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The defective nature of CdSe quantum dots embedded in inorganic matrices

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Abstract: Quantum dots (QDs) embedded in inorganic matrices have been extensively studied for their potential applications in lighting, displays, and solar cells. While a significant amount of research focused on its experimental fabrication, the origin of their relatively low photoluminescence quantum yield has not been investigated yet, although it severely hinders practical applications. In this work, we use time-dependent density functional theory (TDDFT) to pinpoint the nature of excited states of CdSe quantum dots embedded in various inorganic matrices. The formation of undercoordinated Se atoms and non-bridging oxygen atoms at QD/glass interface is responsible for the localization of a hole wavefunction, leading to the formation of low-energy excited states with weak oscillator strength. These states provide pathways for non-radiative processes and compete with radiative emission. The photoluminescence performance is predicted for CdSe quantum dots in different matrices, and validated by experiments. The results of this work have significant implications for understanding the underlying photophysics of CdSe quantum dots embedded in inorganic matrices that would facilitate the fabrication of highly luminescent glasses.

1. Introduction

Semiconductor quantum dots (QDs) were first realized experimentally in glasses¹ in 1981 and later as chemically synthesized colloidal nanocrystals² in 1983. QDs offer tunable photoluminescence (PL), high photoluminescence quantum yield (PLQY), and high color purity, have thus emerged as suitable materials for white LEDs,³ solar cells,⁴ lasers,⁵ etc. QDs feature a large surface-to-volume ratio and high surface energy,

resulting in instability and degradation of emissive properties during storage and use. Therefore, large efforts have been made in the past decades to eliminate surface defects of colloidal QDs, for example through surface passivation or by forming core-shell structures.⁶⁻⁸ Although the PLQY of colloidal QDs can reach almost 100% after efficient passivation,⁹⁻¹⁰ poor stability derived from the introduction of organic ligands remains an important roadblock for its practical application.

Encapsulating quantum dots with an inorganic glass matrix can combine the excellent optical properties of QDs and the high chemical and thermal stability of the glass. Thus, QDs such as CdSe,¹¹⁻¹⁴ PbS,¹⁵ and perovskite QDs,¹⁶⁻²⁰ have been embedded in glasses and attracted a lot of attention. However, the highest reported PLQYs for CdSe and CsPbBr₃ QDs embedded in glass matrices are 48.6%²¹ and 86.9%¹⁸, respectively, much lower than their colloidal counterparts. The poor emissive properties of QDs embedded glasses greatly hinder their commercial applications and the underlying mechanism has not been fully explored yet. However, it is experimentally challenging to probe the structural origin of the low PLQY of QDs due to the dense, insulating, and amorphous nature of glass matrix, and the dimensions of the QD/glass interface.

Instead, molecular simulations have proven to be a reliable approach to investigate the atomic and electronic structure of colloidal QDs. Atomistic modelling methods were used for the characterization of the ground state²²⁻²⁵ as well as excited states²⁶⁻³⁶ of CdSe QDs. Those theoretical studies investigated the origin of defect emission of colloidal QDs and provide a better understanding of QDs photophysics, giving guidance to the experimental design of novel materials, e.g., by the passivation method. Indeed, while significant experimental efforts have been made in research on QDs in glass matrices, theoretical work based on *ab initio* method is still scarce compared to that on colloidal QDs. The size-dependent band gap of QDs in different matrices has been studied based on potential-morphing method (PMM):³⁷ it was found that the confining potential depends exclusively on the nature of the matrix (and not on that of the dot). Furthermore, our own previous work³⁸ suggested that the QDs could not maintain their ideal structure — even at their core — when they were incorporated into glass matrices, in stark contrasts with colloidal QDs (which feature a slight rearrangement for surface atoms and maintain their bulk structure at the core). For CdSe QDs in binary alkali silicate glasses, the breakage of stable 6-member and 4-member Cd-Se rings was observed, with the formation of Se-Na or Cd-O interfacial linkages. The unavoidable strong structural reconstruction contributes to the formation of undercoordinated surface

atoms and non-bridging oxygen atoms at QD/glass interface. Those structural rearrangements are anticipated to exert large effect on its electronic structure and the QD/glass interfacial structure might be the origin of low PLQY. Ground state electronic calculations³⁹ confirmed this hypothesis, demonstrating the nature of the highest occupied molecular orbitals (HOMO) of CdSe QDs embedded in glass matrices were directly affected by the glass. The HOMO was determined by oxygen atoms in $(\text{Na}_2\text{O})_{39}(\text{SiO}_2)_{78}(\text{CdSe})_{33}$ glasses, while it was decided by Se atoms in other glass compositions based on the analysis of density of states (DOS). Besides, the disappearance of the pristine QD structure was verified by atomic structure and bandgap analysis. Consequently, the emission is not from the combination of defect emission and intrinsic emission of pristine QD as commonly proposed. Those works exhibited the striking difference between QDs in colloidal solutions and in glass matrices, which we suggested to be the origin of the diverse luminescence performance. However, the nature of the transition (optically active or forbidden) from HOMO to LUMO (lowest unoccupied molecular orbitals) could not be described by these ground state electronic calculations, and therefore, the photophysics especially the excited states properties of CdSe QDs embedded in glass matrices, still needed to be investigated.

Here, we performed TDDFT method calculations to present computational evidence that CdSe quantum dots embedded inorganic matrices are defective in nature. The presence of the glass matrix inevitably contributes to the significant structural reconstruction of the pristine QDs, resulting in the localization of the hole wavefunction on undercoordinated interfacial Se atoms and non-bridging oxygens. The small overlap between the localized hole and delocalized electron wavefunctions implies a weak oscillator strength of the first excited states, and therefore poor emissive properties of those composites. The photoluminescence quantum yields of CdSe QDs embedded glass samples we fabricated are proportional to the oscillator strength of the lowest-energy transitions calculated. Our results reveal that the essentially unavoidable existence of undercoordinated Se atoms together with non-bridging oxygens at the QDs/glass interface leads to a dense manifold of low-energy states, governing the emission properties of CdSe QDs in inorganic matrices. Our findings further the understanding of QDs embedded glasses and could give guidance to design highly luminescent QDs embedded in glasses as well as colloidal QDs passivated by an inorganic shell.

