Exciton binding in type II CdSe/CdTe quantum dots

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INTRODUCTION

In a conventional solar cell the energy of an absorbed photon in excess of the bandgap is wasted as heat. Multiple exciton generation (MEG) in colloidal quantum dots (QDs) uses this energy to instead produce additional free charges, increasing the photocurrent and cell efficiency [1]. Theoretical predictions indicate that MEG has the potential to enhance the efficiency of a single gap cell from 33% to 42%, Fig 1 [2]. Full realization of this potential requires that the energy threshold for MEG be minimized. An attractive interaction between excitons reduces the threshold by the biexciton binding energy, Bxx, but this has been found to be small (-10meV) for type I QDs [3]. Previous calculations of Bxx in type II CdSe/CdTe QDs have found a large repulsion between excitons [4]. Here, we show that, by taking into account CI, combinations of core diameter and shell thickness can be found for a CdSe/CdTe core/shell QD, Fig 2, that result in large values of Bxx<0.

MODEL

Our theoretical methodology is based on an **k.p** Hamiltonian, with correct atomistic symmetry, C2v, 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 [5]. Excitonic states were found using the full CI method, hat includes explicitly the effects of Coulomb interaction, exact exchange and correlations between many-electron configurations, Fig 3. 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 shell/solvent interfaces. Relevant dipole matrix elements that couple different bands at the Gamma point as well as the dielectric constants of CdSe and CdTe at the transition energies are predicted using ab initio time-dependent density functional theory [6].

RESULTS

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, Fig 4; (ii) the bi-exciton binding can only be predicted with full CI Hamiltonian; (iii) CI predicts bi exciton binding as big as 60 meV with characteristic minimum which is function of shell thicknesses; (iv) by ignoring the dielectric confinement, it is not possible to predict bi-exciton attraction in structures with large shell thickness [5]; (v) by changing the value of the dielectric constant of colloid material the variation in the Bxx binding energy can be also tuned in the region of 100 meV; (vi) for proper estimate of the Bxx inclusion of correlations and surface polarization effects are necessary. We provide the 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-exctiton 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.

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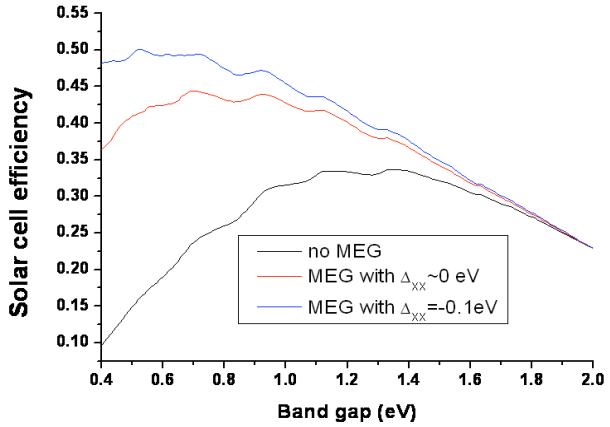

Fig. **1**. Potential benefit of MEG to solar cell efficiency calculated by the Detailed Balance method and without sunlight concentration

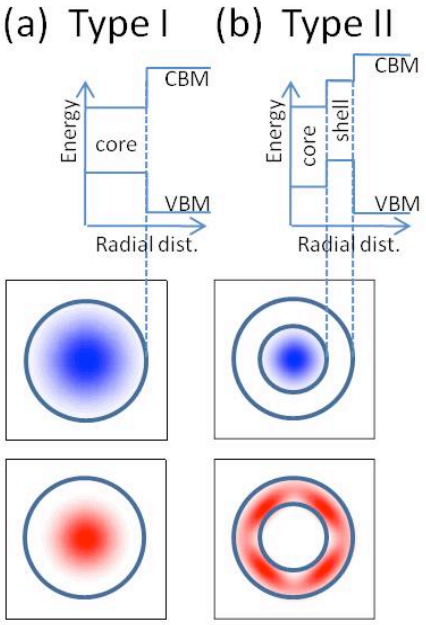

Fig 2. Electronic structure for (a) Type I and (b) Type II QD. (VBM =valence band maximum and CBM=conduction band minimum). In a Type I structure, both carriers reside in the core while for Type II the electron is in the core and the hole in the shell (or vice versa). In a quasi- Type II structure, one carrier is confined to either the core or shell & the other delocalised over the whole QD. The colour maps compare the electron (blue) and hole (red) wavefunctions in Type I and II QDs and were obtained using the 'kppw' code.

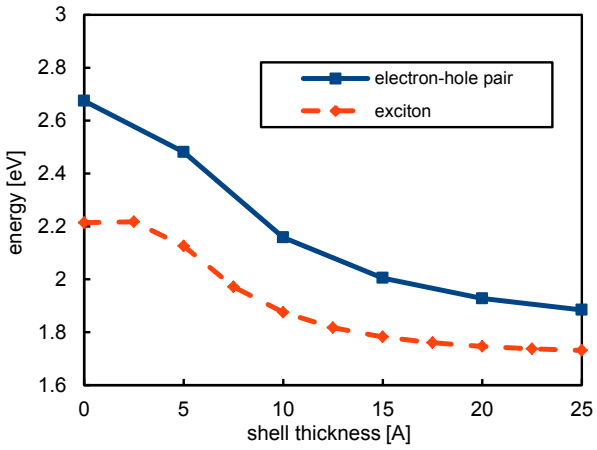

Fig. 3. Effect of Coulomb attraction, exchange and correlations as captured by full CI (diamonds) on the excitonic structure when compared to single particles e0-h0 energy (square) of CdSe/CdTe QDs as a function of shell thickness.

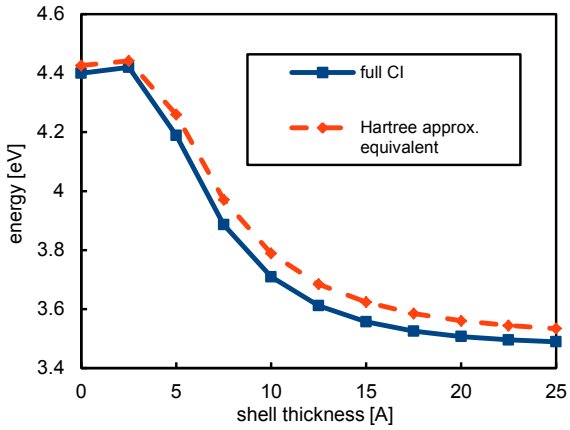

Fig. 4. Effect of correlation and exchange on the bi-exciton energy in CdSe/CdTe QDs as a function of the shell thickness.