Multiple Exciton Generation in Small Si Clusters: A High-Level, Ab Initio Study

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ABSTRACT The electron–hole excitonic nature of high energy states is investigated in neutral and charged Si clusters, motivated by the multiple exciton generation (MEG) process that is highly debated in photovoltaic literature. Silicon forms the basis for much of the photovoltaic industry, and our high-level, first-principles calculations show that at 2–3 times the lowest excitation energy, the majority of optically excited states in neutral Si and Si10 take on multiple exciton (ME) character. The transition from single excitons (SEs) to MEs is not as sharp in Si as in PbSe clusters, but it is much more pronounced than in CdSe. The closer similarity of Si to PbSe than CdSe is unexpected, since Si clusters are less symmetric than PbSe clusters. Charging suppresses MEG in Si clusters; however, the suppression is less pronounced than in PbSe. A strong ME signal is seen already at $5 \times E_g$ upon charging. The low ME thresholds and nearly complete switch from SEs to MEs create a good possibility for efficient MEG in neutral Si nanoclusters and reveal hope that reasonable quantum yields can still be obtained despite charging.

SECTION Dynamics, Clusters, Excited States

The thermodynamic efficiency of solar conversion devices is limited to 32%,¹ with a significant portion of solar energy lost to heat. Semiconductor quantum dots (QDs) have held the promise of higher efficiencies because of the belief that quantum confinement effects can lead to efficient multie exciton generation (MEG).² Besides photovoltaic applications, MEG benefits photoconductive devices, e.g., optoelectronic detectors.³ Multiple mechanism have been proposed for MEG and much controversy remains,⁴ even though most authors agree that MEG occurs as a result of Coulomb interaction between charge carriers. One such mechanism is an inverse Auger process,¹⁵–⁷ commonly known as impact ionization. This mechanism relies on a single, high-energy exciton, which produces a second exciton through a strong Coulomb interaction between electrons and holes. Confinement effects can enhance the likelihood of the inverse Auger process, due to the closer proximity of the charge carrier, by relaxing the momentum conservation requirement of the bulk material, and through the increased spacing between the electronic energy levels. If the spacing becomes mismatched with phonon energies, then the so-called phonon-bottleneck results.¹⁸ The hot-exciton relaxation slows down, creating more time for the inverse Auger process to occur.

Another mechanism is the direct excitation of multiple excitons (MEs).⁹,¹⁰ Here, Coulomb interactions couple ME states with single exciton (SE) states and allow for the direct optical excitation of MEs. This mechanism is independent of the phonon-bottleneck and is supported by the ultrafast MEG time scales.⁹,¹¹ the experiments that show MEG with no phonon-bottleneck,¹²,¹³ and our previous simulations of the ultrafast electron–phonon relaxation¹⁴,¹⁵ and the nature of the photoexcited states¹⁰,¹⁶ in PbSe and CdSe QDs. A third mechanism that has been put forth involves exciting a superposition of SEs and MEs.¹¹,¹⁷ The efficiency of this mechanism depends on the relative dephasing times of SEs and MEs.¹⁸,¹⁹ This mechanism is also consistent with our theoretical calculations on CdSe clusters¹⁰ and accounts for the small modulation in the early time data seen in the experimental signal.¹¹ MEs were observed in a variety of materials. However, conflicting reports of MEG efficiencies were reported.²,⁴,²⁰–²⁹ In a previous paper,¹⁶ we proposed that photoionization of the QD is an important reason for the low quantum yields, especially if MEs are generated by the direct mechanism, compared to the inverse Auger process.³⁰ Our symmetry adapted cluster theory with configuration interaction (SACCI) calculations on PbSe showed that charging the QD creates a possibility for intraband excitations and significantly blue-shifts both SEs and MEs. This blue-shift pushed the MEG threshold to very high energies that are hardly relevant for solar energy harvesting. Uncontrolled charging in QDs can thus result in a devastating decrease in MEG efficiency.

Silicon QDs deserve particular attention, since much of the present photovoltaic industry is already based in Si. Further, Si does not raise toxicity issues that can be concerns with other materials. Recently, Si QDs demonstrated the potential to

Received Date: October 6, 2009
Accepted Date: November 11, 2009
Published on Web Date: November 20, 2009
make solar devices with higher efficiencies than are possible with currently used technologies. Experimental measurements on Si QDs put the threshold of MEG at 2.4 times the first band gap excitation energy ($2.4 \times E_g$) and found a quantum yield of 2.6 excitons per photon at $3.4 \times E_g$. 31 In order for Si QDs to become a viable option in solar devices, a theoretical understanding of MEG in Si QDs is necessary.

