

Effect of Calcium on the Atomic and Electronic Structures of CdSe QDs Embedded Soda-Lime-Silica Glasses

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Abstract: In this work, we have investigated effects of calcium on the atomic and electronic structures of CdSe QDs by *ab initio* molecular dynamics. The increase of CaO content in glass is found to break the linkage between Na and O atoms, while interactions between Cd atoms and non-bridging oxygens are not disrupted. The presence of the CdSe QD promotes the migration of Na atoms from the glass matrix to the interface, and even the interior of CdSe QD, while Ca atoms are only found to be present at the QD/glass interface and in glass matrices far from QD. However, on the basis of radial concentration distribution, the CdSe QD only impacts the structure of glass at short-range near the interface. The increase in CaO content is also shown to increase the HOMO-LUMO gap of CdSe QDs embedded glasses. Our findings can extend understanding of the effect of calcium on the structural and luminescence properties of CdSe QDs embedded glasses.

1. Introduction

Quantum dots (QDs) have stimulated large research interest, because of their size tunable optical and electronic properties. Their appealing properties include narrow emission linewidth and high quantum yields, making them near-ideal nanomaterials for energy conversion and lighting technologies.^{1,2} Compared to colloidal QDs, QDs embedded glasses can combine the excellent thermal, mechanical, and chemical stability of the glass matrix and the remarkable optical properties of QDs. Therefore, QDs embedded glasses have great potentials for applications in the field of LEDs,^{3,4} lasers,⁵ and solar converters.⁶ The emission of CdSe QD covering the entire visible spectral range by controlling the size of nanocrystals, has been extensively studied.⁷⁻¹⁰

However, the practical application of CdSe QDs embedded glasses suffers from their very low quantum yields compared with their colloidal counterparts. It has been proposed the

defects on the interface between QDs and glass matrix is detrimental to the excitonic emission, resulting in the commonly observed defect emission.¹¹ However, origins of the defects have not been clarified so far, which is mainly impeded by the difficulty to probe interfacial atomic structure between CdSe QDs and glass matrix, due to the low concentration of CdSe QDs, the insulating nature of glass, and instability of glass under intense electron beam irradiation. Computational simulations provide an alternative to bring insight into this issue, investigating a system at the atomistic level, which is not directly accessible in experiments. The atomic¹² and electronic structure¹³ of CdSe QDs embedded binary sodium silicate glasses have been explored in our previous studies based on the *ab initio* molecular dynamics. Breakages of CdSe coordination have been found no matter at the QD/glass interface or in the core of CdSe QD, with the formation of Se - Na and Cd - O bonds at the interface. The strong reconstruction of CdSe QD also contributed to changes in their electronic structures. The nature of the highest occupied molecular orbitals (HOMO) was determined by oxygens in some glasses, while it was decided by Se atoms in glasses with different Na₂O/SiO₂ ratios. Therefore, the composition of glasses plays a significant role in the atomic and electronic structure of CdSe QDs.

In our previous study, the investigated glass was limited to sodium silicate glass composed of Na₂O and SiO₂, while the experimentally fabricated glasses were usually multicomponent. The soda-lime-silica system forms the basis for a wide range of commercially important glass products. These compositions are commonly used for the CdSe QDs embedded glasses, although usually additional minor components are present. Therefore, the effect of calcium on the atomic as well as the electronic structure of CdSe QDs embedded glasses is supposed to be investigated. In this paper, we reports the results of an *ab initio* molecular dynamic study of CdSe QDs embedded in (25-x) Na₂O - x CaO - 75 SiO₂ (x = 5, 10, 15, in mol%) system. The Se - Na, Se - Ca, and Cd - O bonds are observed at the QD/glass interface based on the analysis of radial distribution function. The increase in CaO content enhances the stability of CdSe QD but weakens the interaction between O and Na atoms. The existence of CdSe QD leads to the migration of Na atoms from glass matrices to the interface and interior of CdSe QD, while contributes to migration of O atoms and Si atoms from interface to glass matrices. Ca atoms only exist in the interface of QD/glass and in region far from the QD. The effect of CdSe QD on the glass structure are only observed in short-range according to the analysis of radial concentration distribution. With the additional introduction of CaO content, the HOMO-LUMO gap are found to increase and all the frontier orbitals are decided by hybrid QD.

