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First-principles study of the halide-passivation effects on the electronic structures of CdSe quantum dots

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Abstract

We studied the effects of chlorine passivation and iodine passivation on the electronic structures of $\text{Cd}_{33}\text{Se}_{33}$ quantum dots through partial chlorine replacement for surface pseudo-hydrogen atoms, taking the full pseudo-hydrogen-terminated $\text{Cd}_{33}\text{Se}_{33}$ quantum dots as a reference. Our calculations demonstrate that the electrostatic interaction between surface Cd absorbates and halide passivant removes the dangling-bond-derived states of surface Cd atoms. Due to the high electronegativity, Cl passivant needs to coordinate with three Cd atoms to saturate p orbitals to form complete saturation. The modulation of Cl passivants to electronic structures of quantum dots depends on the coordination number of Cl passivants. With coordination number up to three, Cl passivants have less contribution to HOMO state and QDs are more energetically stable. With electronegativity decreasing from Cl to I, I passivants with 2 coordinations have been energetically stable to passivate QDs, leading to relatively inactive surface after passivation. The HOMO states of I-terminated QDs are composed of I 5p and Se 4p.

Keywords: chlorine passivation, iodine passivation, first-principles calculation, coordination number

1 Introduction

Colloidal semiconductor quantum dots (QDs), because of quantum size effect and strain relaxation, have unique physics properties such as energy band-gap tuning, carrier separation and size-dependence optical properties¹⁻³. That tunability enables QDs to optimally match the optical absorption of solar cells to the solar spectrum. In this regard, QDs have been considered as one of the promising materials for photovoltaic devices of the future. The high

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surface-to-volume ratio of QDs leads to the existence of a large number of surface dangling bonds which inject mid-gap states into the band gap. The open-circle voltage, V_{oc} , which is established by two distinct quasi-quantum energy levels, one for electrons and the other for holes, influences the solar cells performance. When the dangling bonds bring in trap states, the photogenerated charges fill into the mid-gap levels instead of those conductive band levels, resulting in reduction of V_{oc} . Moreover, the dangling bonds serve as the centers of electron-hole recombination shortening the life of excitons, which plays a negative role on the short-circuit current, J_{sc} . Consequently, the performance of nanostructured-semiconductor-based photovoltaics is limited by the surface states derived from dangling bonds. To improve solar cell efficiency, a strategy that achieves maximal passivation level is desired to remove the effect of surface dangling bonds.

Experiments have shown that the surface coordinating ligands have a dramatic effect on the band edges^{4,9}. For example, the rate of intra-band relaxation can be slowed down by changing the capping organic ligands⁴. Organic alkylamines⁹ and inorganic multi-semiconductor-shells^{9,10} increase the emission quantum yields by passivating the surface of CdSe QDs. Surface passivants also influences multiple-exciton generation efficiencies⁸. Surface passivation with proper ligands improves quantum efficiency of band edges⁹. Short mercaptopropionic acid achieved a best reported efficiency of 5.6% in organic ligands passivation by reducing the organic ligand interparticle spacing⁷. Much attention has been devoted to organic ligands which are used to lower the recombination loss due to the surface dangling bonds^{4,7,11,12}. However, the bulkiness of the organic ligands that employ long chains (8-18 carbons) prevent organic passivants from passivating other cations on the surface of QDs, leading to low coverage of passivants. That incomplete coverage of organic ligands leaves high density of defect which leads to recombination loss. Monovalent inorganic ligands⁵ was reported recently to offer a better passivation in steric consideration, achieving the efficiency as high as 6.0%. Halide ions, which attached to CdSe QDs through electrostatics interaction, led to different degrees of redispersion and stabilization in polar solvents¹³. Moreover, a hybrid passivation scheme⁶ of short organic ligands and halide anions have improved the solar cells efficiencies of colloidal QDs solar cells as high as 7%.

First principles calculations showed that organic ligands form delocalized orbitals

spreading over the QDs surface and ligands^{12, 14}. Steric interference of neighboring organic ligands affects binding strength between oxygen atoms in the organic ligands and cations on the surface¹¹. Unlike the well-studied effects of organic ligands on both structure and physics properties, the effects of inorganic ligands are rarely studied¹⁵⁻¹⁷. In theoretical studies of nanostructured semiconductors, pseudo-hydrogen (PH) was proposed to passivate each of the dangling bonds with fractional charge of $(8-Z)/4$, where Z is the valence charge of the surface atom¹⁸. With fractional charge, the PH passivants saturate the dangling bonds and remove surface states from electronic structure of band edges¹⁹. However, PH passivants are artificial and do not exist in the real world. There is no way to get the same intrinsic electronic structure as PH passivation case. But, technologically, we can take PH passivation as a reference, which is an ideal strategy to remove the dangling bonds. Experiments have shown that atomic halide ions, with the goal of using the shortest imaginable ligands, passivated QDs^{5, 6, 13}. However, the coordination effects of halide anions on the electronic structure of QDs are still not investigated. Here, we report our results of density function theory (DFT) calculations that reveal the effects of chlorine passivation on the morphology and electronic structure of CdSe QDs. We used $\text{Cd}_{33}\text{Se}_{33}$ cluster, which have been experimentally identified to be one of the smallest CdSe clusters²⁰.

