



# Systematic spatial and stoichiometric screening towards understanding the surface of ultrasmall oxygenated silicon nanocrystal



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## ARTICLE INFO

### Article history:

Received 15 May 2016

Received in revised form 29 June 2016

Accepted 30 June 2016

Available online 2 July 2016

### Keywords:

Silicon nanocrystals

Quantum dots

Electronic properties

DFT calculations

Oxygenated dots

Stoichiometry

## ABSTRACT

In most of the realistic *ab initio* and model calculations which have appeared on the emission of light from silicon nanocrystals, the role of surface oxygen has been usually ignored, underestimated or completely ruled out. We investigate theoretically, by density functional theory (DFT/B3LYP) possible modes of oxygen bonding in hydrogen terminated silicon quantum dots using as a representative case of the Si<sub>29</sub> nanocrystal. We have considered Bridge-bonded oxygen (BBO), Doubly-bonded oxygen (DBO), hydroxyl (OH) and Mix of these oxidizing agents. Due to stoichiometry, all comparisons performed are unbiased with respect to composition whereas spatial distribution of oxygen species pointed out drastic change in electronic and cohesive characteristics of nanocrystals. From an overall perspective of this study, it is shown that bridge bonded oxygenated Si nanocrystals accompanied by Mix have higher binding energies and large electronic gap compared to nanocrystals with doubly bonded oxygen atoms. In addition, it is observed that the presence of OH along with BBO, DBO and mixed configurations further lowers electronic gaps and binding energies but trends in same fashion. It is also demonstrated that within same composition, oxidizing constituent, along with their spatial distribution substantially alters binding energy, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap (up to 1.48 eV) and localization of frontier orbitals.

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## 1. Introduction

Silicon nanocrystals (SiNCs) are very interesting nanomaterials whose potential is still not discovered completely or even understood in many respects. Compared to bulk silicon, the electronic properties of SiNCs are significantly dependent on their size. In general, these properties are extremely sensitive to the surface conditions of nanocrystals such as passivation, functionalization, spatial distribution of passivants, reconstruction etc. Silicon nanocrystals (SiNCs) possess quantum confinement effect, large ratios of surface area to volume, nontoxicity and biodegradability, leading to the use of SiNCs in a variety of fields

such as microelectronics, optoelectronics, photovoltaics, in-vivo bioimaging, photosensitizing, drug delivery, lab-on-chip sensing, photocatalysis, phototherapeutics and much more [1–12]. Free-standing self-assembled SiNCs are often synthesized with surface hydrogen passivation which can be further oxidized [8]. But the role of surface oxygen has been usually ignored or underestimated, despite the evidence given by various experiments [13–15]. Many techniques have been used to explore the oxidation state of the Si atoms involved in bonding with surface oxygen [16–18]. In past years, a lot of efforts have been carried out in order to understand surface chemistry of silicon NCs due to the presence of oxidizing constituents both experimentally and theoretically [19–28]. For example, it was reported earlier [28] that for BBO containing NCs the red shift of band gap is found to be smaller compared to the DBO or complete hydroxylation. Furthermore, for hydroxyl passivation, energy gap is largely dependent on amount of OH on surface and their spatial distribution. Zdetsis et al. [25] demonstrated that BBO leads to more stable nanocrystal with large HOMO-LUMO

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gap and binding energies compared to DBO bonds with which we completely agree. Xiaodong et al. [26] performed similar oxygen treatment to hydrosilylated silicon NCs, where they conclude that BBO and OH hardly change the HOMO-LUMO gap at ground state (which is not true for hydrogen passivated NCs). Nazemi et al. [27] have investigated effect of spatial position and spatial distribution of BBO passivants on absorption spectra of hydrogen passivated NCs. According to their findings, spatial position can significantly effect on HOMO-LUMO gap, optical absorption and localization centers of frontier orbitals with which we agree. However, we have investigated that spatial distribution of DBO, Mix and OH also play vital role on surface chemistry in addition to BBO.

In this study, Si<sub>29</sub> nanocrystal (~1 nm) has been deliberately considered for electronic and cohesive investigations, which is not accidental as was demonstrated in our previous work [25]. Therefore, instead of random selection of oxygen bond formation and selective discussion on their characteristics, we present rather systematic density functional Theory (DFT) study. Hence oxidizing constituents of Bridge-bonded oxygen (BBO), Doubly-bonded oxygen (DBO), hydroxyl (OH) and mixed are examined with respect to their composition stoichiometry (identical isomers) and spatial position (distribution).

It is found that electronic and cohesive characteristics significantly change with (1) concentration, (2) spatial distribution and (3) type of oxygen bonding on the surface of silicon nanocrystals. In general, it is observed that bridge bonded oxygenated nanocrystals along with Mix have higher binding energies and large electronic gap compared to nanocrystals with doubly bonded oxygen atoms which is also true if hydroxyl group is also present. As far as concerned to the stability of NCs, we confirm from our results that BBO containing NCs are more stable than DBO whereas Mix bonding show intermediate behavior.

## 2. Model and approach

Initial structure of oxygen free hydrogen terminated Si<sub>29</sub> nanocrystal is selected from our previous studies [25,29]. In this study, oxygenated Si<sub>29</sub> nanocrystals are constructed while taking special care of stoichiometry in order to present comprehensive and unbiased comparison. Fig. 1 represents some fully relaxed structures with respect to various modes of oxygen bonding and their concentrations. Detailed information about oxygen bond configurations along with spatial positions of those stoichiometrically identical isomers can also be seen in Table 1. As is mentioned above, we have considered various types of oxygen bonding, namely, Bridge-bonded oxygen (BBO or >O), Doubly-bonded oxygen (DBO or =O), hydroxyl (OH) and Mix. We put large emphasis on non-hydroxylated nanocrystals whereas selected cases of hydroxylated nanocrystals are also part of this research.

