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Calculation of structural and optical properties of silicon quantum dots: tuneable absorption energy and negative electron affinity

Ruhan Thirayathorn[1], Pairot Moontragoon[1,2,], Vittaya Amornkitbamrung[1,2], Santi Meansiri[3], Zoran Ikonic[4]*

[1]Department of Physics, Science, Khon Kaen University, Khon Kaen, 40002, Thailand.
[2]Integrated Nanotechnology Research Center (INRC), Deaprtment of Physics, Science, Khon Kaen University, Khon Kaen, 40002, Thailand.
[3]School of Physics, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand.
[4]School of Electronic and Electrical Engineering, University of Leeds, Leeds, UK.
[*]Corresponding author:mpairo@kku.ac.th (P. Moontragoon)

Abstract

The structural and optical properties of hydrogen-terminated silicon quantum dots were investigated by using the Gaussian 09 program. The models of silicon quantum dots assume that the silicon atoms are covalently bonded in diamond crystal structure, with quantum dot diameters varying from 0.8 to 1.6 nanometers. The bonds of silicon atoms at the surface were terminated by hydrogen atoms. The calculations of optimized structures and ground state electronic properties for the quantum dots have been performed using Hartree-Fock with 6-31G* basis set, and the exited states were then calculated by using time-dependent density functional theory (TDDFT) with (B3LYP) hybrid functional. The results show that the hydrogen-terminated silicon quantum dots have tuneable absorption energy, depending on particle size, and the larger particles have lower absorption energy. The calculated UV-VIS spectrum results show that with the quantum dots diameter changing from 0.8 nm to 1 nm to 1.2 nm the absorption peak moves from 5.23 eV (238 nm) to 4.68 eV (264 nm) to 4.03 eV (308 nm). Moreover, the hydrogen-capped silicon nanocrystals also show negative electron affinity (NEA).

Keywords: *Optoelectronics, Colloidal silicon quantum dots, Negative electron affinity.*

1. Introduction

In recent years, colloidal quantum dots (QDs) based on different elements and compounds have attracted intensive research effort for their unique properties, i.e. the energy spectrum of quantum dots can be engineered by controlling the geometrical size, shape, and the strength of the confinement potential. Therefore, they can be used in many applications, such as therapeutic applications as drug delivery agents, bio-imaging luminescent markers, or for targeted cell destruction, and in optoelectronic devices [1-5]. Quantum dots can be fabricated in various ways, such as self-assembled quantum dots by using molecular beam epitaxy (MBE) or metallorganic vapor phase epitaxy (MOVPE), lithography or etching, and organic synthesis [6-7]. However, a possible disadvantage of some dot types is that they are made of materials with high toxicity, e.g. cadmium sulfide, cadmium selenide, and their lead-containing counterparts. Silicon quantum dots are considered as one of promising candidates in this respect, because the material is inexpensive, relatively abundant, non-toxic and it has dominated the microelectronics and photovoltaics industry for many decades. Furthermore, there are recent reports of very high photoluminescence quantum yields, novel synthesis routes, colloidal stability, and absence of cytotoxicity of silicon quantum dots. Therefore, many researchers have studied applications of silicon quantum dots in transistors, solar cells, light emitting diodes (LED), and diode lasers. They have also studied the possibility of using silicon nanoparticles as agents for medical imaging, and as qubits in quantum computing [8-9]. In addition, by combining low dimensional quantum effects and surface engineering, one can overcome the largest weakness of bulk silicon in optoelectronic applications, which is a small absorption coefficient, or a very small emission efficiency, because it is an indirect band gap semiconductor. For example, significant enhancement of light emission efficiency can be accomplished for silicon quantum dots with a size of about 5 nm or less, because of a strong confinement of electrons therein [10-11].

2. Materials and methods

In this work, the structural and optical properties of hydrogen-terminated silicon quantum dots were investigated by using the Gaussian 09 code [12]. The silicon quantum dots model adopted here assumes that silicon atoms are covalently bonded, having a diamond crystal structure, with the dot diameters varying from 0.8 to 1.6 nanometers, as shown in Fig. 1. The dangling bonds of silicon atoms at the surface were terminated by hydrogen atoms. The calculations of optimized structures and ground state electronic properties for quantum dots have been performed using Hartree-Fock with 6-31G* basis set, and the exited states were then calculated by using TDDFT with B3LYP hybrid functional.

