Complementary transport channels in Si-ZnS nanocomposites: first principles simulations

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Search for materials to harvest light

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.

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

[\[M. Zacharias et al., Appl. Phys. Lett. 80, 661 (2002)\]]
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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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**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

![d = 3.3nm Si nanocrystals in SiO2](image)
Si NPs in ZnS: methods and results

- Create structural models for a-ZnS embedded $\text{Si}_{35}, \text{Si}_{66}, \text{Si}_{123}, \text{Si}_{172}$ nanoparticles (NPs) from \textit{ab initio} molecular dynamics (MD)

- Pronounced gap reduction of embedded NPs vs. hydrogenated NPs

- Additional exploratory runs with varying sulfur content

![Graph showing the relationship between NP diameter and $E_{\text{gap-LDA}}$]

- More sulfur $\Rightarrow$ larger gap

- $\text{Zn}_{1-x}\text{Si}_{1+x}$: $x=0.08$

- Stoichiometric ZnS
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*more sulfur => larger gap*

effective gaps at increased EDOS levels depend much less on sulfur content

*S content influences mainly near-gap states*

gaps of Si NPs in SiO\textsubscript{2} shown for comparison [T. Li, G. Galli et al., PRL2011]
Sulfur shell formation on NP surface causes gap reduction

Si NP draws sulfur from the matrix => sulfur shell formation

S atoms at NP surface are typically 3-fold coordinated, due to valence electronic structure: 1 S-Si bond, 2 Zn-S bonds => lone pairs at interface

Lone pairs fall energetically into NP gap, => occupied mid-gap states, NP-HOMO is now an interface state, involving the S lone pairs

In addition: S shell formation leaves small Zn clusters within matrix => Zn clusters introduce near-gap states, tunable by sulfur content

\[
\text{Si NP-surface electron assignment}
\]

\[
\begin{align*}
1/2 & \quad 1/2 & \quad 3/2 & \quad 3/2 & \quad 2 \\
S & & & & \text{lone pair} \\
\text{Si} & & & & \text{NP-surface}
\end{align*}
\]
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Density of states

\[ E [\text{eV}] \]

\[ \text{DOS [a. u.]} \]

- Zn-clusters
- S-shell
- Si states

\[ E [\text{eV}] \]

\[ \text{DOS [a. u.]} \]

- \( \text{Si}_{35} \)
- \( \text{Si}_{66} \)
- \( \text{Si}_{123} \)
- \( \text{Si}_{172} \)
TDDFT-RPA spectra

Embedding Si-NPs into a-ZnS results in red-shifted absorption spectrum, compared to bulk a-ZnS, despite larger Si-NP gap than bulk a-ZnS gap => combination of two „large gap“ systems results in a „small gap“ composite system

**Cause:** interface region (sulfur-shell) dominates properties at small size regime

increasing NP size => increasing red-shift
Band alignment: *type I vs. type II interface*

Integrate local density of states along band edges

**Example of Si-NPs in SiO$_2$:** valence & conduction band edges localized inside Si-NP => type I junction, no charge extraction

NP-LUMO can be pushed above a-SiO$_2$ band edge by compressive strain [T. Li, F. Gygi, G. Galli, PRL 2011] => type II junction, electrons in matrix & holes in NP

Si$_{66}$ in SiO$_2$: type I interface

![Valence band edge](image1)

![Conduction band edge](image2)
Si-NPs in a-ZnS: Complementary transport channels

valence band edge: interface & matrix states

conduction band edge: localized in NP

very small Si-ZnS lattice mismatch (0.3%); type II interface at equilibrium density

At LDA level of theory: electron transport by NP-NP tunneling, hole transport by a-ZnS matrix (needs checking at higher level of theory, currently running GW calculation)

interface chemistry & matrix density dominate NP properties at small NP sizes
Summary

- ZnS-embedded Si nanoparticles feature complementary transport channels with spatially separated pathways for electrons and holes, allowing for long recombination times.

- Band lineup results in hole transport through matrix, electron transport by NP-NP hopping.

- This specific band alignment is desirable because hole transport is always less efficient than electron transport and limits solar cell performance.

- Sulfur shell formation around nanoparticle counteracts quantum-confinement induced gap increase at small sizes => probably interesting for multiple exciton generation?
GW for ZnS-embedded Si$_{35}$

Si$_{35}$ embedded in $3\times 3\times 3$ ZnS-cell exhibits complementary transport channels, but still too large for GW

**Solution**: recreate Zn pseudo-potential, then freeze Zn-3d electrons

electronic properties at fixed atomic structure remain unchanged

reduces $\#e^-$ from 1760 to 902

dielectric eigenpotentials used for calculating dielectric tensor

bulk ZnS band structure with 3d electrons in valence vs. frozen in core

doable now (600 deps in 18h on 8192 cores), new GW code has parallelization over eigenpotentials

currently calculating Lanczos chains
Structure generation

Generate models of ZnS-embedded Si NPs from ab initio MD:

