.

Methods

As physics at the nanoscale shows significant quantum mechanical effects, the properties of molecule-sized nanocrystals cannot be predicted by classical or semiclassical computation methods. To gain insight about the physical properties of nanocrystal built up from couple hundreds of atoms, one has to solve Schrödinger's equation by an appropriately chosen approximative method. I utilized Density Functional Theory (DFT) based methods to study the properties of SiC nanocrystals, as DFT offers a good compromise between predictive power and computational cost. In particular, I performed Time-Dependent DFT (TDDFT) calculations using the PBE0 hybrid exchange-correlation functional which is known to provide reliable and relatively accurate results for Group IV semiconductors and organic molecules.

New scientific results

1. **Color centers in ultrasmall SiC nanocrystals**

   (a) I characterized various transition metal-related color centers in small (1 nm$<d<$2 nm) cubic silicon carbide nanocrystals utilizing computational methods based on density functional theory. I found that these color centers introduce deep defect levels in the HOMO-LUMO gap of the nanocrystal that are localized on the point-defects and provided a group-theoretic description of the symmetries of these states. I demonstrated that the quantum confinement effect is rather weak for these localized states, as the localization and energy of these states shows only a light dependence on the nanocrystal diameter. I also performed the same analysis for the Si-vacancy and divacancy defects and found that localized states of these intrinsic color centers also exhibit weak quantum confinement effect. I calculated the lowest dipole-allowed excitations for both the transition-metal related and the intrinsic defects utilizing adiabatic linear-response time-dependent density functional theory and the PBE0 exchange-correlation functional. The results confirmed that due to the introduction of the color-centers, the size-dependence of the optical gaps of the SiC nanocrystals becomes weak. In addition, our calculations indicated that SiC nanocrystals hosting these color centers are indeed very promising for *in vivo* biological imaging applications as their absorption edge

shifted into the NIR region which is considered the ideal biological window as the absorption and scattering of the blood and tissue is minimal in this energy range [T1,T2,T3].

(b) I determined the geometry relaxation upon excitation of the aforementioned point defects embedded into SiC nanocrystals. I obtained the excited state geometries utilizing the ΔSCF method. I also calculated the dynamical matrix, the vibrational frequencies and normal modes of these systems. This allowed the calculation of the emission lines shapes in the Franck-Condon approximation using the generating function method. I found that the absorption spectra do indeed fall into the NIR range for most of the investigated defects. I identified that the excited state relaxation and vibrational broadening shows a rather drastic size-dependence for the divacancy defect, at least for small nanocrystals. I also calculated the radiative lifetimes of these systems and found that the introduction of point defects lowers the lifetime by orders of magnitudes compared to pristine SiC nanocrystals. I found especially fast relaxation rate for the negatively charged Si-vacancy defect, indicating that the brightness of SiC nanocrystals containing Si-vacancy defects can rival nanocrystals' made of direct band gap semiconductors. These result directly indicate that the introduction of various point defects can greatly enhance the otherwise relatively poor optical performance of the host SiC nanocrystals for *in vivo* biological imaging applications. The proposed color-center containing SiC nanocrystals have excellent biocompatibility, sufficiently small size and strong PL emission in the biological window.

2. **Donor-acceptor pairs in ultrasmall SiC nanocrystals**

   (a) I investigated the optical properties of SiC nanocrystal co-doped with type II Al-N and type I B-N donor-acceptor pairs. I found that similarly to the bulk case, the B_C defect introduces a rather deep acceptor level, the Al_{Si} defect a much shallower one, while N_C donor state remains very close to the conduction band edge oven for very small SiC nanocrystals. I focused on the impact of the quantum confinement effect and the donor-acceptor distance on the optical properties. Aided by density functional theory, time-dependent density functional theory and the ΔSCF method, I was able to show that first excitation energy decreases with both the nanocrystal size and the donor-acceptor distance [T4].