In this paper we investigate the different impacts of PH and halide (Cl and I) passivations on the electronic properties of passivated QDs. For that purpose, we focused on $\text{Cd}_{33}\text{Se}_{33}$ dots capped with chlorine atoms or iodine atoms on topical sites and analyzed the change of corresponding electronic structure. We show that, the electronic interaction between surface Cd absorbates and halide passivants can remove the surface states from dangling bonds of surface Cd atoms. However, the incompletely saturated Cl passivants affect the states of highest occupied molecular orbitals (HOMO). In that case, the effect of chlorine passivation depends on the coordination number of Cl passivants. With the coordination number of 3, the Cl passivants remove surface states and have negligible effect on the HOMO states. In iodine passivations, 2-coordinated I passivant have been energetically stable and, with the energy levels close to those of Cd-Se in QDs, have a great effect on the HOMO states.

2 Methods

In our DFT calculations, we carried out the electronic structure and total energy calculations using the Troullier-Martins pseudopotentials prescription and the Perdew-Burke-Ernzerh of generalized-gradient approximation (GGA) exchange-correlation potential in Siesta package. Double- ζ plus polarization orbitals (DZP) are used as a basis set. The initial quantum dots coordinates are obtained by cutting out from the bulk wurtzite lattice ($a=4.419\text{\AA}$, $c=7.212\text{\AA}$). The supercell with QD locating at the center contains a vacuum region of at least 15\AA , which is large enough to reduce the periodic interactions. All the coordinates of atoms, including passivants, are fully relaxed until the force on each atom is no more than 0.04 eV/\AA . Although the GGA underestimates band gap, we focus specially on the relative change of band-edges as a function of different passivating sites. As a result, the band-gap error has little effect on our fundamental conclusions.

It is noted that, in practical experiments, QDs probably undergo surface reconstruction and, especially the case with no passivation, only a limited number of dangling bonds are left on the surface. That reconstruction changes the bulk-like electronic structures of QDs into surface electronic structures which have a great effect on the performance of QDs. For example, when the stoichiometric CdSe QDs are unpassivated, the electron transfers from cations to anions with surface reconstructing. That reconstruction removes dangling bonds and opens band gap, which is considered as ‘self-healing’ of QDs²¹. However, the self-healing drives sp^3 -like bonds between Cd and Se atoms to become surface bonds, e.g. the surface cations (Cd) perform sp^2 -like bonds with three neighboring anion atoms (Se) on Cd-rich surface. This condition of surface atomic bonds changes the bulky electronic properties to a surface one which has high density of states at the top of valence band. That effect becomes enhanced with size decreasing as the surface-to-volume ratio increases. Moreover, non-stoichiometric CdSe QDs may leave some chemically active bonds at the surface, which have surface states to reduce the energy gap. There are no intrinsic effects from surface reconstruction and non-stoichiometry is not discussed in the current work.

When the surface is unpassivated, inner Cd-Se bonds compel the dangling bonds of surface Cd to be sp^3 hybridized orbitals configuration. PH matches the orientation of dangling bonds to conserve the sp^3 configuration. The PH-terminated QDs have no surface reconstruction. The bonding states, due to the interaction between PH and surface atoms,

locate well below the HOMO state, while the anti-bonding states are above the state of lowest unoccupied molecular orbitals (LUMO). With no change to the intrinsic electronic structure of band-edges, PH passivation removes the effects of surface states. The states of HOMO and LUMO are mostly located within the interior of dot with negligible overlap with the states from PH passivants. Consequently, the electronic structure of band edges is dominated by the intrinsic chemical interaction within the interior of the QDs and independent of the bonds between the surface atoms and the PH passivants. Theoretically, PH passivation also provides a platform to judge a different passivation strategy by comparing it with the PH passivation case.

Previous computational¹¹ and experimental²² studies confirmed that organic ligands bind preferentially to the surface Cd atoms. We focus mainly on the effect of halide ligands binding to Cd atoms. To gain insight into the effect of chlorine passivation, we removed partial PH atoms from the surface Cd atoms at different sites and attached halide atoms (Cl or I) to the dangling bonds. The approach is similar to the replacement of H with O in bond study of SiC²³. Correspondingly, we employed the fully PH-terminated Cd₃₃Se₃₃ quantum dot as a reference to compare with. Because the distances between PH atoms and halide atoms are as large as 4 Å (3.5 Å for the (000 $\bar{1}$)^{II} facet case in chlorine passivation and 3.7 for the (000 $\bar{1}$)^{II} facet case in iodine passivation), the interaction between them could be reasonably neglected in following discussion.

3 Results and Discussions

Compared to the 4-coordination bonding between Cd and Se in wurtzite CdSe crystal, halide atoms prefers 3-coordination bonding with Cd due to the inactive lone pair of s² electrons of halide atoms, as demonstrated by the crystal structure of bulk CdCl₂ and CdI₂. In that consideration, while the charge of one dangling bond of one surface Cd atom is taken as fractional charge of 1/2, that of one halide passivant is taken to be 5/3. There is no perfect coordination combination between surface Cd absorbates and halide passivants to conform the charge balance and coordination number of Cd and halide atoms simultaneously. When one halide atom absorbs at the only dangling bond site of one 3-coordinated Cd atom,

obviously, the structure is unstable due to the incompletely saturated halide atom. The above consideration implies that one halide atom would interact with more than two dangling bonds from Cd to be saturated. When halide atoms attach to surface dangling bonds of QDs, two possible situations should be considered: one is that all surface Cd atoms are fully saturated and the systems keep charge balance (i.e. one halide atom simultaneously passivating two dangling bonds of surface Cd absorbate); the other is that one halide atom coordinates with three cadmium atoms, similar to the bonding in bulk CdCl_2 (or CdI_2) crystal to saturate the p orbitals of halide atoms, leaving one excess electron.