2. Computational Methods

The methodology used here to generate QD/glass models was developed and validated in our previous work, and it is based on a combination of classical and *ab initio* molecular dynamics.¹² Firstly, atoms were randomly placed in a cubic simulation box using the Packmol code,¹⁴ generating an initial configuration of the glass matrix. The total number of atoms in the glass matrix were 1180, 1160, 1140, with the simulation size 25.340 Å,

25.227 Å, 25.112 Å, respectively. Compositions of those glasses are 80 Na₂O - 40 CaO - 300 SiO₂, 60 Na₂O - 40 CaO - 300 SiO₂, and 40 Na₂O - 60 CaO - 300 SiO₂. From this initial configuration, the glass structures were generated using a melt-quenching approach ranging from 6000 K to 300 K, in the NVT ensemble at the target density,¹⁵ with a partial-charge rigid-ion pairwise potential.¹⁶ The molecular dynamics simulations were run using the DL_POLY package.¹⁷ The Coulomb interactions were calculated using the Ewald summation method with a precision of 10⁻⁵ and a real-space cutoff for short-range interactions set to 7.6 Å.

Secondly, the Cd₃₃Se₃₃ QD structure obtained at DFT level in a previous study,¹⁸ was incorporated into this glass matrix, removing glass atoms so interatomic distance between QD and glass matrix were longer than 2.5 Å. The final composition was 68 Na₂O - 17 CaO - 255 SiO₂ - 33 CdSe ($x = 5$), 51 Na₂O - 34 CaO - 255 SiO₂ - 33 CdSe ($x = 10$), and 34 Na₂O - 51 CaO - 300 SiO₂ - 33 CdSe ($x = 15$) (**Figure 1**). The interaction between Cd and Se atoms were described by a Lenard-Jones pairwise potential,¹⁹ while the Lorentz-Berthelot combining rules were used for interactions between glass matrix and QD. After equilibrating at 1000 K with 200 ps NVT and 200 ps NVE dynamics, the whole structures were quenched from 1000 K to 500 K in steps of 50 K, keeping the CdSe QD frozen. Then it was gradually cooled from 500 K to 300 K in steps of 10 K, with all atoms allowed to move. The structures were further equilibrated at 300 K with 200 ps NVT and NVE dynamics.

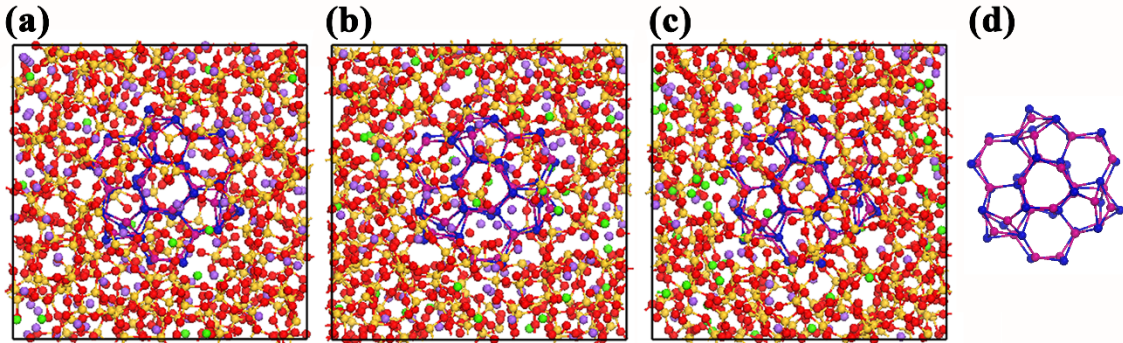


Figure 1 Initial structures of classical molecular dynamics. Glass composition: (a) $x = 5$: 68 Na₂O - 17 CaO - 255 SiO₂ - 33 CdSe, (b) $x = 10$: 51 Na₂O - 34 CaO - 255 SiO₂ - 33 CdSe, and (c) $x = 15$: 34 Na₂O - 51 CaO - 300 SiO₂ - 33 CdSe, (d) pristine QD. The colors of the atoms are: magenta for Cd, blue for Se, purple for Na, green for Ca, red for O, and yellow for Si.