3. Results and discussion

Optimized ground state structures

The optimized structure of the hydrogen-terminated colloidal silicon quantum dots are shown in Fig. 1.

LUMO-HOMO energy gaps and molecular orbital

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of larger quantum dots tend to be localised in the dot interior, while in case of smaller dots they are distributed across whole dots, as shown in Fig. 2. In accordance with typical wave function patterns for size-quantized states, in large quantum dots both the HOMO and LUMO states are localized in the interior, with almost zero amplitude on the surface. The energy spacing between HOMO and LUMO is size-dependent, i.e. the value of the energy gap decreases as the size of the dot increases, as expected, and indicating a weaker confinement for larger dot sizes, as shown in Table 1.

Table 1. HOMO, LUMO energy levels of hydrogen-passivated colloidal silicon quantum dots size of 0.8 nm, 1.0 nm, 1.2 nm, 1.4 nm and 1.6 nm respectively.

size	*HOMO (eV)*	*LUMO (eV)*	*LUMO-HOMO (eV)*
0.8 nm	-9.47	1.84	11.32
1.0 nm	-9.13	1.44	10.57
1.2 nm	-8.71	1.04	9.75
1.4 nm	-8.42	0.78	9.20
1.6 nm	-8.24	0.64	8.88

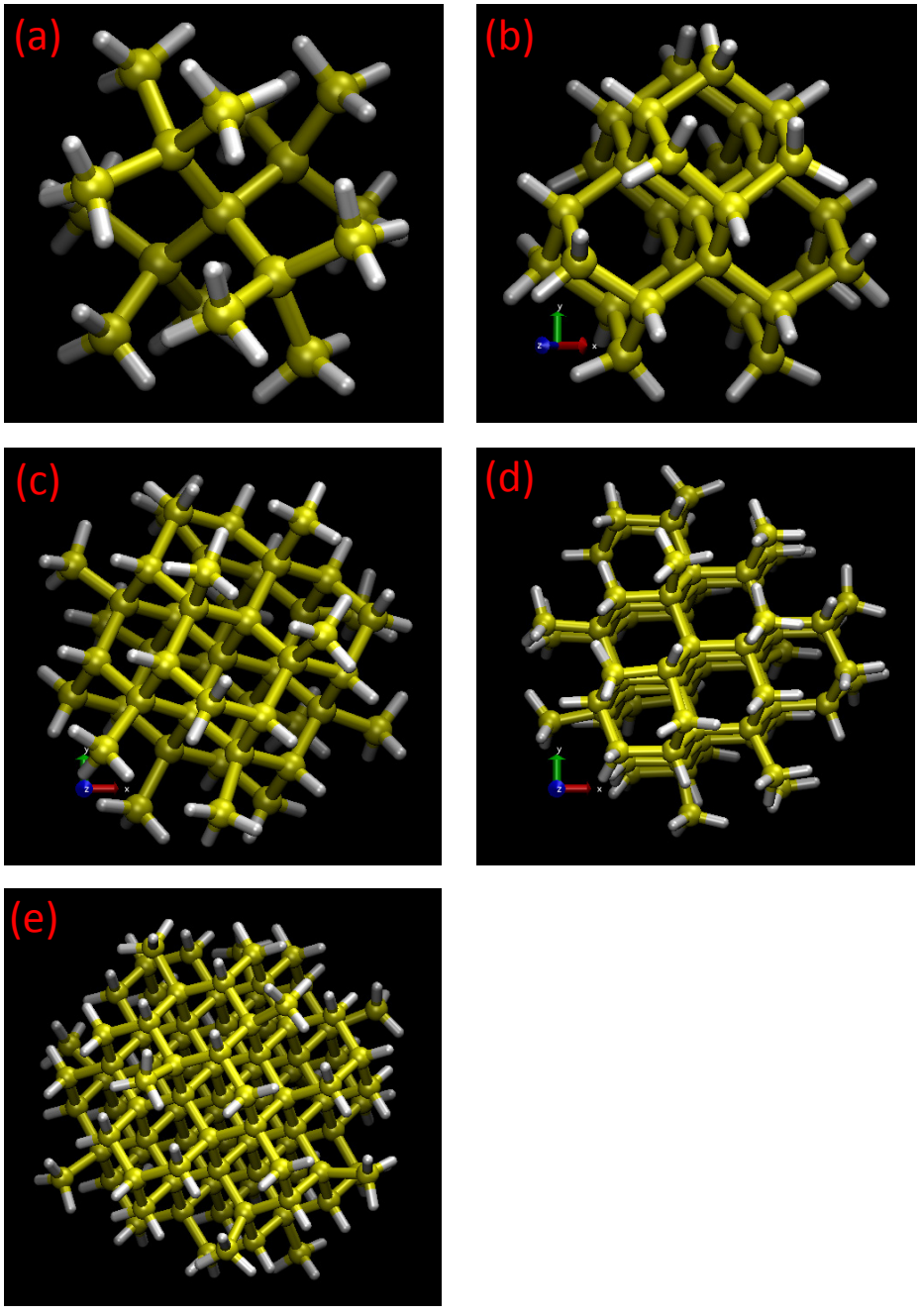

Figure 1. The hydrogen-terminated colloidal silicon quantum dots, size of (a) 0.8 nm (b) 1.0 nm (c) 1.2 nm, (d) 1.4 nm, and (e) 1.6 nm when yellow represents Si atoms and gray represents H atoms.