The Cd positions on the surface are marked as shown in Fig.1: A1, A2 and A3 indicate 3-coordinated Cd atoms, each with only one dangling bond to be passivated; B1 and B2 label 2-coordinated Cd atoms, each with two dangling bonds to be passivated. In general, taking chlorine passivations for example, the local structures to be passivated are classified into four categories: (i) one Cl atom passivates two dangling bonds from one 2-coordinated Cd atom (B1 or B2 sites); (ii) one Cl atom simultaneously passivates two dangling bonds from two 3-coordinated Cd atoms (A1 or A2 sites); (iii) one Cl atom passivates two dangling bonds from one 2-coordinated Cd atom and another one from one 3-coordinated Cd atom (A2 and B2 sites); (iv) one Cl atom passivates three dangling bonds from three 3-coordinated Cd atoms (A1 site) on $(000\bar{1})$ surface. In cases i, ii, and iii, Cd and Cl atoms conform the 8-valence electrons rule, which means that the QDs keep charge balance between cation and anion atoms, leaving the coordination number of Cl passivant less than 3. And case iv breaks charge balance, with one excess electron from cations (Cd), but saturates the Cl passivant with coordination number of 3. In case iii, there are other combinations (for example, B2 and A3 sites) which involve PH atoms to bond with Cl passivants, when Cl passivants absorb at the sites. We ruled those combinations out as unstable structures, for the reason that, just with surface Cd atoms, the Cl passivants can not be stable and need neighboring PH atoms to coordinate with.

Based on the relaxed structures, the configuration of the above four cases can be divided into two categories: (i) for mono-dentate of Cl passivant, i.e. one Cl passivant coordinating to one 2-coordinated Cd atom, the addition of Cl lead to no obvious surface reconstruction to the

wurtzite structure of QDs (see discussion in section 3.1); (ii) for multi-dentate of Cl passivant, i.e. one Cl passivant coordinating to more than one surface Cd atom, the addition of Cl affects the bond length of a few Cd-Cd pairs and results in surface reconstruction to some extent (see discussion in section 3.1).

3.1 Chlorine passivation with nearly valid Eight-valence electrons rule

When one chlorine atom coordinates with one 2-coordinated cadmium atom (B1 or B2 site in Fig.1) on $(0001)^I$ or $(11\bar{2}0)^I$ facet, the passivation maintains the surface of QDs the same configuration as bulk wurtzite CdSe. Due to the dominant ionic bonding character, the interaction between the Cl passivants and surface Cd atom is electrostatic interaction which passivates dangling bonds. The electrostatic interaction pushes the surface states from dangling bonds of cations down below the HOMO state, even not as deep as those in PH-terminated cases. In addition, because of the electrostatics interaction, the bond lengths between Cl passivants and surface Cd absorbates become important (see Table 1). We find that the bond lengths between surface Cd absorbates and Cl passivants get longer as the coordination number of Cl passivants increases. The energy gap is composed of the bonding state and anti-bonding state of Cd-Se in PH passivation case. However, in Cl passivation cases, the bonding state from surface Cd absorbates and incompletely saturated Cl atom (except for $(000\bar{1})^{III}$ case) slightly perturbs the HOMO states of QDs, depending on the coordination number of Cl passivants. In incompletely saturated Cl passivations, energy level of bonding state of Cd-Cl, which depends on bond length of Cd-Cl, is higher than those of Cd-Se and occupies the HOMO states of QDs. And the energy gap is bigger with shorter bond length of Cd-Cl (see Table 1). Detail will be discussed below.

Generally speaking, all passivation cases have LUMO similar to PH-terminated QDs. With negligible overlap with Cl passivants, the LUMO states mainly locate at the interior Cd atoms (see Fig. 2). The energy level of anti-bonding state of Cd-Cl are higher than that of interior Cd-Se. Passivated surface Cd atoms and incompletely saturated Cl passivants do not lead to surface states to the LUMO states. As a result, the LUMO states of QDs are composed of intrinsically anti-bonding state of Cd-Se and the incompletely saturated Cl passivants have

negligible effect on the LUMO states.

With mono-dentate of Cl passivant, the HOMO states of QDs with Cl-passivation on $(0001)^I$ facet and $(11\bar{2}0)^I$ facet are composed of the incompletely saturated Cl 3p orbitals (see Fig. 2), partially mixing with neighboring Se 4p orbitals. The states of Cl 3p orbitals are above those of the intrinsic Cd-Se of QDs. Although Cl passivants remove the surface states of dangling bonds of surface Cd atoms, the incompletely saturated Cl passivants lead to new surface states. The relatively high density of Cl 3p states actually leaves the QDs unstable, and the QDs prefer to lower the energy level of the Cl p orbitals through surface structure relaxation. As a result, $(0001)^I$ facet and $(11\bar{2}0)^I$ facet are the last possible sites which Cl passivants absorb.