Finally, after equilibrating the systems using the classical molecular dynamics described above, the resulting structures were employed as the initial configurations for *ab initio* molecular dynamics, with interatomic forces calculated at the density functional theory (DFT) level, using the CP2K code.²⁰ The PBE exchange-correlation function was used.²¹ For Na, Ca, Cd, and Se, we used short-range molecularly optimized double- ζ single polarized basis sets (DZVP-MOLOPT-SR-GTH), while for O and Si we used a double- ζ

single polarized basis set (DZVP-MOLOPT-GTH).²² The plane wave cutoff and relative cutoff was set to 600 Ry and 40 Ry, respectively. The structure was quenched from 500 K to 300 K in steps of 50 K, with a total 10 ps *ab initio* molecular dynamics run at a time step of 2 fs. The production run was conducted in the NVT ensemble at 300 K for 10 ps. For each system, 500 configurations were selected at equal interval from a 10 ps production run of *ab initio* molecular dynamics simulations. Among those, 50 configurations were picked to perform the calculation and analysis of the electronic structure of CdSe QD embedded glasses. We used the nonlocal PBE0-TC-LRC²³ exchange-correlation functional with a cutoff radius of 4.0 Å. Moreover, the computational cost of nonlocal functional calculations can be reduced using the auxiliary density matrix method (ADMM).²⁴

3. Results and Discussion

The final configurations of the *ab initio* simulations are shown in **Figure 2**. Compared to the pristine CdSe QD in the initial structure (**Figure 1d**), we see that CdSe QD undergoes a strong structural reconstruction, similar in nature to what was previously observed in other QD/glass systems.^{12,13} In pristine QD, Cd atoms (Se atoms) are 3-coordinated with Se atoms (Cd atoms) on the surface, while Cd atoms (Se atoms) are 4-coordinated with Cd atoms (Se atoms) in the core. For the CdSe QDs in glass matrices, the breakage of stable 6-membered Cd-Se rings is observed with the formation of 1- or 2-coordinated Cd atoms or Se atoms at the interface. It is hard for the CdSe QD to maintain its bulk structure even in the core.

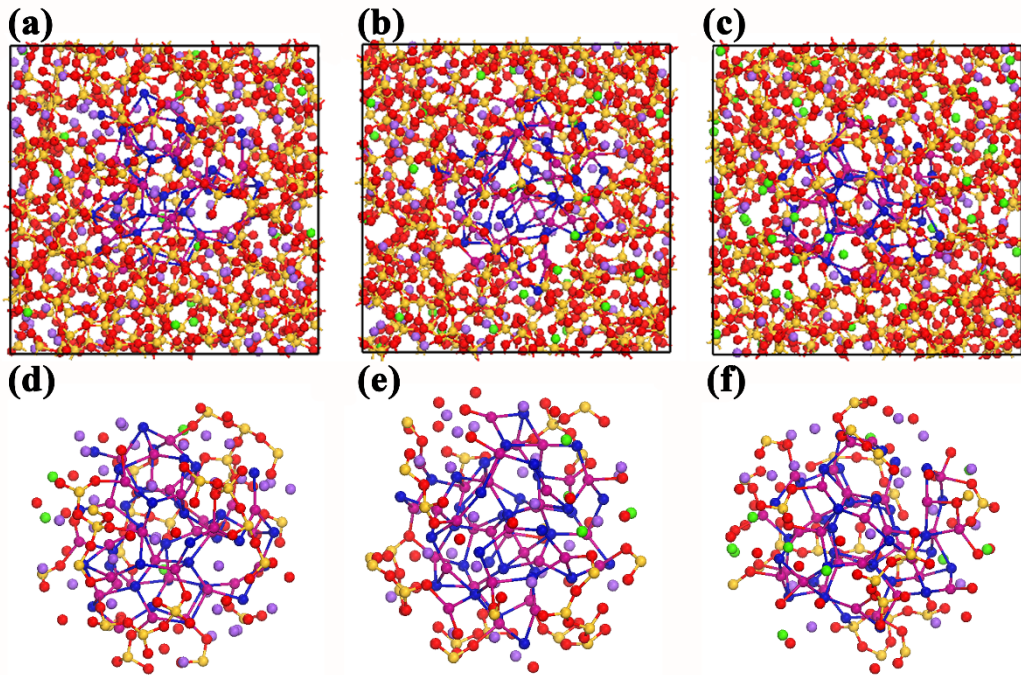


Figure 2 Final structures from the *ab initio* molecular dynamics simulations. Glass composition: (a) $x = 5$: 68 Na₂O - 17 CaO - 255 SiO₂ - 33 CdSe, (b) $x = 10$: 51 Na₂O -

34 CaO - 255 SiO₂ - 33 CdSe, and (c) $x = 15$: 34 Na₂O - 51 CaO - 300 SiO₂ - 33 CdSe. (d)-(f): Partial enlargement of the final structure corresponding to (a)-(c), respectively.