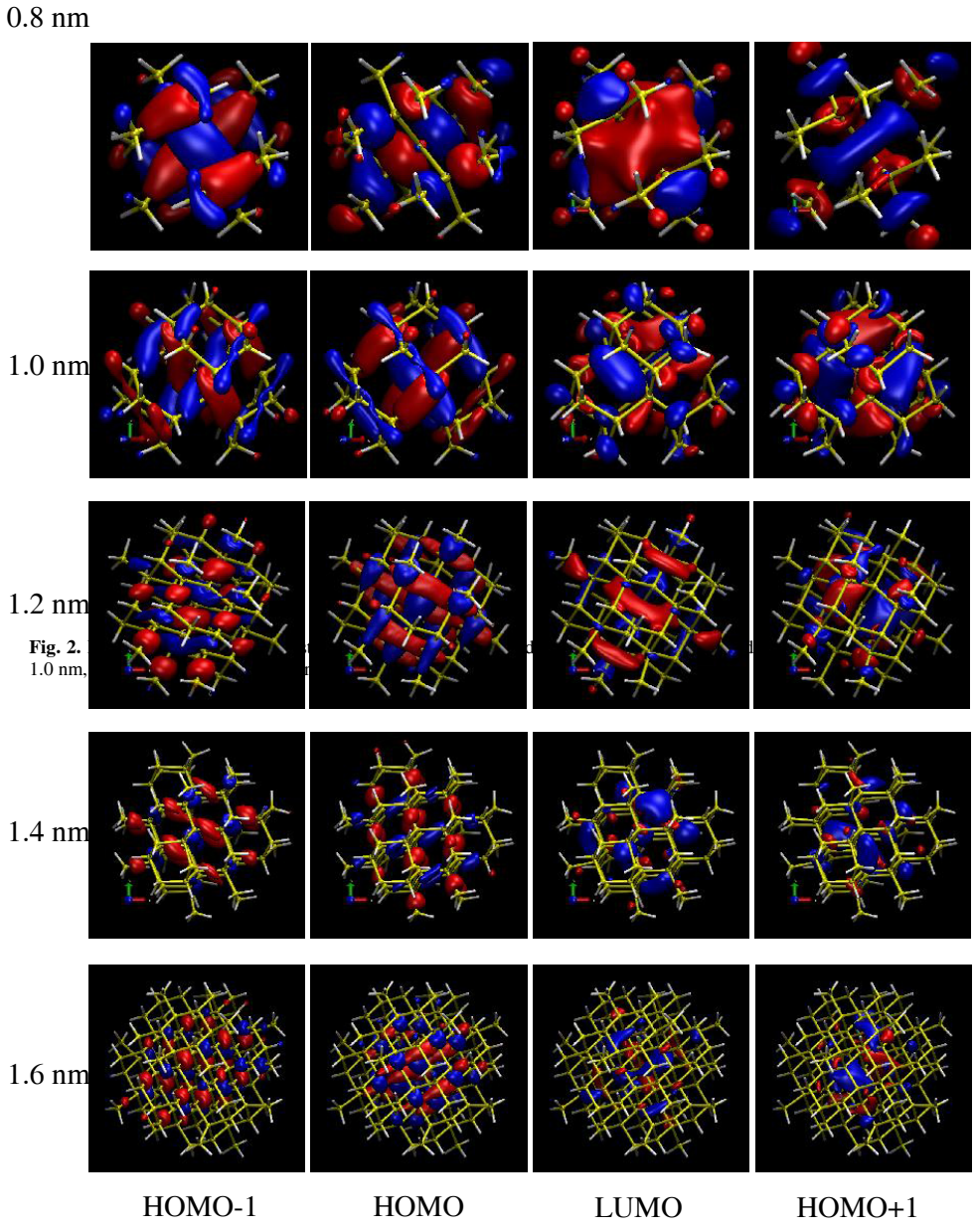

Figure 2. Molecular orbital spatial distribution of hydrogen-capped colloidal silicon quantum dots size of 0.8 nm, 1.0 nm, 1.2 nm, 1.4 nm and 1.6 nm respectively.

Electron affinity

Electron affinity defined as the amount of energy released when an electron is added to a neutral atom or molecule to form a negative ion, i.e.

$$EA = E^{N} - E^{N+1}$$

when EA EA is electron affinity energy, E^{N} is energy of neutral system and E^{N+1} is energy of negative ion system. According to Table 1, Fig. 3, calculated by using Hartree-Fock with 6-31G* basis set, and Koopmans theorem, i.e. the first ionization energy of a molecular system is equal to the

negative of the orbital energy of the highest occupied molecular orbital (HOMO), and electron affinity is equal to the negative of lowest unoccupied molecular