For example, in case of non-hydroxylated Si<sub>29</sub>O<sub>6</sub>H<sub>24</sub> nanocrystal, six BBO atoms are introduced in first subgroup Si<sub>29</sub>(>O)<sub>6</sub>H<sub>24</sub>, six DBO atoms are introduced in second subgroup Si<sub>29</sub>(=O)<sub>6</sub>H<sub>24</sub> and in third subgroup a mixture of three BBO and three DBO atoms Si<sub>29</sub>(>O)<sub>3</sub>(=O)<sub>3</sub>H<sub>24</sub> with exactly 50% ratio which keeps composition stoichiometry. Similar technique has been adopted for other non-hydroxylated nanocrystals where number of oxygen atom varies from O<sub>2</sub> to O<sub>10</sub> with even distribution. For hydroxylated nanocrystals, OH group is introduced in addition to the configuration adopted above. For example, in Si<sub>29</sub>O<sub>10</sub>H<sub>24</sub> nanocrystal, six BBO atoms are introduced in first subgroup Si<sub>29</sub>(>O)<sub>6</sub>H<sub>20</sub>(OH)<sub>4</sub>, six DBO atoms are introduced in second subgroup Si<sub>29</sub>(=O)<sub>6</sub>H<sub>20</sub>(OH)<sub>4</sub> and in third subgroup a mixture of three BBO and three DBO atoms are introduced Si<sub>29</sub>(>O)<sub>3</sub>(=O)<sub>3</sub>H<sub>20</sub>(OH)<sub>4</sub> etc. In contrast with previous example of non-hydroxylated NCs, four hydrogen atoms have been replaced with four OH group. For comparison we have

also included oxygen free hydrogen passivated Si<sub>29</sub> nanocrystal i.e. Si<sub>29</sub>H<sub>36</sub> (Table 1).

Spatial position or spatial distribution of oxidizing constituents, analogous to their stoichiometry, alters surface chemistry which cannot be neglected. Hence, structures are further divided into three categories depending upon the position of oxygen bonds while keeping their composition same. The choice of spatial position is strongly dependent on the availability of suitable silicon atom and their vacant neighborhood which can be saturate and avoid dangling bond. In this process no repetition is involved, hence, all possible combinations are included in this study (Table 1). Due to the different configurations of nanocrystals depending on the number of oxygen atoms, their orientations and spatial distribution, symmetry of the structures differs compared to the symmetry of original structure i.e. T<sub>d</sub>, which is obvious.

All calculations in this work are based on density functional theory (DFT) using the hybrid exchange-correlation functional of Becke, Lee, Yang and Parr (B3LYP) [30]. This functional has been shown to efficiently reproduce the band structure of a wide variety of materials, including c-Si, with no need for further numerical adjustments [31]. Convergence criteria for the SCF energies and for the electron density (rms of the density matrix), were placed at 10<sup>-7</sup> au, whereas for the Cartesian gradients the convergence criterion was set at 10<sup>-4</sup> au. The whole system was relaxed in the geometry optimization at the same time by demanding that the total force (average and maximum) on each atom be practically zero, i.e. smaller than 10<sup>-4</sup> a.u. Our calculations were performed with the TURBOMOLE [32] suite of programs using Gaussian atomic orbital basis sets SVP [4s3p1d] for Silicon and [3s2p1d] for Oxygen [33].

## 3. Results and discussion

### 3.1. Cohesive properties

We have calculated binding/atomization energy of oxygenated silicon nanocrystal using following expression [25]:

$$BE_{NC} = N_{Si}E(Si) + N_OE(O) + N_H E(H) - E_{NC} [Si_{N_{Si}}O_{N_O}H_{N_H}] \quad (1)$$

where  $E_{NC} [Si_{N_{Si}}O_{N_O}H_{N_H}]$  is total energy of nanocrystal,  $E(Si)$ ,  $E(O)$  and  $E(H)$  are the energies of silicon, oxygen and hydrogen atoms (with respect to vacuum) and  $N_{Si}$ ,  $N_O$ , and  $N_H$  are the number of silicon, oxygen and hydrogen atoms.

Fig. 2 shows binding energy per heavy atom with respect to the number of oxygen atoms on the surface of silicon nanocrystals. Further details about composition, binding energies and electronic gap etc for all NCs can be seen in Table 1. In general, regardless of any interspecies comparison, the binding energy decreases with increasing number of oxygen atoms on the surface of silicon nanocrystals. As we can see in Fig. 2(a) that BBO.P1 have highest binding energy values and DBO.P1 (and DBO.P2) have lowest binding energy values whereas all other configurations including mixed ones have intermediate values. Hence structural stability of BBO.P1 is not only higher compared with other spatial positions of BBO but also other form of oxygenation (DBO and Mix). It is interesting and rather clear from Fig. 2 that spatial position of DBO does not effect binding energy. However, in case of three different spatial positions of Mix oxygen configurations which contain both BBO and DBO, variation in binding energy is influenced mainly by the presence of BBO.

For clearer interpretation of binding energy comparison, we sorted out our results in further two groups. Hence, Fig. 2(b) and (c) show nanocrystals with highest and lowest binding energy values respectively, extracted from Fig. 2a. The difference in binding energies for NCs with BBO and DBO is larger in 2(b) compared with 2(c).

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