Based on the analysis of radial distribution function (RDF) obtained over the *ab initio* molecular dynamics, the first-neighbor peaks for Si - O (**Figure 3a**), O - Na (**Figure 3b**), O - Ca (**Figure 3c**), and Se - Cd (**Figure 3d**) pairs are found at 1.64 Å, 2.36 Å, 2.27 Å and 2.63 Å, respectively, consistent with experimental and theoretical values.^{19,25} Looking into the QD/glass interface, the formation of O - Cd, Se - Na and Se - Ca bonds observed visually is confirmed by the analysis of RDF for those pairs (**Figure 4**). Although there are some fluctuations of the interatomic distance of each pair in different glass composition, the first-neighbor peak is located near 2.25 Å (**Figure 4a**), 2.98 Å (**Figure 4b**), and 3.00 Å (**Figure 4c**) for O - Cd, Se - Na, and Se - Ca, respectively. The interatomic distances for Cd - O bonds were found to be 2.25 Å based on the extended X-ray absorption fine structure spectroscopy (EXAFS) analysis of CdSe QDs embedded glasses.²⁶ The Se - Na and Se - Ca distances observed in the heavier alkaline earth complexes with a phosphinoselenic amides were 3.01 Å and 2.99 Å, respectively (characterized by single crystal X-ray diffraction).²⁷