orbital (LUMO), the silicon quantum dots show a negative electron affinity (NEA) [13]. The electron affinity energy is decreasing when size of the nanoparticle is increasing. Therefore, the silicon quantum dots may be a promising material for novel applications such as photoemitters, secondary electron emitters, and cold-cathode emitter devices.

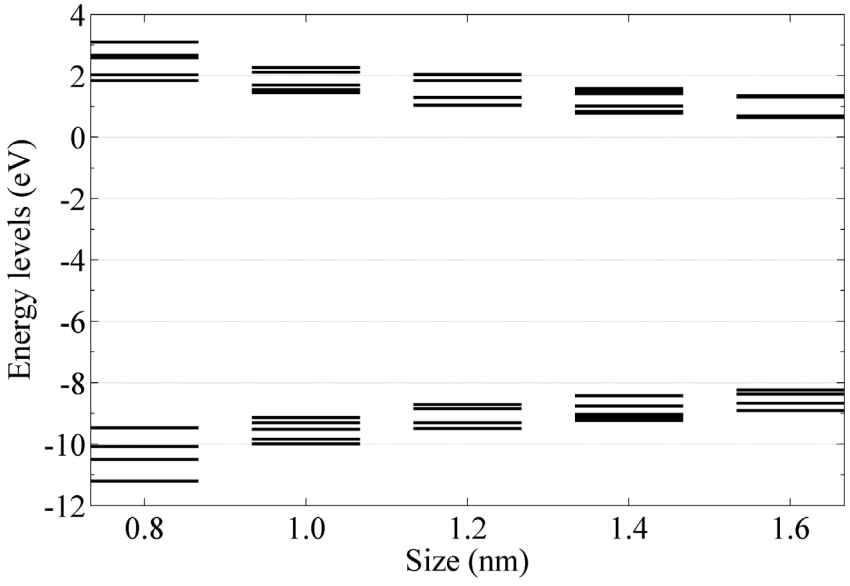

Figure 3. HOMO and LUMO energy levels of hydrogen-capped colloidal silicon quantum dots size of 0.8 nm, 1.0 nm, 1.2 nm, 1.4 nm and 1.6 nm respectively.

Electronic absorption spectra

According to the calculated results, the hydrogen-terminated silicon quantum dots have a tuneable absorption energy, depending on particle size, lower energies corresponding to larger dots, and these energies are always well above the band gap of bulk silicon, as shown in Table 2.