In the case of $(000\bar{1})^{II}$ (or $(01\bar{1}0)^{II}$) facet passivation, the bond lengths between Cl and 3-coordinated Cd atoms is shorter than the Cd-Cl distance in bulk CdCl_2 (2.70 Å). The HOMO states also contain contribution from Se 4p and Cl 3p states. Although $(000\bar{1})^{II}$ and $(01\bar{1}0)^{II}$ cases reduce the contribution from Cl 3p states to the HOMO states, that mixture breaks the symmetry of distribution of HOMO states in PH-terminated case. Moreover, the spatial wavefunction distribution of top HOMOs shows that those wavefunctions have significant contribution from the surfaces Cl passivant of QDs. Compared with PH-terminated case, those 2-coordinated Cl atoms significantly affect the electronic structure of band edges. Consequently, the HOMO states of $(000\bar{1})^{II}$ and $(01\bar{1}0)^{II}$ cases are mixture of Se 4p and Cl 3p states in comparison with that of Se 4p states in PH-terminated case. In that consideration, Cl passivants in bidentate cases (i.e. $(000\bar{1})^{II}$ and $(01\bar{1}0)^{II}$ cases) remove surface states of surface Cd absorbates but perturb the HOMO states of QDs. Compared with the mono-dentate case of Cl passivation, those bidentate cases lower the energy level of Cl passivants, which is still higher than that in the tridentate case (see discussion in section 3.2).

Figure 3 shows the schematic bonding picture of charge balance cases. The above discussed Cl passivation cases, conforming the 8-valence electrons rule, remove the dangling-bond-derived states. The LUMO states of Cl passivation cases can be considered as

that of PH-terminated case, which means that Cl passivants remove the dangling-bond-derived states and have negligible perturbation to the LUMO states of QDs. However, the passivation effect of Cl passivation on band edges is not as strong as that in PH passivation, and the contribution of Cl passivants to HOMO states can still be clearly observed, depending on the coordination number of Cl passivants. But the energy levels of the bonding states of the coupling surface Cd and incompletely saturated Cl passivants are higher than those of the bonding state between Cd and Se atoms. As shown in Fig. 2, for all Cl passivation cases, the incompletely saturated Cl passivant, i.e. the coordination number of Cl passivant less than three, have a great perturbation to the HOMO states. Though Cl passivants can passivate, to a large extent, the dangling bonds of surface Cd absorbates in all cases, the p orbitals of Cl atoms need three neighboring Cd atoms to be saturated. However, the charge balance consideration (i.e. conforming all atoms 8-valence electrons rule) leaves the coordination number of Cl passivants less than three. And the mixture of Cl 3p states and Se 4p states composes the HOMO states of QDs, and the coordination number of Cl passivants influences wavefunction distribution of HOMO states by changing the saturation extent of Cl passivants. As a result, the energy levels of bonding states of Cd-Cl in charge-balance Cl passivations are not certainly below that of intrinsic bonding state of Cd-Se but can be considered as a function of coordination number of Cl passivants. With the coordination number of Cl passivants increasing, the energy level of bonding states of Cd-Cl gets deeper. The system that one chlorine atom coordinates with two 3-coordinated Cd atoms is more stable than the system that one chlorine atom coordinates with only one 2-coordinated Cd atom. But the most stable case should correspond to the Cl passivants interacting with 3-coordinated Cd atoms. The HOMO states with incompletely saturated Cl p orbitals are expected to have negative effect on the performance of QDs-based devices.

3.2 Chlorine passivation with 3-coordinated Cd atoms

The effective Cl passivation depends on the distance between Cl passivant and surface Cd absorbates. Only in the case of (000 $\bar{1}$) facet passivation, one chlorine atom can directly bond to three 3-coordinated Cd atoms (A1 site) in a distance of 2.83 Å, 4.8% larger than the calculated Cd-Cl bond length (2.70 Å) in bulk CdCl₂. In such a case, a HOMO-LUMO gap is

2.50 eV, 0.03 eV larger than the gap for the case of one chlorine atom passivating two 3-coordinated Cd atoms on the $(000\bar{1})^{\text{II}}$ facet (see Table 1). Though the charge balance of QDs is broken, the chemical bonding from Cl-Cd interaction acts as ‘ligand potential’ to passivate the dangling bonds of three Cd atoms and remove surface states, leaving one excess electron. As shown in Fig. 4 (a), although the excess charge pushes the Fermi energy up close to the LUMO states as n-type doping, ‘ligand potential’ pushes surface states derived from dangling bonds of three surface Cd atoms below the HOMO states and the tridentate saturates the Cl passivant. Unlike dangling bonds, the excess electron shifts Fermi energy level but does not inject new surface states into the band gap. As a result, one chlorine atom passivates three 3-coordinated surface Cd absorbates.

Due to the large difference in the electro-negativities between Cl and Cd, Cl 3p and Cd 5s have weak p-s mixing in the upper valence band in CdCl_2 crystals. Consequently, the Cl 3p occupied states form the top of the valence band, which is near 1 eV deeper than that of PH-terminated $\text{Cd}_{33}\text{Se}_{33}$ QDs, and the mixing Cd 5s - Cl 3p unoccupied states form the bottom of the conduction band²⁴. As shown in Fig 4 (b) and (c), in $(000\bar{1})^{\text{III}}$ case, the HOMO wavefunction of QD locates at Se sites and has no overlap with Cl passivant, and the LUMO wavefunction slightly overlaps with Cl passivant. The 3-coordination, as that in bulk CdCl_2 crystals, saturates Cl passivant and lowers the energy level of Cl 3p states below HOMO state, so that the HOMO states locate at those interior Se atoms of QDs. Energetically, the passivation of one Cl passivant bonding with three 3-coordinated Cd atoms is more stable than those passivations of one Cl passivant bonding with less Cd atoms because the latter incompletely saturates Cl and leads to higher energy states of the Cl passivants.