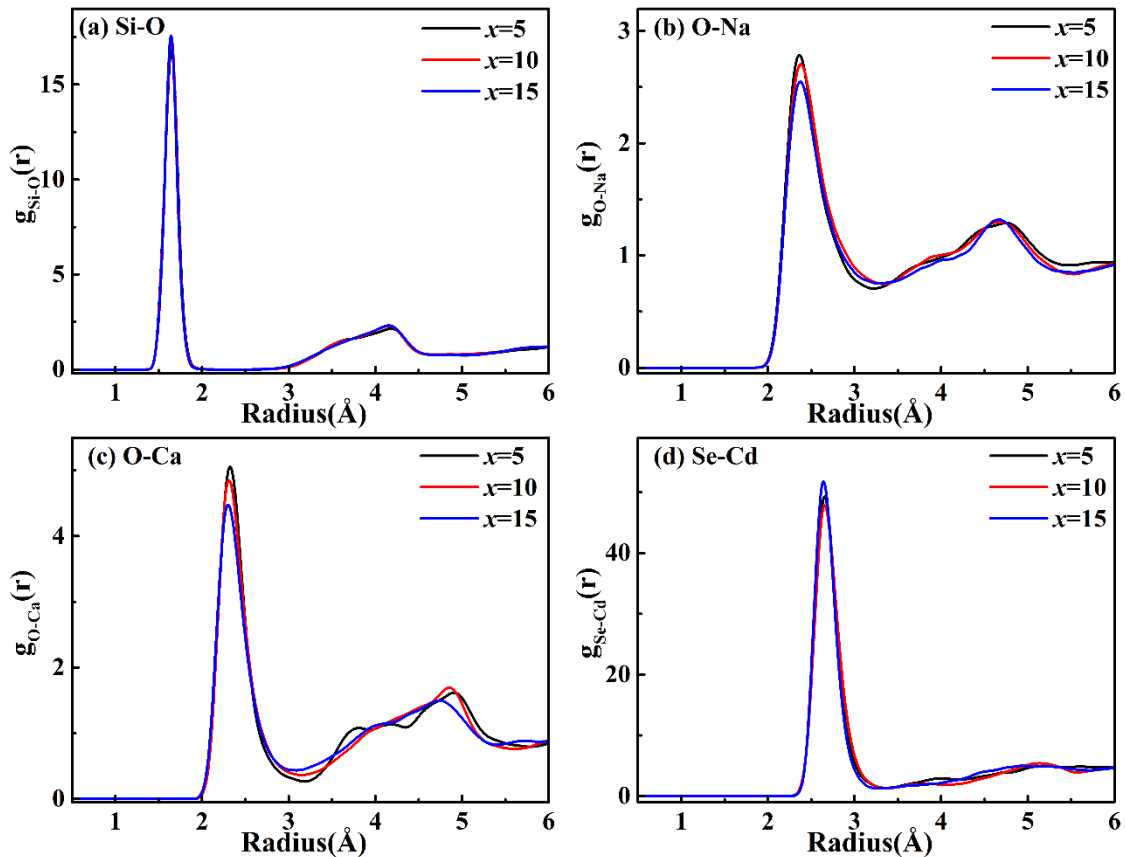


Figure 3 Radial distribution functions for (a) Si - O, (b) O - Na, (c) O - Ca, and (d) Se - Cd pairs, averaged over the *ab initio* molecular dynamics trajectories for CdSe QD embedded in (25- x) Na₂O - x CaO - 75 SiO₂ glasses. The black, red and blue lines represent the glass composition with x equal to 5, 10 and 15, respectively.

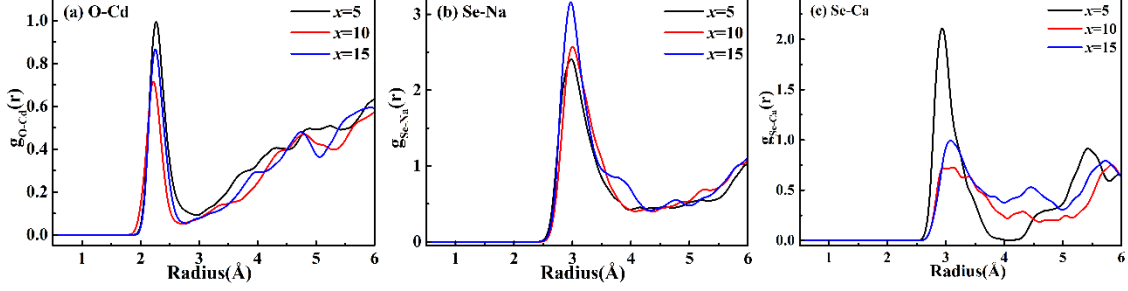


Figure 4 Radial distribution functions for (a) O - Cd, (b) Se - Na, and (c) Se - Ca pairs, averaged over the ab initio molecular dynamics trajectories for CdSe QD embedded in $(25-x) \text{Na}_2\text{O} - x \text{CaO} - 75 \text{SiO}_2$ glasses. The black, red and blue lines represent the glass composition with x equal to 5, 10 and 15, respectively.

Furthermore, we explored the coordination environment of oxygen atoms (**Figure 5**). With the increase of CaO content in the glass, we observe that the ratio between the number of O atoms coordinated with Na atoms and total number of O atoms decreases, while that of O atoms coordinated with Ca atoms increases. However, the ratio between the number of O atoms bonded with Cd atoms and the total number of oxygen atoms only slightly fluctuates with the increase of CaO content (**Figure 5a**). To get a deeper insight into this coordination, we divide oxygen atoms into two groups: non-bridging oxygen atoms (NBO) and bridging-oxygen atoms (BO). The ratio between the number of BO and oxygen atoms is estimated to be 83.5% based on the ratio between glass modifiers and glass formers, which is slightly higher than 73% in our model due to the presence of CdSe QD (**Figure 5b**). It is visible that calcium ions compete with sodium ions to coordinate with BO and NBO (**Figure 5c**). Additionally, BO are more likely to be surrounded with Na ions, while Ca ions are favored by NBO, consistent with previous studies.^{15, 28-29} Almost all Cd ions interact with NBO rather than with BO, and these interactions are not impacted by the increase of CaO content. These trends can be explained by the single-bond strength of each pair. The non-directional ionic Na - O bonds are weaker than the Ca - O bonds due to the high field strength of Ca atoms with higher valence and smaller radius. However, the external shell of Cd^{2+} contains 18 electrons, resulting the strong polarization of oxygen atoms. Therefore, the single-bond strength of each pair increases in the order of O - Na, O - Ca, and O - Cd.