In this letter, we present the results of state-of-the-art quantum chemical calculations as applied to neutral, anionic, and cationic Si$_7$ and neutral Si$_{10}$ QDs. SAC-CI, 32 as implemented within the Gaussian 03 software package, 33 is a high-level computational tool that begins with Hartree–Fock (HF) and uses a cluster expansion to explicitly include correlation effects in the ground-state wave function. Operators are then applied to this correlated ground state producing excited states with both single- and multie excitonic character. This method goes beyond linear-response time-dependent HF and density functional theory (DFT), which remain in the single-particle picture and thus have difficulty producing states consisting of MEs.

The very large computational cost of the calculations performed here severely limits the size of the QDs. We have previously shown through HF band structure analysis that the results from the small QDs can be generalized, at least qualitatively, to larger QDs. 10 The SAC-CI method is much more sophisticated than the effective mass theory 11 and pseudopotential approaches. 6, 7, 21 The atomistic, semiempirical pseudopotential method suggests that conclusions obtained for small QDs should hold for QDs up to 3 nm in diameter. 21 In this method, Fermi’s golden rule was used to calculate exciton–bixciton transition rates and to estimate the number of excitons produced by a single photon at different energies. The SAC-CI results described below fit nicely with the pseudopotential trend for excitons produced per photon (see Figure 4 in ref 21).

The QDs used in this study are shown in Figure 1. Optimized geometries of the Si$_7$ and Si$_{10}$ QDs were obtained using ground-state DFT with the B3LYP functional and the LANL2dz basis set. The structures used in the present study agree with those used in previous studies on Si$_7$ and Si$_{10}$ clusters. 34–37 The optimized geometry of the neutral seven-atom Si QD was used for both the anion and the cation calculations.

The SAC-CI calculations were performed with all valence orbitals included in the active space and a pseudopotential for the core electrons. Both the singles and doubles (SD) and general (GEN) SAC-CI methods were employed in the calculations. The GEN method includes higher-order excitation operators and achieves a higher degree of accuracy for the description of multielectron processes, but at a substantially greater computational cost. The LANL2dz and LANL2mb basis sets were utilized for the calculations and have been shown previously to give similar results. 10

For the neutral Si$_7$ cluster, all 587 possible excited states using the SD method and the LANL2dz basis were calculated, with the highest excitation energy at 11.4 eV. Calculation of 2100 excited states up to an excitation energy of 14.9 eV using the GEN method and the LANL2mb basis was also performed on the neutral Si$_7$ cluster. The SD method was used for quantum chemical calculations as applied to neutral, anionic, and cationic Si$_7$ and neutral Si$_{10}$ QDs. SAC-CI, 32 as implemented within the Gaussian 03 software package, 33 is a high-level computational tool that begins with Hartree–Fock (HF) and uses a cluster expansion to explicitly include correlation effects in the ground-state wave function. Operators are then applied to this correlated ground state producing excited states with both single- and multie excitonic character. This method goes beyond linear-response time-dependent HF and density functional theory (DFT), which remain in the single-particle picture and thus have difficulty producing states consisting of MEs.

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The Si$_7$ anion and cation calculations used the closed-shell dianion and dication as reference states, respectively. After correlating these reference ground states, excited state cation doublet wave functions were created via coupled ionization and excitation. 2400 excited states were calculated for both the anion and cation using the GEN method and the LANL2dz basis with maximum excitation energies of 16.9 and 15.3 eV, respectively. These energy ranges included 800 excited states for both the cation and the anion. For all the GEN calculations, the contribution from excitations higher than double was never more than 5%.

Figure 1 shows the SAC-CI calculated electronic spectra for the QDs studied. The SD and GEN methods produce similar peak positions up to the limit of the number of excited states for the SD method for the seven-atom cluster (Figure 1a,b). The use of a larger basis set results in a slight red-shift of the spectra, although this is not immediately obvious by looking at the spectra, as there are fewer possible states with the minimal basis set and thus the spectra of the larger basis set
appears blue-shifted comparatively. The red-shift becomes more apparent in Figure 2, which explicitly shows the energies of all excited states. As expected, the spectrum of the larger 10-atom cluster is red-shifted compared to Si7. Charging the QD causes a blue-shift of the spectra, which can be seen by comparing spectra c and d with spectrum b in Figure 1. The blue-shift is more pronounced in the anion.

