

# Effect of Large Bi-Exciton Binding Energy in CdSe/CdTe QD MEG Solar Cells

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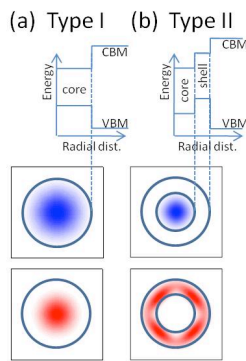
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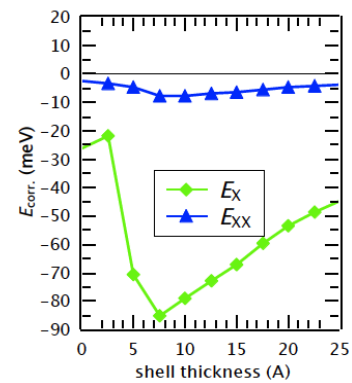
By increasing the exciton-exciton attractive (so called the bi-exciton, Bxx) interaction in colloidal QD's, a low threshold, relative to QD's optical gap ( $E_g$ ), can be achieved which is essential for increasing the efficiency on the multi-exciton generation (MEG) solar cells [1]. In conventional QDs, with type I band alignment this threshold depends mainly on the ratio between electron and hole effective masses. The core/shell QDs with type II band alignment offers extra degree of freedom in mediating the Coulomb interaction between charges in such structures, Fig. 1. Preliminary experimental studies on CdSe/CdTe QDs have shown that type II QDs can exhibit giant attractive X-X interaction energies, in the order of  $\sim 0.1$  eV. This is a key development since it has been recognized that X-X attraction reduces the threshold for MEG by Bxx. Theoretical predictions indicate that MEG has the potential to enhance the efficiency of the single gap material from 33% (the Shockley-Queisser limit) to 42% [2], and a reduction in MEG threshold, via attractive Bxx, by as little as 0.1 eV could lead to 50% efficiency.

To assess faithfully the potential of Bxx on the efficiency, a theoretical methodology was established, based on an 14-band  $\mathbf{k}\cdot\mathbf{p}$  Hamiltonian, with correct atomistic symmetry,  $C_{2v}$ , of the zinc-blend material, which incorporates the effects of band mixing between the p-bonding, s-anti-bonding and p-anti-bonding states, spin-orbit interaction, crystal-field splitting, strain between core/shells and piezoelectric potentials [3]. Excitonic states were found using the full Configuration interaction method, that includes explicitly the effects of Coulomb interaction, exact exchange and correlations between many-electron configurations. In setting up the full CI, particular attention was paid to accurate modeling of the dielectric constant variation through the structure as well as surface polarization effects on core/shell and QD/colloid interfaces. Relevant dipole matrix elements that couple different bands at the  $\Gamma$  point as well as dielectric constants of CdSe and CdTe at the transition energies are predicted using ab initio time-dependent density functional theory [4].

By changing the QD's CdSe/CdTe core size and shell thickness we have concluded that: (i) using the Hartree approximation alone, it is not possible to predict the Bxx binding in structures with type II shells; (ii) the bi-exciton binding can only be predicted with full CI Hamiltonian; (iii) CI predicts bi exciton binding as big as 70 meV for with characteristic minimum occurs for structures with 0.5 nm thick shell, Fig. 2; (iv) by ignoring the dielectric confinement, it is not possible to predict bi-exciton attraction for the structures with shell thickness  $> 0.75$  nm [5]; (v) by changing the value of the dielectric constant of colloid material from 1 to 2 the variation in the Bxx binding energy is as big as 100 meV; (vi) for proper estimate of the Bxx inclusion of correlations and surface polarization effects are necessary while effect of self-polarization is negligible. Based on Aufbau principle, we provide the quantum mechanical explanation for contra-intuitive appearance of the bound bi-excitons with inclusions of shells in terms of stronger reduction in the Columbic repulsion among holes in the bi-exciton then reduction of the e-h attraction, which is consequence of 4 fold degeneracy of the h-ground state imposed by symmetry of the structure.



**Fig. 1** Schematic of CV and VB band edges and electron and hole ground state quantum confining in: (a) QD with core only that is also type I, and (b) QD with core and shell that are type II aligning.



**Fig. 2** Correlation energy of  $E_X$  (solid circles) and  $E_{XX}$  (solid squares) as a function of shell thickness in CdSe/CdTe core/shell QD.

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