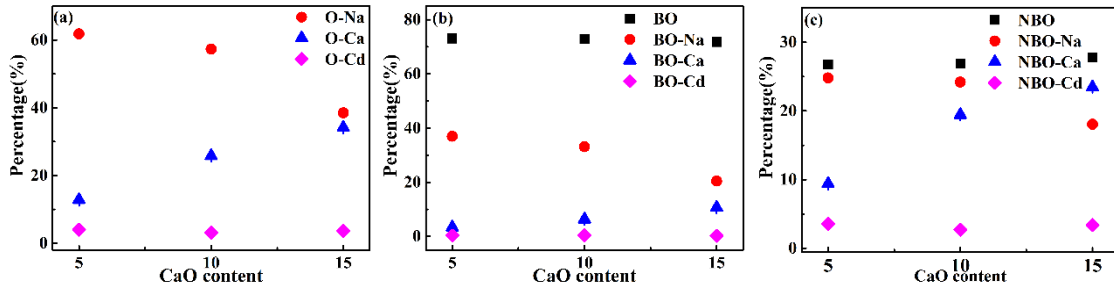


Figure 5 500 configurations obtained by 10 ps production run were divided into 5 blocks, and the coordination environment of O atoms were analyzed for each block. The error bars represent standard deviation. (a) The ratio between the number of oxygen atoms

coordinated with Na atoms, Ca atoms or Cd atoms and the total number of oxygen atoms. (b) The ratio between the number of bridging oxygens (BO), BO coordinated with Na atoms, BO coordinated with Ca atoms or BO coordinated with Cd atoms and the total number of oxygen atoms. (c) The ratio between the number of non-bridging oxygens (NBO), NBO coordinated with Na atoms, NBO coordinated with Ca atoms or NBO coordinated with Cd atoms and the total number of oxygen atoms.

The coordination environment of Se atoms in the different systems was also investigated. All the Se atoms are bonded with Cd atoms, while the Na atoms tends to bond preferentially with Se atoms than Ca atoms (**Figure 6a**). The percentage of Se atoms coordinated with Na atoms decreases from 80.50%, 76.81% to 67.21% with the increase of CaO content, while the percentage of Se atoms interacted with Ca atoms increase from 11.25%, 12.44% to 19.83%. In the initial configuration (**Figure 1**), 63.64% of Se atoms are 3-coordinated with Cd atoms and 36.36% of Se atoms are 4-coordinated with Cd atoms. stable SeCd_3 and SeCd_4 units are observed, replaced by the formation of unstable SeCd_2 and SeCd_1 units (**Figure 6b**). Meanwhile, it is apparent that the stability of CdSe QD improved with the addition of CaO, consistent with the final geometrical structure shown.

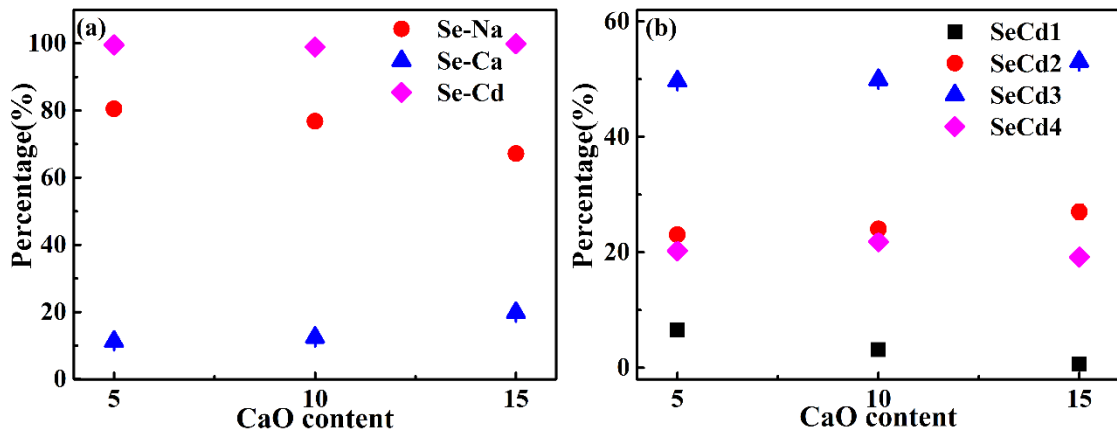


Figure 6 500 configurations obtained by 10 ps production run were divided into 5 blocks, and the coordination environment of Se atoms were analyzed for each block. The error bars represent standard deviation. (a) The ratio between the number of Se atoms coordinated with Na atoms, Ca atoms or Cd atoms and the total number of Se atoms. (b) The ratio between the number of Se atoms 1-coordinated, 2-coordinated, 3-coordinated or 4-coordinated with Cd atoms and the total number of Se atoms.