2. Results and Discussions

The fully relaxed structure of a pristine $\text{Cd}_{33}\text{Se}_{33}$ quantum dot in vacuum, with 21 three-coordinated Se or Cd atoms on surface and 12 four-coordinated Se or Cd atoms in the core, was generated by DFT calculations, as in the method used in our previous work (**Figure 1a**).⁴⁰ The non-local PBE0 hybrid exchange-correlation functional was employed, which has been proved to provide rather accurate geometry and excited states description comparable to experimental finding based on extensive benchmarking tests on CdSe QDs.^{28, 36, 41} — for further details on how we generated the model and calculated the absorption spectra, see the Methods section. With our chosen methodology, the first absorption peak (**Figure 1b**) is located at 525 nm (2.36 eV), redshifted compared to the experimental value of 415 nm (~ 2.99 eV).⁴² We do not intend to reproduce the exact value of the experimentally observed absorption peak, but rather to probe impact of inorganic matrices on a relative energy scale. **Figure 1b** also displays the density of transitions, which was obtained by applying Gaussian broadening to the calculated excitation energies. The high density of transitions with small oscillator strength indicates the optically forbidden states, as shown at higher energies (~ 425 nm) than the first absorption peak.

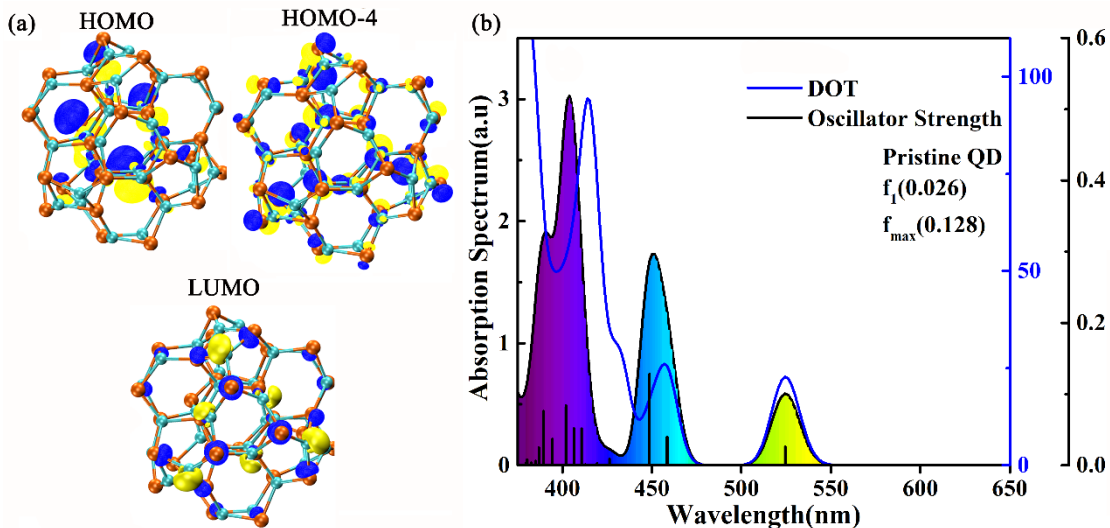


Figure 1 Molecular orbitals and absorption spectrum of pristine $\text{Cd}_{33}\text{Se}_{33}$ quantum dot. (a) The lowest-energy transition almost originates from HOMO to LUMO transitions with the oscillator strength equal to f_l . The excited state with the maximum oscillator strength (f_{max}) across 100 calculated transitions is mainly from HOMO-4 (low lying occupied orbital (HOMO-n)) to LUMO. The color of the atoms in CdSe QD are cyan for Cd and orange for Se. Blue and yellow regions denote positive

and negative sign of wave functions, respectively. (b) Absorption spectrum (black line, shaded) and density of transitions (blue line). Black vertical bars show individual excited states, with the values for the oscillator strength shown at the right y -axis.

The HOMO to LUMO transition contributes to 98.58% of the lowest-energy transition with a weak oscillator strength equal to 0.026. In the pristine QD, the HOMO is found to be localized on the 3-coordinated surface Se atom (**Figure 1a**), while the LUMO is delocalized due to the heavier effective mass of holes. For the brightest peak with the highest oscillator strength (0.128), it is dominated by the HOMO-4 to LUMO transition. The HOMO-4 is more delocalized than the HOMO, resulting in the spatial overlap of electron and hole wavefunctions, leading to a significant absorption intensity.

Then, we incorporated the pristine QD into glass matrices of varying composition: 25 Na₂O–75 SiO₂, 33Na₂O–67SiO₂, 20 Na₂O–5 CaO–75 SiO₂, and 15 Na₂O–10 CaO–75 SiO₂ (in mol%), respectively, serving as an initial structure for molecular dynamic (MD) simulations (**Figure S1**). These QDs embedded glasses are labeled as Q25N75S, Q33N67S, Q20N5C75S and Q15N10C75S (**Table S1**). The atomic structures of those glasses were generated by a combination of classical MD and *ab initio* MD (AIMD). Compared to the pristine QD, the final configuration (**Figure 2**) of the production run demonstrates significant reconstruction of CdSe QD, with breakage of the stable CdSe₄ or SeCd₄ units and formation of undercoordinated Cd or Se atoms at the interface (**Figure S2**). It was found the 2-coordinated surface Se atoms are responsible for the dark, surface-associated excitations, even in a stoichiometric CdSe QD with perfect ligand passivation.³⁶ Therefore, we hypothesize that the observed structural reconstruction will have a remarkable impact on the optical properties of CdSe QDs embedded glasses compared to pristine QD.