3.3 Iodine passivation on QDs

The chemical bonding between Cl passivants and surface Cd atoms could remove surface states derived from the dangling bonds of surface cations, even in the case of charge balance broken (see Section 3.2). However, because of the high electronegativity of Cl, the Cl passivant needs three Cd atoms to form a tridentate ligand to be well saturated. With only few sites on QDs’ surface providing three sufficient cations to coordinate, the vast majority of Cl

passivants tend to interact with cations from the surfaces of neighboring QDs to be saturated. Recent experiment¹³ reported that the CdSe QDs with Cl passivants tend to aggregate but those with Br or I passivants have no obvious changes in the QDs size and show no sign of aggregation, which seems partly consistent with our conclusions. Figure 5 plots the electronic structures of QDs passivated by I atoms on (0001)^I, (000 $\bar{1}$)^{II}, and (000 $\bar{1}$)^{III} facets, respectively. I passivants could remove the surface dangling states and broaden energy gap (see Fig. 5a). Meanwhile, I passivant with mono-dentate ligand also leads to new surface states above the bonding states of Cd-Se in (0001)^I case. With bidentate of I passivants, the chemical bonding from I-Cd lowers the energy level of the I passivants and the HOMO states are composed of the mixture of I 5p and Se 4p in (000 $\bar{1}$)^{II} case. However, even I passivants dangling with three Cd coordinations, the HOMO states are still composed of the mixture of I 5p and Se 4p in (000 $\bar{1}$)^{III} case (see Fig. 5b). This is partly different from the case in chlorine passivation.

Because of the difference in electronegativity of Cl from I and the varying bond lengths, the chemical bonding from I-Cd is expected to be weaker than that from Cl-Cd. Consequently, the energy levels of bonding states of I-Cd are not as deep as those of Cl-Cd. The HOMO states in (000 $\bar{1}$)^{III} case, which are composed of I 5p and Se 4p, demonstrate that the coordination number of I passivants have less effect on the HOMO states in iodine passivation than that in chlorine passivation. In chlorine passivation, the energy levels of bonding states of Cd and 3-coordinated Cl atoms fall deeper in energy than those of the bonding states of Cd and Se atoms within QDs, but the incompletely saturated Cl passivants have relatively energy levels, which are even comparable with the energy levels of bonding states of Cd-Se in QDs (see Fig. 2). To lower the activity of the incompletely saturated Cl passivants, the Cl passivants tend to interact with nearby especially neighboring cations, leading to the aggregation of QDs. However, in iodine passivation, due to the electronegativity decreasing, the energy levels of Cd and 3-coordinated I atoms are intrinsically comparable with the energy levels of bonding states of Cd-Se in QDs. And the coordination number of I passivants has less effect on the saturation of I passivants than that of Cl passivants, because the passivation of one I passivant to only two 3-coordinated Cd

atoms has already been stable in iodine passivation cases. Therefore, QDs with 2-coordinated I passivants have weak interaction with cations from neighboring QDs, leaving no obvious aggregation in the size.

In PH-terminated case, PH atoms, exactly matching the direction and fractional charge of dangling bonds, perfectly passivate surface cations. The bonding states and anti-bonding states from PH and surface atoms can be pushed down deep into the valence band and up into the conduction band, respectively. Organic ligands usually passivate surface atoms with surface reconstruction, which leads to charge transfer from cation to anion atoms. The binding between organic ligands and 2-coordinated Cd atoms is always stronger than that between organic ligands and 3-coordinated Cd atoms. In addition, the effect of organic ligands depends on the binding capacity of the ligand to the QD as well as steric inter-ligand interactions¹². However, after removing the surface states derived from dangling bonds of cations of QDs, the effect of Cl passivation depends mainly on the coordination number of Cl passivants. The incompletely saturated Cl passivants may affect electronic structure of band edges, while completely saturated Cl passivants have little effect on edge states. For small QDs, the different coordination environment of Cl passivants may lead to different distribution of HOMO states, which potentially affects the efficiency of QD-based device. Compared with the organic ligand passivation based on binding capacity and complex surface reconstruction, halide passivants perfectly present a better passivation due to electrostatic interaction⁵. Moreover, due to the different preferred absorbate sites, which is the fact that organic ligands prefer to absorbing one 2-coordinated cations and that halide passivants prefer to binding with more than one 3-coordinated cations, a hybrid of organic and halide ligands can improve the efficiency of solar cells⁶. Steric locations which halide passivants absorb may compensate the organic-ligand-uncovered surface to improve the coverage and thus the passivation of QDs.

4 Conclusion

In summary, we have investigated the electronic structures of QDs passivated by Cl and I passivants based on DFT calculations. Our calculations demonstrate that, unlike the perfect coordination number match in PH passivation, Cl passivants need to form 3-coordination to be completely saturated, while the electrostatic interaction between Cl and Cd atoms can

passivate dangling bonds of surface Cd atoms, even in the case of charge balance broken. The Cl passivation may lead to somewhat changes in electronic structure of QDs, depending on the coordination number of Cl passivants. With coordination number of Cl passivants increasing, the HOMO state has less contribution from Cl passivants and the QDs get energetically more stable for lower the energy level of Cl passivants. Incompletely saturated Cl passivants may interact with cations of neighboring QDs and, thus, result in the aggregation. With electronegativity decreasing from Cl to I, the states of I passivants 5p compose HOMO states of passivated QDs and have effect on the electronic structure. And 2-coordinated I passivants have been energetically stable, resulting in no obvious aggregation of QDs. Our analysis seems helpful to explain the passivation of organic and inorganic ligands that could potentially improve the coverage and the efficiency of QDs, in addition to the steric consideration.