An additional observation is the Ca atoms tend to distribute on the spatial region far from the CdSe QD (**Figure 2**). Therefore, the radial concentration distribution of each element was calculated (**Figure 7**). Taking the geometric center of CdSe QD as the origin, the radial concentrations are calculated as the ratio between the number of atoms of each element and the volume of ball with radius r . The QD boundary are defined as the most external region of CdSe QD. Compared with the initial structure, the concentration of O

atoms and Si atoms are lower within the QD boundary, demonstrating the O atoms and Si atoms are more likely to distribute far from the QD region. However, an opposite trend is observed with the concentration of Na atoms within QD boundary higher than that of initial structure. Moreover, no Ca atoms are found in the interior of CdSe QD. We can draw a conclusion that the existence of CdSe QD terminates the Si-O network at the interface and promote the migration of Na atoms from glass matrices to the interior of CdSe QD. The migration of Ca atoms is complex. The radial concentration profile near the CdSe QD of final configuration is slightly higher than that of initial configuration with the composition of x equal to 5 and 15, while it is tiny smaller than that of initial structure with $x = 10$. Due to the high field strength and high coordination number between Ca atoms and O atoms, Ca atoms are hard to move in glass matrices. It should be noted that the concentration of each element is equal to that of initial structure at $r = 14 \text{ \AA}$, reflecting that the presence of CdSe QD can only have an impact on the short-range scale and the glass matrices far from the QD can keep their pristine status. We also calculated the radial concentration of 500 configurations and took an average. The results shown in **FigureS1** are consistent with the findings described above.

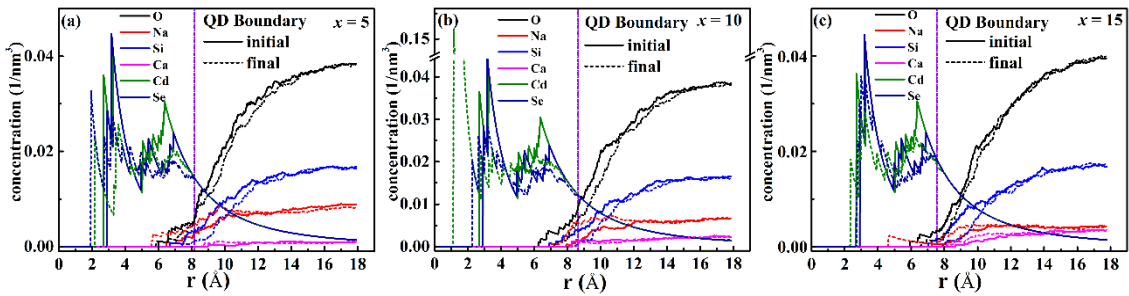


Figure 7 Radial concentration distribution of O atoms (black line), Na atoms (red line), Si atoms (blue line), Ca atoms (magenta line), Cd atoms (green line) and Se atoms (navy line) of the initial configuration of classical molecular dynamics (solid line) and the final configuration (dash line) obtained by *ab initio* molecular dynamics. The glass composition: (a) $x = 5$, (b) $x = 10$, and (c) $x = 15$. The origin is the geometric center and the QD boundary (purple vertical dash line) is the most external region of CdSe QD.

The electronic structure was also studied to probe the impact of calcium. The average HOMO-LUMO gap increases from 2.26 eV, 2.40 eV to 2.42 eV when x changes from 5 to 15 (**Figure 8a-c**). Therefore, the addition of CaO content in glass matrices can increase the HOMO-LUMO gap of CdSe QDs embedded glasses. According to the radial concentration distribution, the CdSe QDs embedded glasses can be spatially divided into three parts: hybrid QD, hybrid glass and pristine glass. Strong structural reconstruction happens in CdSe QD, resulting in geometrical structure different from pristine QD, which we called hybrid QD here. Meanwhile, the existence of CdSe also contribute to the rearrangement of atomic structure of glasses, leading to the formation of hybrid glass near the QD/glass interface, while the structure of glass far from CdSe QD keep their pristine status. The density of states of 50 configurations selected from AIMD production run

were calculated and similar conclusions can be drawn. Based on the analysis of density of states, the HOMO and LUMO is decided by the Se and Cd atoms, respectively. Therefore, the frontier orbitals are entirely determined by hybrid QD. This finding is different from our previous work,¹³ while the HOMO was determined by hybrid glasses with the glass matrix composition 33 Na₂O – 67 SiO₂. Therefore, calcium also plays a different role in determining the electronic structure of CdSe QDs embedded glasses.