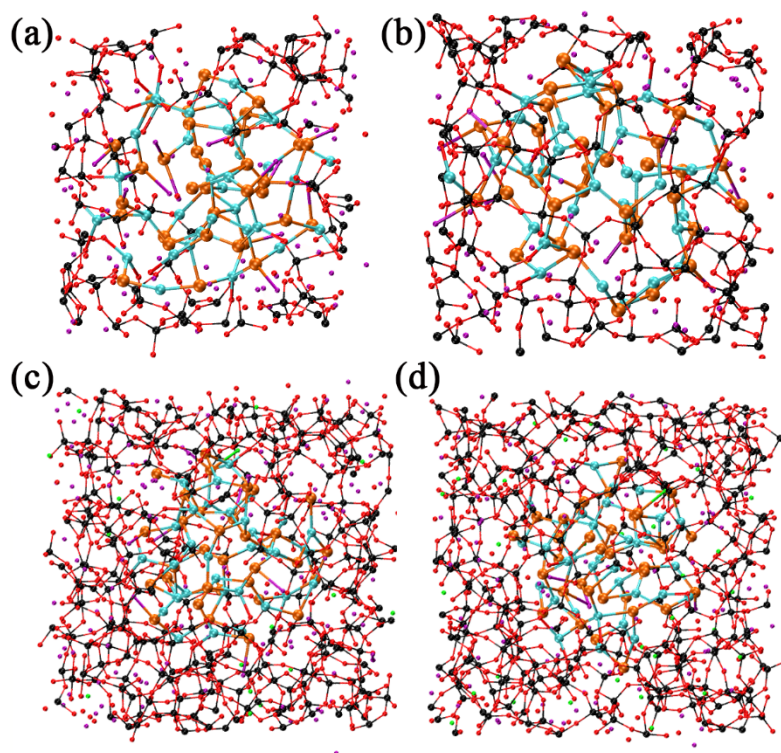


Figure 2 Final configuration of $\text{Cd}_{33}\text{Se}_{33}$ quantum dot embedded in different glasses, taken from AIMD. Glass composition: (a) 25 Na_2O –75 SiO_2 –33 CdSe , (b) 33 Na_2O –67 SiO_2 –33 CdSe , (c) 20 Na_2O –5 CaO –75 SiO_2 –33 CdSe , and (d) 15 Na_2O –10 CaO –75 SiO_2 –33 CdSe . The structure of hybrid QD is distinctly different from pristine QD, with a great ratio of undercoordinated surface atoms and breakage of stable CdSe_4 or Cd_4Se units even in the core (The structure of hybrid QD are solely illustrated in **Figure S2**). The color of the atoms are: Cd in cyan, Se in orange, O in red, Si in black, Na in purple, Ca in green.

TDDFT calculations using the final configuration of each AIMD exhibit the distinct excited states characteristics of CdSe QD embedded in different glass matrices (**Figure 3 and Table S2**). The first immediate observation is that the first absorption peak is shifted compared with pristine QD. The solvent effect has been extensively discussed in colloidal QDs experimentally and theoretically:^{35, 43-49} the relatively larger dielectric constant of semiconductor QDs compared to organic solutions gives rise to a dielectric confinement effect,⁵⁰⁻⁵¹ leading to the enhancement of exciton binding energy and oscillator strength. As a result, the first absorption peaks are often blue-shifted for colloidal QDs in polar solutions. Although the glass matrices can be considered as a “polar solution” to some extent (**Table S3**), the shift of the first absorption peak does

not have the same tendency as colloidal QDs. The dielectric constant of silicate glasses⁵² is higher than that of CdSe QD,⁵³ contributing to the disappearance of dielectric confinement effect. Therefore, the blueshift of the first absorption peak are not observed in some of the surrounding glasses.

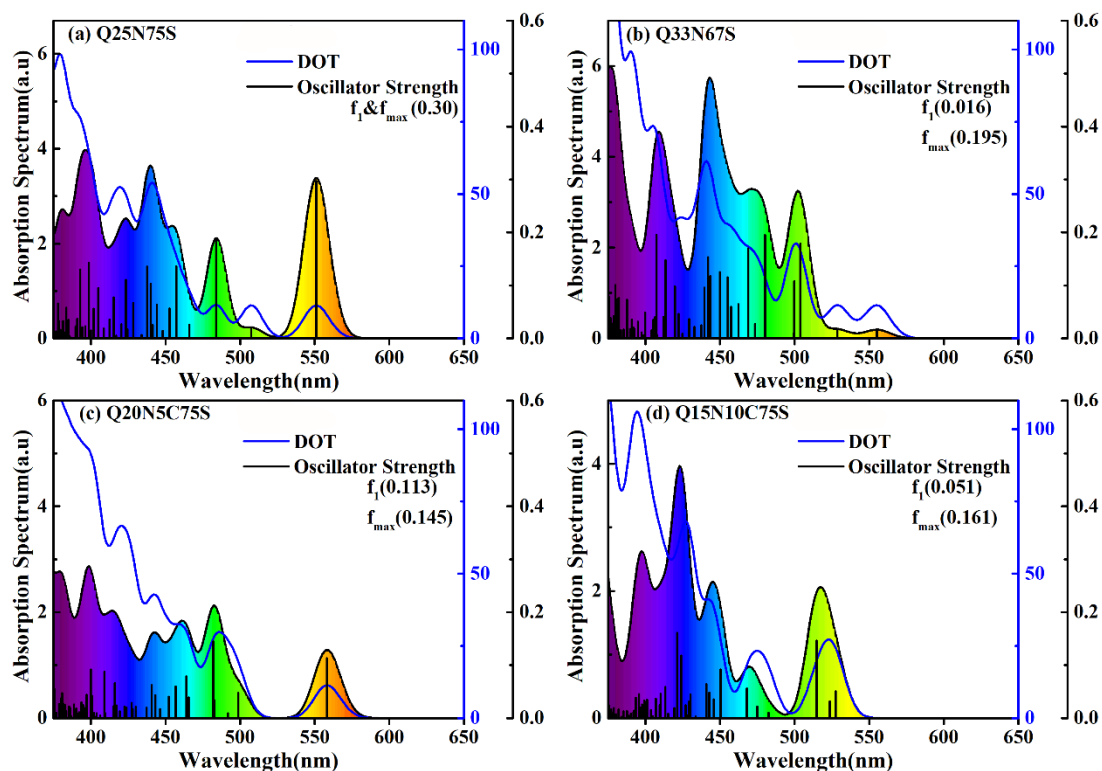


Figure 3 Absorption spectrum of $\text{Cd}_{33}\text{Se}_{33}$ quantum dot embedded in glass matrices. The calculated structure is the final configuration of the 10 ps AIMD production run (**Figure 2**). The first absorption peak is red-shifted compared to that of the pristine quantum dot, and the oscillator strength of the lowest-energy transition varies depending on the composition of glass matrices.