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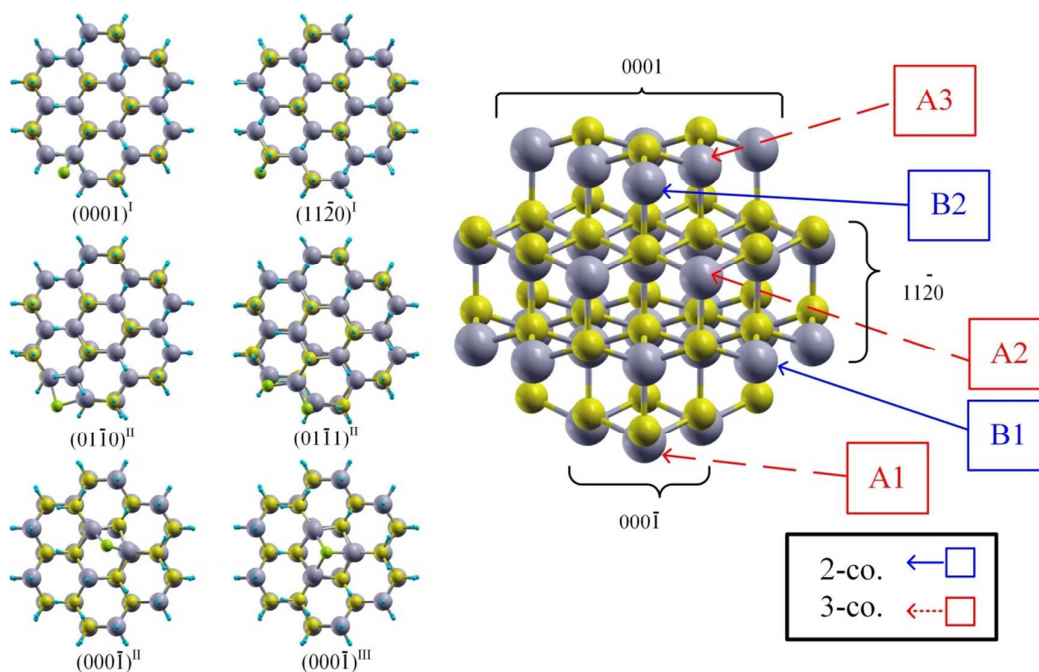


Fig.1 Calculated structures of Cl passivation on $(0001)^{\text{I}}$, $(11\bar{2}0)^{\text{I}}$, $(01\bar{1}0)^{\text{II}}$, $(000\bar{1})^{\text{II}}$ facets of $\text{Cd}_{33}\text{Se}_{33}$ QDs, with the superscript of roman numbers (i.e. I, II and III) standing for the coordination number of Cl passivants. And $(01\bar{1}1)^{\text{II}}$ case stands for one Cl atom passivating Cd atoms of A2 and B2 sites and $(000\bar{1})^{\text{III}}$ stands for one Cl atom passivating three Cd atoms at A1 site. Cd, Se, Cl and PH atoms are colored grey, yellow, green and blue, respectively. $(000\bar{1})^{\text{II}}$ and $(000\bar{1})^{\text{III}}$ cases take the view from the bottom, while the other 4 cases from the top.

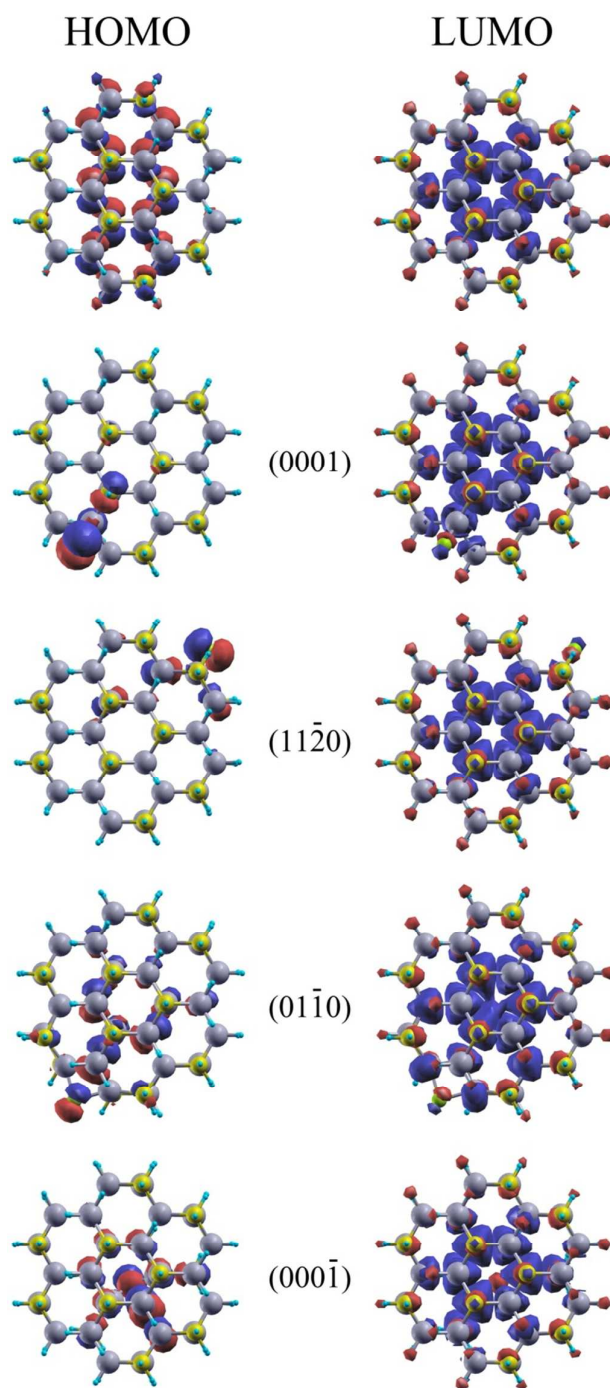


Fig. 2 HOMO (left column) and LUMO (right column) of Cl-passivated $\text{Cd}_{33}\text{Se}_{33}$ QDs at Γ point.