   (b) I utilized the ΔSCF approach to calculate the excited state geometries of co-doped SiC nanocrystals, and calculated the vibrational frequencies and normal modes. Employing the results of these calculations I determined the PL emission spectra of for both the Al-N and B-N donor-acceptor pair. Combining these results with the previously determined trend regarding the size dependence of the optical properties, I conclude that SiC nanocrystals co-doped with B-N are very promising for applications in *in vivo* biological imaging.

3. **Anhydride formation on the surface of SiC nanocrystals** My calculations confirmed that the experimentally observed change in the IR spectra and PL emission of SiC nanocrystals upon annealing the samples over 370 K can indeed be explained by the formation of anhydride groups from neighboring carboxyl groups on the surface of SiC nanocrystals. I calculated the IR density of states for various possible anhydride configurations, and identified that the measured IR double band originates from carboxyl groups bonding to (111) facets of the SiC nanocrystal. Utilizing density functional theory, I was able to demonstrate the impact of deprotonated carboxylate groups on the optical properties which explained the blue-shift experienced at higher temperatures [T5].

4. **Optical properties of SiC nanocrystals with different surface chemistries** Utilizing density functional theory and time-dependent density functional theory, I investigated the surface-chemistry dependence of the optical properties of SiC nanocrystals. I showed that Si-OH groups do not play an important role in the emission spectra, while C-OH groups introduce a relatively deep defect level above the HOMO of the nanocrystal. In addition, I demonstrated that the substitution of Si-OH groups by Si-COOH groups further reduces the optical gap even though the surface related defect level remains localized on the C-OH groups. I was able to explain this by the charge transfer between the COOH groups and nanocrystal utilizing a simple phenomenological model. I created a model for reoxidized SiO_2-like surface of SiC nanocrystals and found that the emission of these systems are blue-shifted compared to the as-prepared samples. My results are in good agreement with the outcome of experiments performed simultaneously [T6].

List of publications

[**T1**] Near-infrared luminescent cubic silicon carbide nanocrystals for in vivo biomarker applications: an ab initio study
Bálint Somogyi, Viktor Zólyomi, and Adam Gali
Nanoscale **4** 7720-7726 (2012)

[**T2**] Introducing Color Centers to Silicon Carbide Nanocrystals for In Vivo Biomarker Applications: A First Principles Study
Bálint Somogyi, Viktor Zólyomi and Adam Gali
Mater. Sci. Forum **740-742** 641-644 (2013)

[**T3**] Transition Metal Defects in Cubic and Hexagonal Polytypes of SiC: Site Selection, Magnetic and Optical Properties from ab initio Calculations
V. Ivády, B. Somogyi, V. Zólyomi, A. Gällström, N.T. Son, E. Janzén, and A. Gali
Mater. Sci. Forum **717-720** 205-210 (2012)

[**T4**] Computational design of in vivo biomarkers
Bálint Somogyi and Adam Gali
Journal of Physics: Condensed Matter **26** 143202 (2014)

[**T5**] Chemical Transformation of Carboxyl Groups on the Surface of Silicon Carbide Quantum Dots
Zsolt Szekrényes, Bálint Somogyi, Dávid Beke, Gyula Károlyházy, István Balogh, Katalin Kamarás, and Adam Gali
The Journal of Physical Chemistry C **118** 19995-20001 (2014)

[**T6**] Identification of Luminescence Centers in Molecular-Sized Silicon Carbide Nanocrystals
Dávid Beke, Tibor Z. Jánosi, Bálint Somogyi, Dániel Á. Major, Zsolt Szekrényes, János Erostyák, Katalin Kamarás, and Adam Gali
The Journal of Physical Chemistry C **120** 685-691 (2016)

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Wang, Y., Hu, R., Lin, G., Roy, I., and Yong, K.-T. (2013). Functionalized quantum dots for biosensing and bioimaging and concerns on toxicity. *ACS Applied Materials & Interfaces*, 5(8):2786–2799.