Table 2. The calculated wavelengths and optical transitions of hydrogen-passivated colloidal silicon quantum dots size of 0.8 nm, 1.0 nm and 1.2 nm respectively.

Size	Energy (eV)	Wavelength (nm)	Oscillation strength
0.8 nm	5.12	242.1	0.0418
	5.23	237.0	0.0013
	5.45	227.3	0.1398
1.0 nm	4.60	269.3	0.0006
	4.69	264.6	0.0029
1.2 nm	4.02	308.1	0.0403
	4.03	307.5	0.0001
	4.05	306.1	0.0054

The calculated absorption spectra (which belong to the UV range for these, relatively small diameter dots) show that quantum dots with a diameter of 0.8 nm have peak absorption at about 5.23 eV (238 nm), those with a diameter of 1.0 nm have peak absorption at about 4.68 eV (264 nm), and for 1.2 nm quantum dots this is at about 4.03 eV (308 nm), as shown in Fig. 4. It should also be noted that the oscillator strengths of various transitions are non-zero, but are generally rather small (except in one case in the smallest dot diameter considered). This indicates that, even in the absence of k-selection rule that exists in bulk, Si dots are not strongly active optical media. However, even with this limitation there still may be a scope for using the silicon quantum dots for novel applications such as bio-labeling and optoelectronic devices.

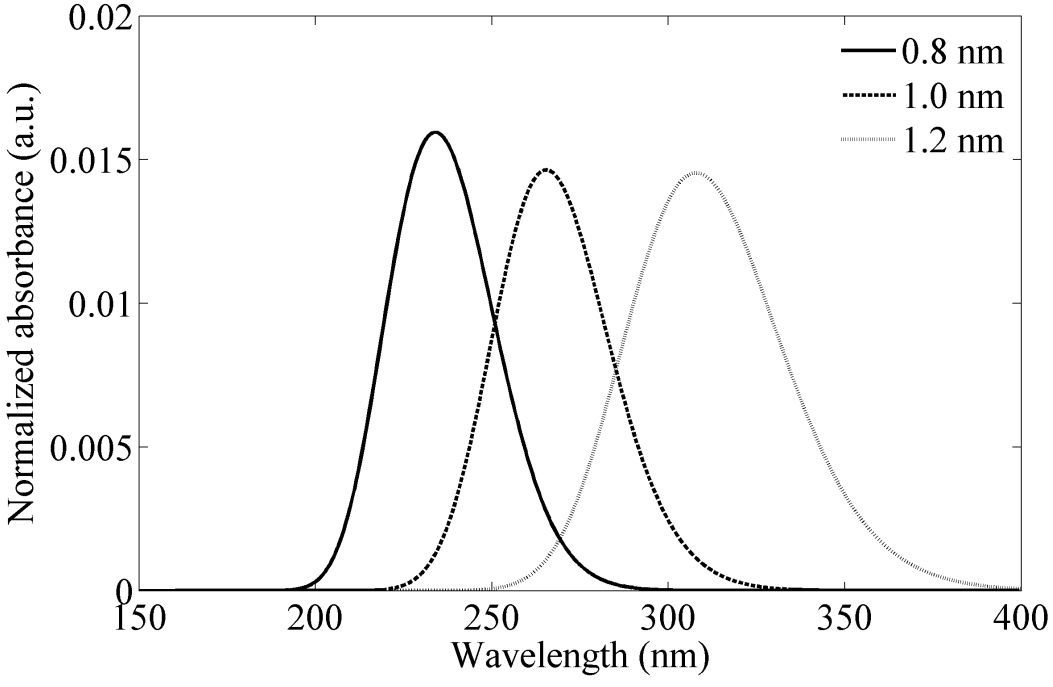

Figure 4. Calculated absorption spectra of hydrogen-capped colloidal silicon quantum dots size of 0.8 nm, 1.0 nm, and 1.2 nm respectively.