Besides, the oscillator strength of the lowest-energy transition ranges from 0.30 to 0.016 depending on the composition of glass matrices. In particular, the oscillator strength of the Q33N67S glass is much lower than that of other compositions (**Figure 3b**), which can be explained by the analysis of computed energy levels and charge density distribution of frontier orbitals.

The ground-state electronic structure calculation predicts that the HOMO of the Q33N67S glasses is mainly determined by the oxygen atoms in glass matrices (**Figure 4**) while the Se atoms play a dominate role in determining the HOMO for other compositions. Meanwhile, the LUMO of CdSe QDs embedded glasses is decided by

the Cd atoms. Therefore, the frontier orbitals are spatially separated in Q33N67S glasses, indicating little possibility of hole and electron recombination even if the HOMO to LUMO transition is optically active. The excited state calculation further confirms this finding, as the first excited states transition is mainly derived from HOMO to LUMO transition, which is optically active but with weak oscillator strength in Q33N67S glasses (**Figure 3b**).

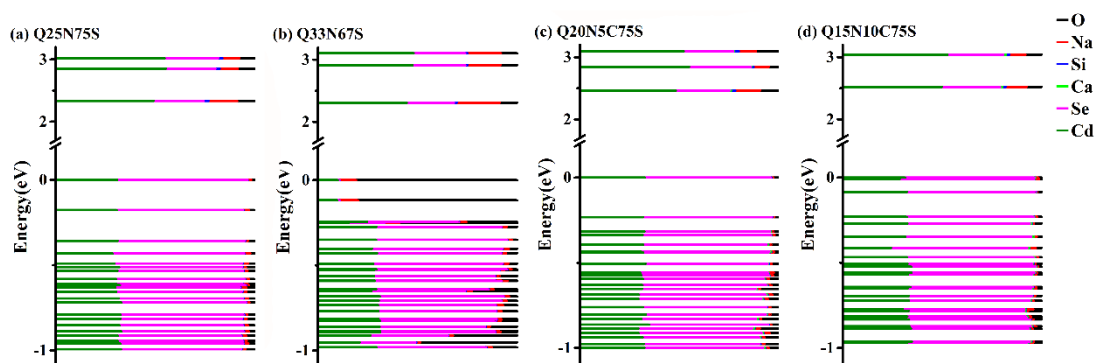


Figure 4 Computed electronic structure of the CdSe QDs embedded in glasses. The calculated structure is the final configuration of the 10 ps AIMD production run. Each line corresponding to a molecular orbital and HOMO was set at 0 eV. Each color represents the contribution of a type of atom for a given molecular orbital. Apparently, the HOMO of Q33N67S is mainly determined by O atoms, rather than Se atoms in other compositions.

The charge density distributions (depicted on **Figure 5** and **Figure 6**) are consistent with the computed energy levels. In Q25N75S glasses, the lowest-energy transition is mainly ascribed to the transition from HOMO (**Figure 5a**) to LUMO (**Figure 5b**), which is distributed on the undercoordinated surface atom of the hybrid QD. It is noteworthy to mention that both orbitals are distributed on some interfacial oxygens, indicating the hybridized nature of frontier orbitals (**Figure S3** in detail). The oscillator strength of the first excited states (also the brightest state with the maximum oscillator strength f_{\max}) are enhanced compared to the pristine QD, due to the improved overlap between the hole and electron wavefunctions. The absorption spectra and distribution of charge density of frontier orbitals are also calculated for some representative configurations from the production run of AIMD (**Figure S4**). It is clear that the multiple interactions between glass matrices and QD lead to different atomic structure of hybrid QD, hence the diverse excited states are observed for Q25N75S glasses. In some configurations, the first absorption peak is blue-shifted (**Figure S4c**), rather than

red-shifted, compared with pristine QD (**Figure S4a** and **S4b**). The oscillator strength of the first excited state transition also slightly fluctuates and the charge density distribution exhibits similar features. All these observations point to a consistent result: the lowest-energy transition is optically active and the frontier orbitals are mainly distributed on surface Se atoms.

However, in Q33N67S glasses, the HOMO is almost localized on the non-bridging oxygen atoms at the QD/glass interface (**Figure 5c** and **Figure S3c**), while the LUMO is mostly delocalized on the hybrid QD (**Figure 5d** and **Figure S3d**) with a small portion on non-bridging oxygen atoms. The small spatial overlap between the electron and hole wavefunctions indicates the weak oscillator strength of the lowest-energy transition. A weakly interacting electron and hole pairs for CdS QDs in phosphate glass were experimentally observed by optically detected magnetic resonance (ODMR) spectroscopy, suggesting a localized state at the surface of CdS QD.⁵⁴ The origin of this interfacially - localized state could not be clarified by the ODMR, however, non-bridging oxygen atoms might be the source according to our study. For this composition, the HOMO-2 orbital is still localized on the interfacial non-bridging oxygen atoms (**Figure S5a**). It changes to simultaneous distribution on hybrid QD and interfacial non-bridging oxygen atoms (**Figure S5b**) for HOMO-3 orbital, which corresponds to the 3rd excited states transition with an oscillator strength equal to 0.18. The brightest peak with the maximum oscillator transition is located at 2.58 eV (6th excited states transition), principally originating from the transition from HOMO-5 (**Figure S5d**) to LUMO. The HOMO-5 orbital is mostly distributed on the hybrid QD. It is clear that the charge density distribution shifts from the glass matrices to the hybrid QD gradually with the decrease of energy of occupied orbitals. Before the brightest peak, there is a number of low-energy states with weak oscillator strength, demonstrating the possibility of absorption tail.