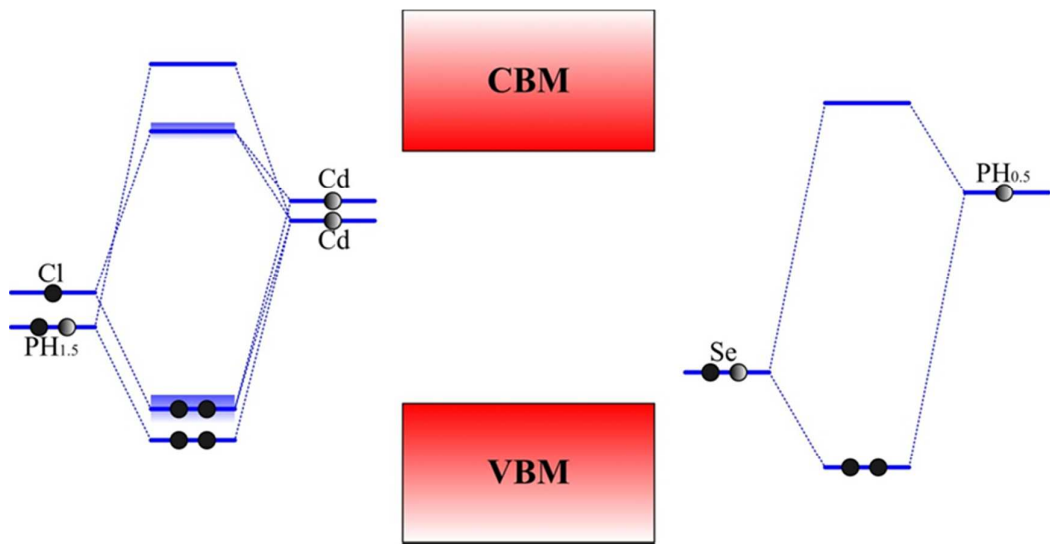


Fig. 3 Schematic bonding picture of PH passivation and Cl passivation

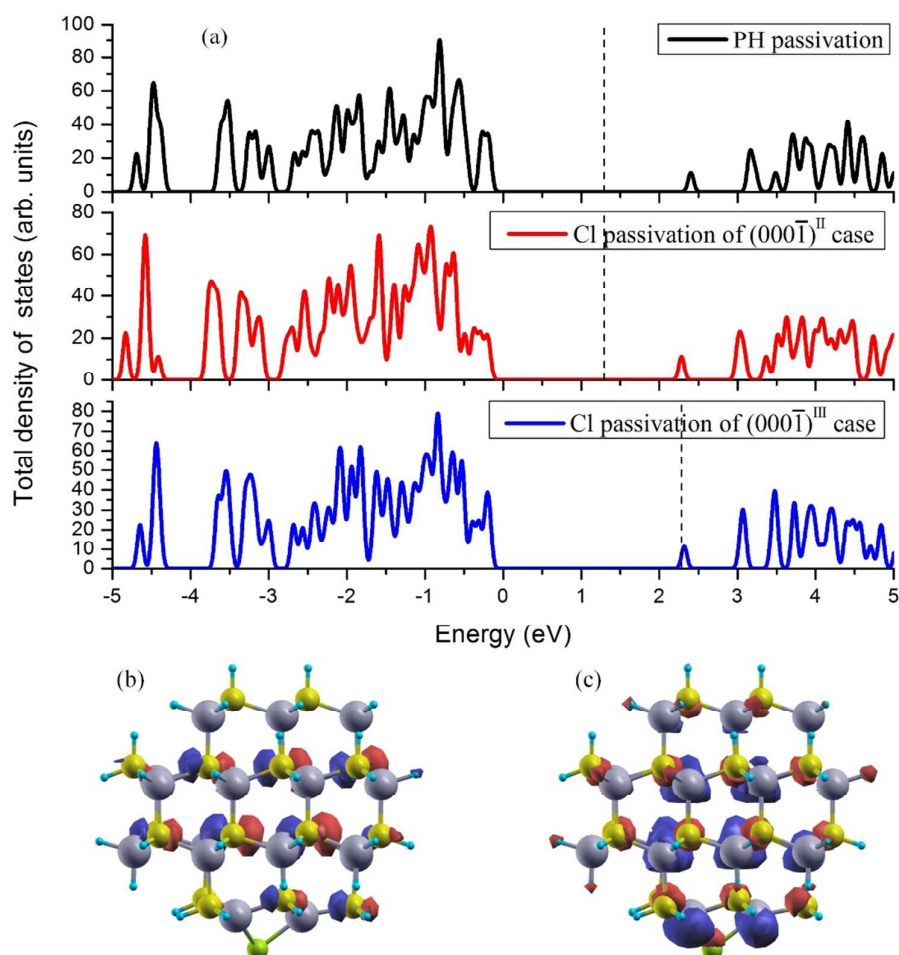


Fig. 4 Density of states and chlorine passivations on $(000\bar{1})$ surface (a) The total density of states (DOS) of $\text{Cd}_{33}\text{Se}_{33}$ QDs with $(000\bar{1})$ surface passivated by PH, one Cl bonding to two 3-coordinated Cd atoms in $(000\bar{1})^{\text{II}}$ case, and one Cl bonding to three 3-coordinated Cd atoms in $(000\bar{1})^{\text{III}}$ case, respectively. The zero of energy is aligned with the top of the valence band. And the dashed line indicates the Fermi levels for each case. (b) and (c) are the wavefunction distribution of HOMO and LUMO states for the $(000\bar{1})^{\text{III}}$ case.