Both charged clusters also show a greater absorption intensity at lower energies, a feature not seen in the neutral QD. These lower energy absorption regions in the charged QD can be attributed to the added electronic transition possibilities that become available due to the extra (missing) electron (Figures 3 and 4). The 10-atom Si cluster shows much greater optical activity at low energy than any of the seven-atom clusters and has a broader spectrum. This is due to the lower symmetry of Si10 as compared to Si7, resulting in more allowed transitions. In general, there is high absorption intensity, for both size clusters, in the energy range in which MEG is likely to occur (i.e., $> 2 \times E_g$).

The fraction of excited states that are MEs is plotted in Figure 2 as a function of the excitation energy for the neutral QDs. These data are obtained by summing the squares of the expansion coefficients corresponding to double and higher-order excitations from the SAC-CI calculations. The GEN calculation shows the onset of MEG to be approximately $2 \times E_g$, while the SD calculations put the threshold at closer to $3 \times E_g$. This range is in agreement with the threshold recently estimated from ultrafast transient absorption spectroscopy, which put the MEG threshold at $2.4 \pm 0.1 \times E_g$.31 For both the SD and GEN calculations in Si7, there is an extended region of superpositions of SEs and MEs before the excited states become predominantly MEs. This is a combination of the behaviors seen in our previous study of CdSe and PbSe QDs.10

The 10-atom Si cluster, however, shows a sharper transition from SEs to MEs. This behavior is reminiscent of the PbSe cluster, which showed an abrupt and complete transition from SEs to MEs.10 This result is somewhat unexpected, since PbSe shows a much higher symmetry in the geometric and electronic structure, compared to Si QDs. A priori, on the basis of the lower geometric symmetry, one may have expected a closer similarity between Si and CdSe clusters. The analogy between the Si and PbSe clusters can be attributed to the common $s,p$-orbital origin of the valence electrons. In comparison, the valence electrons of the Cd atom include $d$-orbitals in addition to the $s$ and $p$-orbitals. The $d$-electrons create a wider range of possibilities for the high energy excitations in CdSe. One can expect that nanoclusters made of Ge, which belongs to the same group in the Periodic Table as Si, also exhibit a complete transition from SEs to MEs. This, combined with the high optical activity seen in the electronic spectra of the QDs at energies where MEs dominate the excited states, implies that MEG should be fairly efficient in Si QDs, a claim that is backed up by the experimental observations.31

Figure 2. The fraction of MEs in the excited states of the neutral QDs calculated from the squares of the SAC-CI expansion coefficients corresponding to double and higher-order excitations. The abbreviations hold the same meanings as in Figure 1. MEs appear in both QDs at energies 2–3 times the first excitation energy and become predominant at higher energies.

Figure 3. Breakdown of the contributions of different transitions to the excited states in the anionic seven-atom Si QD from the GEN SAC-CI calculation with the LANL2dz basis set. The addition of an extra electron in the conduction band (CB) allows for transitions to occur within the CB, causing a blue-shift in the onset of ME transitions relative to the neutral cluster (Figure 2).
The fact that the onset of MEGs in neutral clusters occurs at about twice the lowest excitation energy can be rationalized by a simple energy argument. The Coulomb coupling and mixing between SEs and MEs become strongest when the two types of states come to resonance, since the energy denominator in a corresponding perturbation theory expression becomes small. In addition to this most obvious factor, other conditions may play a role and shift the onset to higher energies. In particular, symmetry selection rules may require electron–hole transitions that are symmetric with respect to the Fermi energy. In such a case, the threshold moves closer to 3 times the gap. Generally, coupling and mixing of states causes lower levels to decrease and higher levels to increase in energy. Hence, the mixing pushes MEs up and low-energy SEs down. Given no symmetry selection rules, the shift of the threshold above two gaps is directly related to the strength of the Coulomb electron–hole interaction that causes the SE/ME mixing.