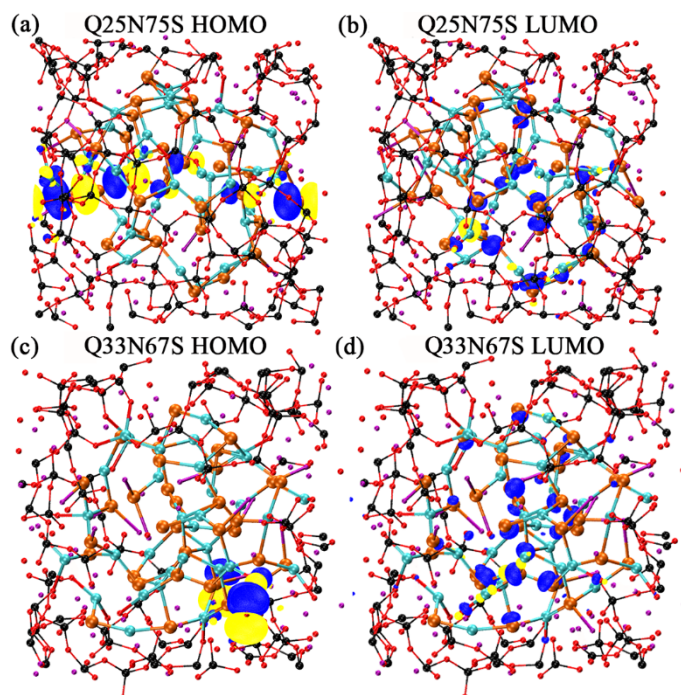


Figure 5 Molecular orbitals of CdSe quantum dots embedded in inorganic glass matrices. The distribution of charge density of Q25N75S and Q33N67S glasses. The HOMO is localized on the non-bridging oxygens at QD/glass interface in Q33N67S glasses, while the LUMO is delocalized on CdSe QD, indicating the weak oscillator strength of the lowest-energy transition due to the small overlap of hole and electron wavefunctions. A drawing of partial enlargement is provided in Figure S3.

Based on our previous work³⁹, the HOMO of most of the configurations were decided by non-bridging oxygen, while it was determined by Se atoms in 7 out of 50 configurations of Q33N67S glasses. To check this, we selected another 4 configurations to conduct further TDDFT calculations (presented in **Figure S6** and **Figure S7**). In most configurations, a weakly absorptive tail due to a dense manifold of low-lying states before the brightest peak can be observed, regardless of whether the HOMO is localized on interfacial non-bridging oxygen or uncoordinated surface Se atoms (**Figure S7a** and **S7b**). Although the oscillator strength of the lowest-energy transition is bigger in some configurations of Q33N67S glasses, it is still lower than that of Q25N75S glasses.

Moreover, the oscillator strength of the first excited states transition of Q20N5C75S and Q15N10C75S glasses are also higher than that of Q33N67S glasses. Based on the analysis of charge density distribution of molecular orbitals contributing to the lowest-energy transition (**Figure 6** and **Figure S8**), the hybridized nature of those orbitals is

clear with most of them distributed on surface Se atoms and a small portion on non-bridging oxygen atoms. The localization of HOMO for Q20N5C75S and Q15N10C75S glasses is not as significant as Q33N67S glasses, resulting bigger overlap of electron and hole wavefunctions.

