Solar nanocomposites with complementary charge extraction pathways for electrons and holes: Si embedded in ZnS

S. Wippermann, M. Vörös, F. Gygi, A. Gali, G. Zimanyi, G. Galli
Nanocomposites based on Si nanocrystals embedded in a charge transport matrix are promising candidates for light absorbers in quantum dot based 3rd generation photovoltaics architectures.

\[ d = 3.3 \text{nm} \] Si nanocrystals in SiO$_2$

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Key problems:
- Ensure efficient charge transport and low recombination rates
- Understand interplay between interface structure, quantum-confinement, defects

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Search for materials to harvest light

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**Si nanocrystals in ZnS:**
- ZnS is earth-abundant, non-toxic and features a favourable band-alignment with Si at least for planar heterointerfaces
- Investigate Si-ZnS nanocomposites from *first principles*

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Embedding Si nanocrystals in a-ZnS

Create structural models for a-ZnS embedded Si\textsubscript{35}, Si\textsubscript{66}, Si\textsubscript{123}, Si\textsubscript{172} nanoparticles (NPs): replace spherical region (1.1 - 1.9 nm) in 4x4x4 ZnS unit cell and amorphize ZnS matrix using \textit{ab initio} molecular dynamics (MD).

DFT-LDA (Qbox) \(E_C = 80\) Ry, \(\tau = 2\) fs, \(T = 2400\) K, Si atoms free to move for \(T < 600\) K, 10-20 ps MD.
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DFT-LDA (Qbox) $E_C = 80$ Ry, $\tau = 2$ fs, $T = 2400$ K, Si atoms free to move for $T < 600$ K, 10-20 ps MD

Different starting geometries, equilibration & cooling times lead to very similar structures

Formation of sulfur-shell on Si-NP surface observed

=> Examine interface structure
Sulfur shell formation introduces new mid-gap states

3-fold coordinated interfacial sulfur: achieves noble gas state with 1 S-Si, 2 S-Zn bonds and 1 lone pair
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=> pronounced gap-reduction of embedded NPs

![Graph showing gap-reduction of embedded NPs](image)
Si nanoparticles (NPs) in SiO$_2$: *type I junction*

- Si NPs embedded in SiO$_2$ form a type I junction with their silica host.
- Valence and conduction band edges localized inside Si NP $\Rightarrow$ no charge transport.
- NP LUMO may be pushed above SiO$_2$ CBM by compressive strain [T. Li, F. Gygi, G. Galli, PRL 2011].
Si nanoparticles (NPs) in ZnS: type II junction

Si NPs in ZnS form a type II junction at equilibrium density

Charge-separated transport channels for electrons and holes may facilitate charge extraction and suppress recombination

Hole transport through host matrix, highly desirable for solar cells

valence band edge

conduction band edge

ZnS CBM
Si NP LUMO
ZnS VBM
Si NP HOMO
Si nanoparticles in ZnS: band alignment

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  - Formation of type II interface between Si NP and a-ZnS matrix, if, and only if, sulfur content is above a certain threshold.
  - DFT-LDA band offsets reliable?
    => calculate band offsets in GW approximation.

- Calculate band edge energies as a function of the radial distance from the center of the NP.
 GW for large systems

Calculation, storage & inversion of dielectric matrix $\varepsilon$ is major computational bottleneck $\Rightarrow$ spectral representation of $\varepsilon$ (RPA)

$$\tilde{\varepsilon} = \sum_{i=1}^{N} \tilde{v}_{i} \lambda_{i} \tilde{v}_{i}^{H} = \sum_{i=1}^{N} \tilde{v}_{i} (\lambda_{i} - 1) \tilde{v}_{i}^{H} + I$$

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Calculating eigenvectors/values does NOT require explicit knowledge of the matrix itself; knowing the action of $\varepsilon$ on an arbitrary vector is sufficient

In linear response: $(\varepsilon - I) \Delta V_{SCF} = -v_c \Delta n$

Charge density response $\Delta n$ to perturbation of self-consistent field $\Delta V_{SCF}$ can be evaluated from density functional perturbation theory

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Orthogonal iteration procedure to obtain eigenvector/-value pairs, using $\Delta V_{SCF}$ as trial potentials

In RPA fast monotonous decay of dielectric eigenvalue spectrum

Single parameter $N_{eig}$ to control numerical accuracy

No summation over empty states, no inversion

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D. Rocca, H.-V. Nguyen, T.A. Pham (UCD)
Band alignment from many body perturbation theory (GW)

GW calculations possible for a system as large as Si$_{35}$Zn$_{81}$S$_{100}$
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Many body corrections in GW approximation introduce mainly a rigid shift

$\Rightarrow$ confirms type II alignment
Summary

Investigated 1.1 - 1.9 nm Si nanocrystals embedded in a-ZnS using ab initio MD and quasiparticle calculations in GW approximation.

ZnS-embedded Si nanocrystals form a type II junction with the ZnS host in sulfur-rich conditions.

Band edges localized in different portions of nanocomposite => charge-separated transport channels for electrons and holes.

Solar Nanocomposites with Complementary Charge Extraction Pathways for Electrons and Holes: Si Embedded in ZnS

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