4. Conclusion

The structural and optical properties of hydrogen-terminated silicon quantum dots, with diameters of 0.8 to 1.6 nm, were investigated by using the Gaussian 09 code. The HOMO and LUMO of the larger quantum dots are located in the dot interior, while those for smaller dots extend across the whole dots. The LUMO energy level of these nanocrystals is higher than the vacuum energy level. The calculated absorption spectra show that quantum dots with diameters of 0.8 nm have absorption peak at about 5.23 eV (238 nm), diameter of 1.0 nm have absorption peak at about 4.68 eV (264 nm), and for 1.2 nm quantum dots this is at about 4.03 eV (308 nm). The absorption wavelength is decreasing when the size of the quantum dots increase. These results

indicate that hydrogen-passivated silicon quantum dots have tunable emission or absorption wavelength.

5. Acknowledgement

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6. References

[1] Pairot Moontragoon, Zoran Ikonic and Paul Harrison, "Band structure calculations of Si–Ge–Sn alloys: achieving direct band gap materials", Semicond. Sci. Technol. 22, 742 (2007).

[2] Jianwei Liu, Folarin Erogbogbo, Ken-Tye Yong, Ling Ye, Jing Liu, Rui Hu, Hongyan Chen, Yazhuo Hu, Yi Yang, Jinghui Yang, Indrajit Roy, Nicholas A. Karker, Mark T. Swihart, and Paras N. Prasad, "Assessing Clinical Prospects of Silicon Quantum Dots: Studies in Mice and Monkeys", Acs. Nano, 8, 7303 (2013).

[3] F. Maier-Flaig, J. Rinck, M. Stephan, T. Bocksrocker, M. Bruns, C. Kubel, A. K. Powell, G. A. Ozin, and U. Lemmer, "Multicolor Silicon Light-Emitting Diodes (SiLEDs)", Nano Lett, 13, 475 (2013).

[4] Qi Wang, Yongping Bao, Xiaohong Zhang, Paul R. Coxon, Upali A. Jayasooriya, and Yimin Chao, "Uptake and Toxicity Studies of Poly-Acrylic Acid Functionalized Silicon Nanoparticles in Cultured Mammalian Cells", Adv. Healthcare Mater., 1, 189 (2012).

[5] Daniel P. Puzzo, Eric J. Henderson, Michael G. Helander, ZhiBin Wang, Geoffrey A. Ozin, and Zhenghong Lu, "Visible Colloidal Nanocrystal Silicon Light-Emitting Diode", Nano Lett., 11, 1585 (2011).

[6] Melanie L. Mastronardi, Frank Hennrich, Eric J. Henderson, Florian MaierFlaig, Carolin Blum, Judith Reichenbach, Uli Lemmer, Christian Kubel, Di Wang, Manfred M. Kappes, and Geoffrey A. Ozin, "Preparation of Monodisperse Silicon Nanocrystals Using Density Gradient Ultracentrifugation", Journal of the American chemical society, 113,11928 (2011).

[7] Melanie L. Mastronardi, Florian Maier-Flaig, Daniel Faulkner, Eric J. Henderson, Christian Kübel, Uli Lemmer, and Geoffrey A. Ozin. "Size-Dependent Absolute Quantum Yields for Size-Separated Colloidally Stable Silicon Nanocrystals", Nano Lett., 12, 337 (2012).

[8] Kai-Yuan Cheng, Rebecca Anthony, Uwe R. Kortshagen, and Russell J. Holmes, "Hybrid Silicon Nanocrystal-Organic Light-Emitting Devices for Infrared Electroluminescence", Nano Lett. 10, 1154 (2010).

[9] Kai-Yuan Cheng, Rebecca Anthony, Uwe R. Kortshagen, and Russell J. Holmes, "High-Efficiency Silicon Nanocrystal Light-Emitting Devices", Nano Lett., 11, 1952 (2011).

[10] Katerina Dohnalova, Alexander N Poddubny, Alexei A Prokofiev, Wieteke DAM de Boer, Chinnaswamy P Umesh, Jos MJ Paulusse, Han Zuilhof and Tom Gregorkiewicz, "Surface brightens up Si quantum dots: direct bandgap-like size-tunable emission", Light: Science & Applications, 2, e47 (2013).

[11] David Jurbergs and Elena Rogojina, "Silicon nanocrystals with ensemble quantum yields exceeding 60%", Appl. Phys. Lett. 88, 233116 (2006).

[12] Gaussian 09, Revision A.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

[13] A. Szabo, and Neil S. Ostlund, "Modern Quantum Chemistry: Introduction to advanced electronic structure properties", Dover Publications, New York, 1996.