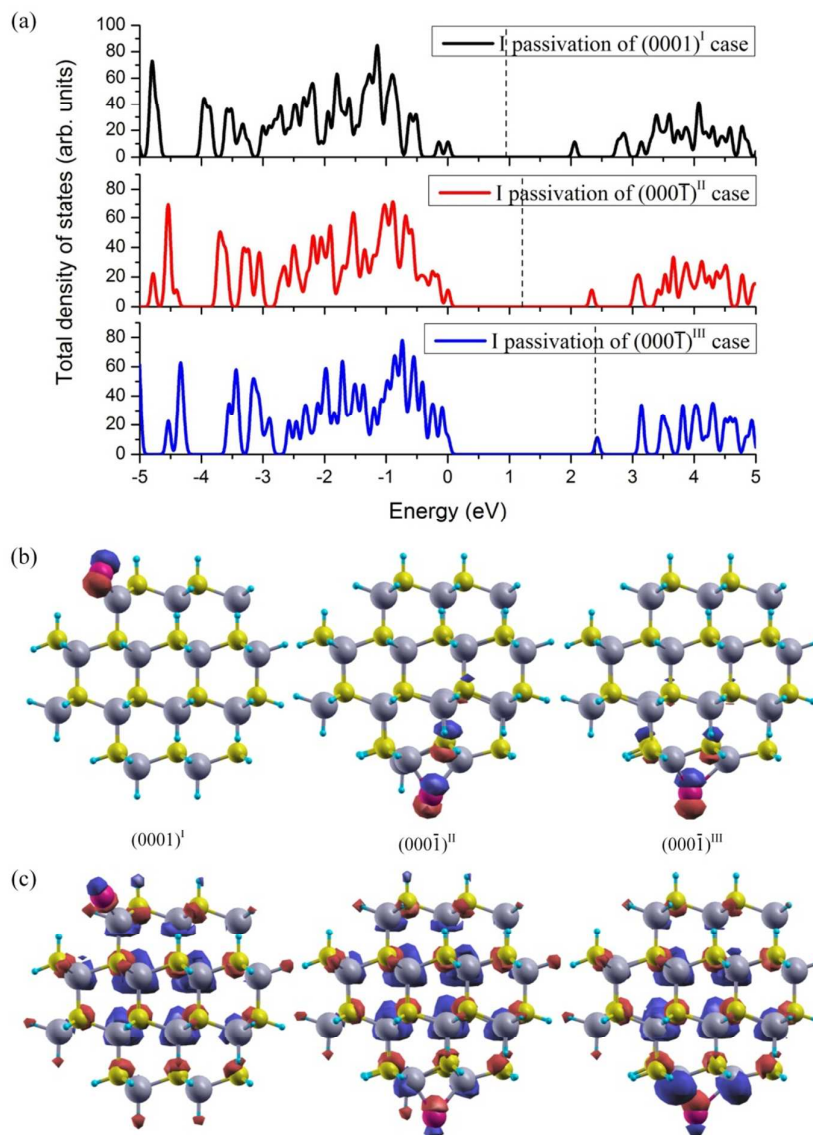


Fig. 5 Density of states and iodine passivations on (0001) and (000 $\bar{1}$) surface (a) The total density of states (DOS) of Cd₃₃Se₃₃ QDs with passivated by PH, one I bonding to one 2-coordinated Cd atom in (0001)^I case, one I bonding to two 3-coordinated Cd atoms in (000 $\bar{1}$)^{II} case, and one I bonding to three 3-coordinated Cd atoms in (000 $\bar{1}$)^{III} case, respectively. The zero of energy is aligned with the top of the valence band. And the dashed line indicates the Fermi levels for each case. (b) and (c) are the wavefunction distributions of HOMO (middle panel) and LUMO states (bottom panel) for the three cases.

Table 1: Calculated energy gap and bond length of Cd₃₃Se₃₃ quantum dot with PH passivation, Cl passivation and I passivation on topical facets. Energy Gap is the energy difference between the HOMO state and LUMO state. Bond length is estimated based on the distance between the passivants and surface Cd absorbates.

		Chlorine passivation						Iodine passivation		
	PH	(0001) ^I	(11 $\bar{2}$ 0) ^I	(01 $\bar{1}$ 0) ^{II}	(000 $\bar{1}$) ^{II}	(01 $\bar{1}$ 1) ^{II}	(000 $\bar{1}$) ^{III}	(0001) ^I	(000 $\bar{1}$) ^{II}	(000 $\bar{1}$) ^{III}
Energy Gap (eV)	2.58	2.53	2.49	2.43	2.47	2.40	2.50	2.06	2.33	2.42
Bond Length (Å)	1.88	2.35	2.37	2.65	2.65	2.57/2.70	2.83	2.66	2.94	3.14