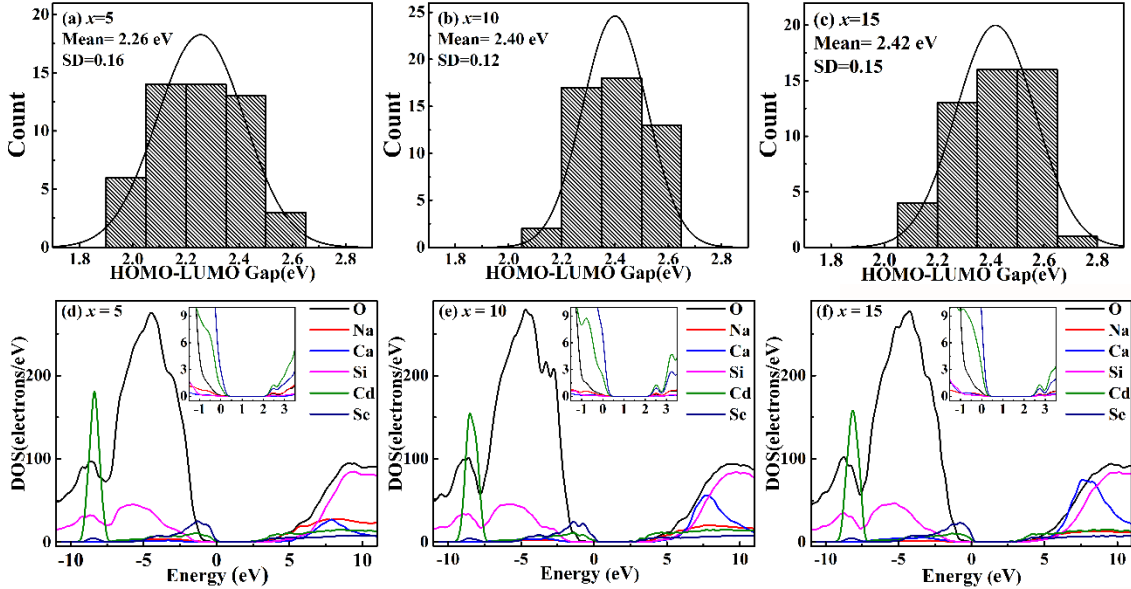


Figure 8 HOMO-LUMO gap distribution of 50 configurations of the *ab initio* molecular dynamics production run of glasses with x equal to (a) 5, (b) 10, and (c) 15. Density of states of the final configuration from the *ab initio* molecular dynamics production run. (e-f) Composition of $x = 5, 10,$ and $15,$ respectively.

4. Conclusion

In this work, we have investigated the effect of calcium ions on the atomic and electronic structures of CdSe QDs embedded soda-lime-silica glasses by *ab initio* molecular dynamics. The Se – Na, Se – Ca, and Cd – O coordination is observed at the QD/glass interface with breakage of stable 6-membered Cd – Se rings within the QD. With the increase of CaO content in the surrounding glass matrices, the stability of the CdSe QD is enhanced. Based on the analysis of coordination environment of oxygen atoms, the interaction between non-bridging oxygens (NBO) and Na atoms is weakened, while the interaction between NBO and Cd atoms is not impacted, upon increase of CaO concentration. On the other hand, Se atoms are more likely to bond with Na atoms than Ca atoms. According to the analysis of radial concentration distribution, although both Na and Ca atoms are glass modifiers, they exhibit different behavior in our molecular dynamics simulations. The Na atoms tend to migrate from the glass matrix towards the interface, even in the interior of CdSe QDs, while Ca atoms only localize at the interface. The presence of the CdSe QDs in the glasses also promotes the migration of O atoms and Si atoms from the interface into glass matrices. Meanwhile, we see that the presence of the CdSe QDs only affects the short-range atomic structure of glasses at interface, and the

glass far from CdSe QD can maintain its pristine status. The HOMO-LUMO gap increases with the additional introduction of CaO contents in the glass matrix, and the frontier orbitals are both determined by the hybrid QD.

Supporting Information

Radial concentration distributions averaged over the *ab initio* molecular dynamics trajectory.

Acknowledgements

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