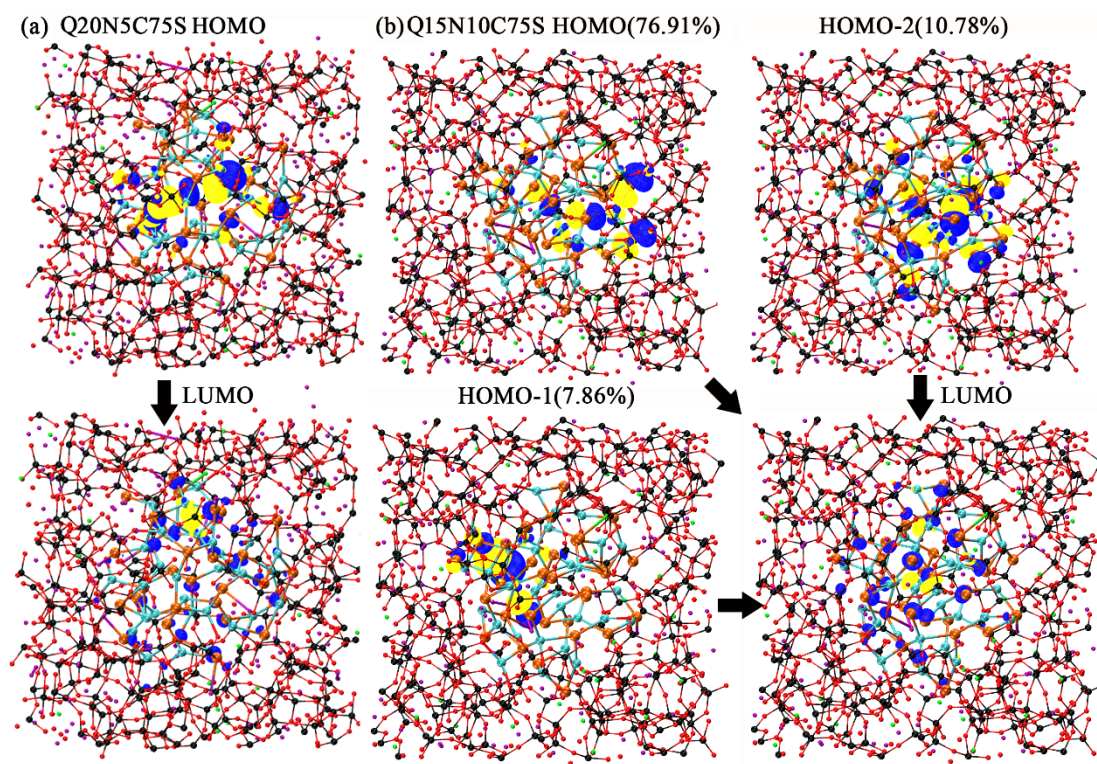


Figure 6 Molecular orbitals of CdSe QDs embedded in inorganic glass matrices. (a) The charge density distribution of the HOMO (top left) and LUMO (bottom left) of Q20N5C75S glasses. (b) The charge density distribution of the HOMO, HOMO-1, HOMO-2 and LUMO of Q15N10C75S glasses. The percentage represents the contribution of transition from each orbital to LUMO of the lowest-energy transition. All contributions higher than 5% are listed. All the charge densities of frontier orbitals are mainly distributed on Se atoms with a small portion on interfacial non-bridging oxygens, reflecting the hybridized nature of those frontier orbitals. A drawing of partial enlargement is provided in **Figure S8**.

It is well known that the timescale of electrons relaxation to the band edge states is in picosecond range, while the emission is in nanosecond range. As such, it is reasonable to assume that emission takes place from the lowest-energy states if it is optically active (large oscillator strength), since it is much faster than the nonradiative recombination via interband multiple phonon processes. However, if the lowest-energy states are

optically weak (small oscillator strength) or even completely inactive, it takes much longer for radiative emission; in this case, non-radiative processes can take place and even quench the emission. Therefore, the oscillator strength of the lowest-energy transition (which is inversely proportional to the radiative time) could be used as an indicator of the emission efficiency of the QDs.^{27, 31} In terms of experimental characterization, the PLQY is a common index to represent emission efficiency. Therefore, based on our calculations, the PLQY of the glasses is expected to decrease in the order of Q25N75S, Q20N5C75S, Q15N5C75S, and Q33N67S according to the oscillator strength of the first excited state transition.

To test the validity of our model, glasses with nominal composition (mol%) of 25 Na₂O–75 SiO₂–1 CdSe, 33 Na₂O–67 SiO₂–1 CdSe, 20 Na₂O–5 CaO–75 SiO₂–1 CdSe, and 15 Na₂O–10 CaO–75 SiO₂–1 CdSe were experimentally fabricated (see supporting information for details about fabrication and characterization methods). For all glass samples, the first excitonic absorption peaks are located at 444 nm (**Figure 7a**). Moreover, the absorption tails are obvious in Q33N67S, Q20N5C75S, and Q15N10C75S glasses. In **Figure 3**, a number of low-energy states with weak oscillator strength below the brightest peak are observed in glasses except for Q25N75S glasses, indicating that the absorption tail originates from those states, consistent with the experimental findings.

A Raman peak at 205 cm⁻¹ was observed for all samples, in good agreement with the longitudinal optical phonon of CdSe (**Figure 7d**).⁵⁵ Based on the first excitonic absorption peak using empirical equation,⁵⁶ the calculated size of the CdSe QD formed in glass specimen is 1.9 nm, which is bigger than that of pristine Cd₃₃Se₃₃ (1.3 nm) and hybrid Cd₃₃Se₃₃ (~1.6 nm) in our computational model. It is hard to synthesize CdSe QD with small size in glass matrices and this size was the smallest one we could achieve experimentally: our models based on Cd₃₃Se₃₃ already contain around 1100 atoms in total (including the glass), which is at the limit of computationally accessible systems. So one might question the relevance of our results to realistic CdSe QDs formed in glasses. Goldzak et al.³⁶ tested the size dependence of the excited states of Cd₃₃Se₃₃ (1.3 nm), Cd₃₈Se₃₈ (1.4 nm) and Cd₉₁Se₉₁ (2 nm). These authors found that the number of low-energy states below the brightest state were likely to be larger with the increase radius of CdSe QD. This observation suggests that the localization of hole on undercoordinated Se atoms seems to be more obvious for CdSe within the experimental range.