MEs can exist in any kind of system, for instance, hydrocarbon molecules. However, there are several important differences between inorganic semiconductors and molecules. On the practical side, molecular excitation energies are much higher than those of inorganic clusters, and beyond the solar spectrum. Exciton binding energies are strong in molecules, and it is hard to break photoexcited states into individual charge carriers. Hence, MEs in individual molecules have little relevance for photovoltaic applications. On the fundamental side, molecular SE and ME energies are substantially affected by the strong excitonic and electron–phonon interactions. Periodic structure of a cluster favors screening of the excitonic Coulomb interaction. Geometries of soft molecules relax upon excitation much more than those of rigid semiconductors. Therefore, one can expect substantial quantitative differences in MEG thresholds and efficiencies between molecules and clusters.

As with our previous study of PbSe QDs, we explored the effect of charging on MEG in Si clusters. Figures 3 and 4 give a pictorial analysis of the character of the excited states of the Si7 anion and cation, respectively. Charging the QD opens up the possibility for intraband transitions to occur, those being transitions within the CB for the anion and the VB for the cation. The new transitions significantly shift MEG to higher energies and are responsible for the higher optical activity seen at lower energies in the calculated electronic spectra of the QDs (Figure 1).

It can be seen in Figures 3 and 4 that intraband transitions dominate at low energies. Single excitations across the band gap become important at energies that are higher than those in the neutral QD (Figure 2). Even then, the excited states are highly mixed and involve single electron transition of both intraband and bandgap character. Two electron transitions start to occur at $5 \times E_g$ in the anion and $3 \times E_g$ in the cation. The $3 \times E_g$ cation transitions are not MEs, but combinations of VB transitions and SEs. MEs appear in both systems at $5 \times E_g$. They are strongly mixed with the VB/SE transitions.

Calculations for charged clusters here emphasize that charging does indeed have a substantial effect on MEG. This conclusion obtained earlier with PbSe is now confirmed with Si. However, the quenching of MEG is not as severe in Si as in PbSe. The MEG threshold in the charged Si clusters is lower than in the charged PbSe, both in absolute energy units and in multiples of $E_g$. The earlier onset of MEG in the charged Si clusters is encouraging for robust and efficient MEG. It is rationalized by the smaller number of valence electrons in Si atoms, compared to Se in PbSe and both Cd and Se in CdSe. The smaller number of electrons per atom accelerates the transition from single to multiple excitations as a function of energy.

The molecular orbital analysis of the MEG blueshift in charged dots (see insets in Figures 3 and 4) leads us to predict similar effects in a number of other situations. For instance, a dangling chemical bond on a surface caused by a missing ligand or a surface defect generates an odd electron in a VB or a CB. As a result, low energy two-electron excitations will be dominated by the intraband/SE transitions, and the MEG threshold will move up in energy, just as in the charged dots. If the overall QD is neutral, but a charge moves from the core to a surface trap, the core will behave as a charged dot. In the orbital picture, ME transitions involving the trapped charge will start at a low threshold. However, they will be optically inactive, since the overlap of the trap and core orbitals in the transition dipole matrix elements will be zero.
Finally, we would like to comment on the apparent discrepancy between experiment and theory. Our theory shows that charging attenuates the MEG efficiency. On the other hand, charging can magnify the MEG efficiency deduced from experimental data. The discrepancy is easily rationalized, since the theory and experiment focus on two different processes. We consider the effect of charging on the nature of photoexcited states, while the analysis of the experiments considers the effect of charging on Auger-type processes that follow photoexcitation. Charging allows a parallel Auger process that contributes to the experimental signal and, hence, can lead to misinterpretation of the data. Ignoring the additional process may suggest a higher MEG yield. Our conclusion that charging decreases the probability of exciting a state that has a strong ME character is independent of the Auger process analysis.

To recapitulate, we have shown with high-level, ab initio calculations that excited states in Si QDs become predominantly MEs at energies greater than $2 \times E_g$. The threshold that we calculate for MEG is in agreement with experimental measurements. For both clusters studied, there is a region of superpositions of SEs and MEs before MEs become completely dominant. The region of superpositions is more narrow, and the transformation from SEs to MEs is sharper in the larger cluster. One can expect that multiple MEG mechanisms are active in the superpositions region, and that the direct mechanism becomes more important at higher energies. Confirming our results for charged PbSe clusters, charged Si clusters show a quenching of MEG and a blue-shifting of ME threshold. The high-energy excited states of the Si nanoclusters resemble those of PbSe rather than CdSe clusters, in spite of the lower symmetry of Si compared to PbSe. Analytic theory suggests that the conclusions obtained for small clusters should hold for QDs up to 3 nm in diameter. The reported results are encouraging and indicate that efficient MEG can occur in nanoscale Si.

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