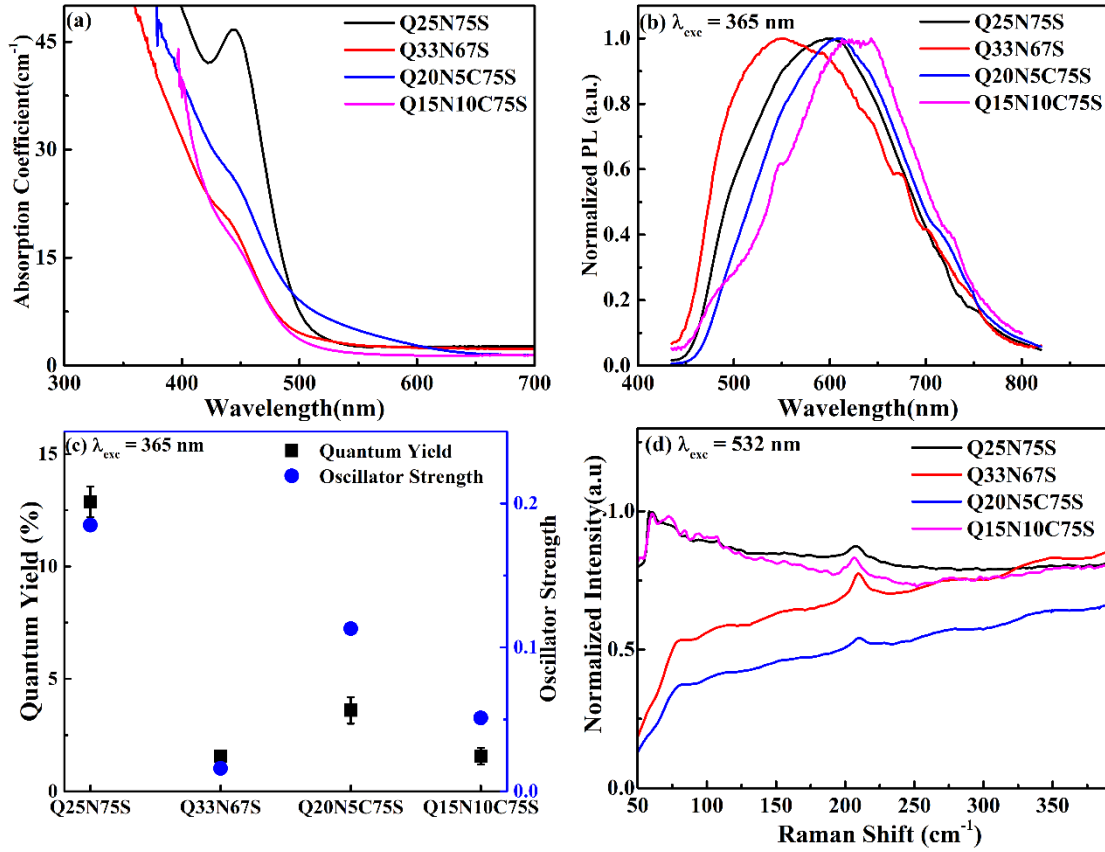


Figure 7 (a) Absorption spectra, (b) Normalized photoluminescence spectra (recorded under 365 nm excitation), (c) Quantum yield (left y -axis) and oscillator strength (right y -axis) of the lowest-energy states in our model, and (d) Raman spectra (recorded under 532 nm excitation) of Q25N75S, Q33N67S, Q20N5C75S, and Q15N10C75S glasses heat-treated at 530°C for 20 h, 480°C for 20 h, 560°C for 10 h and 580°C for 40 h, respectively. The error bar reflects the standard deviation of the measurement of PLQY. The PLQYs of the experimental fabricated glass samples are consistent with the oscillator strength as computational simulation predicted.

Although the position of the absorption peak of those glass samples are the same, the emission peak are located in different range under 365 nm light excitation (**Figure 7b**), indicating the various low-energy surface states of CdSe QD in glass matrices. Besides, the PLQY is 12.87%, 1.57%, 3.6% and 1.57% for Q25N75S, Q33N67S, Q20N5C75S and Q15N10C75S glasses, respectively (**Figure 7c**). As the oscillator strength of the lowest-energy transition can be an indicator of emissive properties, the tendency of the PLQYs in experiments are the same as the oscillator strengths in our computational simulation, validating the accuracy of our model.

The large Stokes shift, the broad full width at half maximum (FWHM) of emission

peaks as well as the low PLQYs, demonstrate the disappearance of intrinsic emission from the pristine QD. Those observations can be explained by our model. First of all, the dense manifold of low-energy states below the brightest peak provide intermediate states for the relaxing of electrons, explaining the observed bigger Stokes shift. Secondly, the micro region of CdSe QD embedded glasses is inhomogeneous due to the fluctuation of temperature and composition during realistic fabrication, leading to various interaction between the CdSe QD and glass matrices. The luminescence of the CdSe QD embedded glasses is originated from the combination of emission from those micro regions. According to our simulation, the excited states of hybrid QD in different glass matrices is diverse. For example, based on the oscillator strength and excitation energy of the lowest-energy transition of the configuration in **Figure S4** and **Figure S6**, the combination of emission from those configurations can be obtained, exhibiting similar broad emission with experimental findings (**Figure S9**). Therefore, the observed broad emission and large FWHM is derived from the various structure of hybrid QD. Finally, the unavoidable structural construction contributed to the formation of undercoordinated Se atoms or Cd atoms at QD/glass interface and breakage of Cd–Se bonds even in the core, resulting in the disappearance of pristine QD. At the same time, the presence of CdSe QD also leads to the inevitable formation of non-bridging oxygen atoms at the interface. The undercoordinated Se atoms and non-bridging oxygen atoms give rise to the localization of hole wavefunction, further decreasing the overlap between electron and hole wavefunctions and forming low-energy states with weak oscillator strength. Those low-lying states with very long emission lifetimes give a larger window for non-radiative processes to decrease PLQY. The disappearance of pristine QD and the inherent undercoordinated Se atoms or non-bridging oxygen atoms at QD/glass interface are the origin of low PLQYs of CdSe QD embedded in glass matrices.

One may question that why the PLQY of Q25N75S glasses is smaller as the oscillator strength is much higher than pristine QD. It may be attributed to the limitation of our model. For one thing, the size of CdSe QD (~1.9 nm) in experiment is much bigger than the pristine CdSe QD (~1.3 nm), the number of low-energy states with small oscillator strength increases with the QD radius,³⁶ suggesting the localized interfacial states are more severe in experiments range. We also note that our atomistic model is a simplified model with a perfect CdSe QD initially incorporated into the glass matrices. However, the real atomic structure is far more complicated such as vacancy and non-

stoichiometric QD, not being considered in our model. These defects may also decrease the PLQYs of CdSe QDs embedded in glasses.

3. Conclusion and perspectives

In conclusion, our theoretical results pinpoint the origin of the low PLQY of CdSe QDs embedded in inorganic matrices. By simulating the Cd₃₃Se₃₃ QD embedded in various glasses, we observed the formation of undercoordinated Se atoms and non-bridging oxygen atoms at QD/glass interface, leading to the localization of the hole wavefunction. The overlap between those localized states and delocalized electron states are small, resulting in a dense manifold of low-energy lying states with weak oscillator strength, further providing large opportunities for non-radiative processes hindering radiative emission. The glass matrices therefore have significant impact on the emissive properties of CdSe QD embedded in glasses indicated by the different excitation energy and oscillator strength of the lowest-energy excited states. The experimentally measured PLQYs of QD/glass system are in good agreement with our theoretical simulations, demonstrating the validity of our model.

Our results may provide guidance for both experimentalists and theorists to address the long-troubled low PLQY problem, paving the way for practical application of QD embedded in inorganic matrices ranging from LED to next-generation displays. We suggest that the composition of glass matrices, and especially the presence of the non-bridging oxygen atoms, is crucial to the luminescent properties. Glass matrices with low ratio of glass modifiers are found to exhibit better optical performance, which is one direction to adjust the glass composition. Additionally, although it is tough to passivate QD in glasses, the passivation method focused on non-bridging oxygen atoms and Se atoms are supposed to be effective. It also can be applied to passivate the colloidal QDs with inorganic shell such as SiO₂. As is a common method to calculate the radius of CdSe QD in glasses based on the absorption peak, our results also suggest the bandgap can be different for QD with the same size in different glass matrices. Therefore, this suggested caution in using these empirical equations.

Finally, our present computational work focused on stoichiometric QDs, while non-stoichiometric QDs are more common in reality. The Se-rich CdSe QD was found to have poor photoluminescence performance compared to Cd-rich CdSe QD and stoichiometric QDs.³¹ It is worthy of considering this imperfect QD embedded in glasses and the semiconductor material is not limited to CdSe, PbS or perovskite QD.

Another obvious extension would involve exploring faster computational methodologies to investigate the excited states of QDs with larger sizes, directly within the experimental range. The combining of machine learning with DFT calculation may be one solution to solve this problem.

4. Methods

Creating the atomic structure of CdSe QDs embedded in inorganic matrices

The generation of CdSe QD embedded in glass matrices is involved in 3 steps as developed in our previous study.³⁸ Firstly, the glass matrices with composition of 25 Na₂O–75 SiO₂, 33 Na₂O–67 SiO₂, 20 Na₂O–5 CaO–75 SiO₂, and 15 Na₂O–10 CaO–75 SiO₂ (mol%) were generated by classical MD using the DL_POLY code.⁵⁷ A partial-charge rigid-ion pairwise potential developed by Pedone et al.⁵⁸ was used to perform the simulations. The Coulomb interactions were calculated using the Ewald summation method⁵⁹ with a precision of 10⁻⁵, and a real-space cutoff for short-range interactions set to 7.6 Å. The initial configurations were obtained by randomly placing the atoms in a cubic simulation cell, with the density consistent with experimental values. The final configurations were generated by a melt-quenching approach in NVT ensemble. The initial structure was heated up gradually in steps of 1000 K with a 60 ps MD run at each temperature from 300 K to 6000 K. After equilibration of the liquid at 6000 K during 400 ps, the system was cooled gradually in steps of 500 K with a 60 ps MD run at each temperature from 6000 K to 300 K. A further 200 ps NVT simulation was carried out at 300 K, together with a 200 ps NVE simulation in order to equilibrate the structure. Secondly, a perfect Cd₃₃Se₃₃ QD was incorporated into the obtained glass matrices, served as the initial configuration for classical MD. Some atoms were removed from the glass matrices to keep the interatomic distance between CdSe QD and glass matrices longer than 2.5 Å. The number of the atoms of resulted structure (**Table S1**) was 30 Na₂O–90 SiO₂–33 CdSe, 39 Na₂O–78 SiO₂–33 CdSe, 68 Na₂O–17 CaO–255 SiO₂–33 CdSe, 51 Na₂O–34 CaO–255 SiO₂–33 CdSe, as shown in **Figure S1**. The interatomic interactions in CdSe QD were described by a Lenard-Jones pairwise potential validated in CdSe nanocrystals,⁶⁰⁻⁶¹ and the Lorentz-Berthelot combining rules were used for the interactions between the CdSe QD and glass matrices. The whole structure was firstly equilibrated at 1000 K using 200 ps of NVT dynamics and followed by 200 ps NVE of dynamics. Then it was cooled gradually from 1000 K to 500 K, while keeping CdSe frozen to keep the integrity of CdSe QD. Subsequent cooling from 500 K to 300 K took

place in steps of 10 K, with all atoms allowed to move. Finally, the structures were equilibrated at 300 K with 200 ps of NVT and NVE dynamics.

Thirdly, the final configuration of classical MD was used as initial configuration for AIMD using the CP2K code.⁶² The PBE exchange-correlation functional at the Generalized Gradient Approximation level were employed.⁶³ For Na, Ca, Cd and Se, a short-range molecularly optimized double- ζ single polarized basis set (DZVP-MOLOPT-SR-GTH) was used, while for O and Si we used a double- ζ single polarized basis set (DZVP-MOLOPT-GTH).⁶⁴⁻⁶⁵ The plane wave cutoff and relative cutoff were 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 AIMD run at each temperature with a time step of 2 fs. The production run was conducted in the NVT ensemble at 300 K for 10 ps.

Electronic structure calculation of CdSe QDs embedded in inorganic matrices

The final configuration of the AIMD run (**Figure 2**) was used to conduct a ground-state electronic structure calculation. The PBE0-TC-LRC exchange correlation functional⁶⁶ with a cutoff radius of 4 Å was employed to calculate the molecular orbitals of those configurations within the auxiliary density matrices method (ADMM).⁶⁷ The same basis set and cutoff were employed in the electronic structure calculations as the AIMD run. The absorption spectra were calculated using linear response time-dependent density functional theory (TDDFT) as implemented in CP2K code, with the same functional and basis set as used in ground-state calculations. The excitations of the first 100 electronic transition states were calculated. The obtained oscillator strength and excitation energy were broadened by the Gaussian function with a line width of 35 meV to obtain the absorption spectra. The excitation energies were also broadened with the same linewidth to calculate the density of transitions.

Representative input files for the calculations are available online at <https://github.com/fxcoudert/citable-data>

Supporting Information

The absorption spectra, and plots of frontier molecular orbitals of some representative configurations together with the details of experimental and characterization method are presented in supporting information. The TDDFT input files and geometry structure in .xyz format used for TDDFT calculations are attached.

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