- Si NPs in ZnS: lattice mismatch 0.84% (theory) vs. 0.33% (experiment)
- cubic 4x4x4 ZnS cell, replace Zn/S by Si in spherical region, rule of mixing for density
- choose radii and center to ensure NPs with maximum symmetry & minimum number of surface dangling bonds => Si\textsubscript{35}, Si\textsubscript{66}, Si\textsubscript{123}, Si\textsubscript{172} (1.1, 1.3, 1.6, 1.9 nm)
- QBox: norm-conserving DFT-LDA, $E_C = 80$Ry, $\tau = 2$fs, $T = 3600$K
- MD for ~10ps, cooling rate of 0.25K/fs
**Density functional theory (DFT):**

**Hohenberg-Kohn theorem:**

\[ E_{XC}[n] \approx E_{XC}^{LDA}[n] = \int n(r) \epsilon_{XC}^{hom}(n(r)) dr \]

\[ E_e[n] = T_0[n] + \frac{1}{2} \int \frac{n(r)n(r')}{|r-r'|} dr dr' + \int n(r)V(r) dr + E_{XC}[n] \]

[Walter Kohn, Nobel Prize for chemistry in 1998]

**Starting point:** initial geometry

<table>
<thead>
<tr>
<th>external potential</th>
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<tbody>
<tr>
<td>interatomic forces</td>
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\[ \left\{-\frac{\nabla^2}{2} + \int \frac{n(r')}{|r-r'|} dr' + V(r) + \frac{\delta E_{XC}^{LDA}}{\delta n(r)} \right\} \psi_j(r) = \epsilon_j \psi_j(r) \]

\[ n(r) = \sum_j |\psi_j(r)|^2 \]

**Structurally relaxed ground-state**

Starting from the initial geometry of a molecule or material, DFT calculations proceed through the following steps:

1. **Starting point:** initial geometry
2. **External potential**
3. **Interatomic forces**
4. **Kohn-Sham self-consistent electron structure**
   - Solve the Kohn-Sham equation to obtain the electron density function \( n(r) \)
5. **Structurally relaxed ground-state**
   - The ground-state properties are determined after structural relaxation.
6. **Vibrational and thermal properties**
7. **Electronic properties**
8. **Spectroscopic and transport properties**

[Density functional theory provides a way to calculate the electronic structure of materials, including ground-state properties and various other properties like vibrational and thermal characteristics.]
Excited states (GW/BSE)

- DFT disregards screened e$^-$-e$^-$ interaction and e$^-$-h interaction for excited states $\Rightarrow$ band gap underestimation, wrong distribution of spectral weights.

- Perturbative approaches for including screening (GW) and e$^-$-h interaction (Bethe-Salpeter), starting from Quantum Liouville equation:

$$i \frac{d\rho(t)}{dt} = [\hat{H}(t), \hat{\rho}(t)] \quad \rho(r, r', t) = \sum_v \phi^*_v(r, t) \phi_v(r', t)$$

$$\int \hat{H}(r, r', t) \phi(r', t) dr' = \left(-\frac{1}{2} \nabla^2 + v_H(r, t) + v_{ext}(r, t)\right) \phi(r, t)$$

$$+ \int \Sigma(r, r', t) \phi(r', t) dr'$$

Self-energy:

$$\Sigma_{COH}(r, r') = \frac{1}{2} \delta(r - r') W_p(r, r')$$

$$\Sigma_{SEX}(r, r', t) = -\sum_v \phi_v(r, t) \phi^*_v(r', t) W(r, r')$$

- Time-dep. perturbation, i.e. electromagn. field
- Statically screened Bethe-Salpeter equation (BSE)
- Screened Coulomb interaction
Excited states (GW/BSE)

To correct for DFT’s band gap underestimation, quasiparticle energies can be obtained in GW approximation from

$$\Sigma_{GW}(r, r'; i\omega) = \frac{1}{2\pi} \int G(r, r'; i(\omega - \omega')) W(r, r'; i\omega') d\omega'$$

Screened Coulomb interaction required (in random phase (RPA) approx.)

$$W(r, r') = \int \epsilon^{-1}(r, r'') v_c(r'', r') dr''$$

Bottleneck: calculation, storage & inversion of dielectric matrix is very computationally demanding, involves large sums over empty states and is hard to converge

Solution: spectral representation of RPA dielectric matrix; obtain matrix from directly calculating eigenvectors and eigenvalues

$$\tilde{\epsilon} = \sum_{i=1}^{N} \tilde{v}_i \lambda_i \tilde{v}_i^H = \sum_{i=1}^{N} \tilde{v}_i (\lambda_i - 1) \tilde{v}_i^H + I$$

=> no summation over empty states, no inversion, storage of eigenvector/-value pairs only!
How to calculate the screening

1. Obtaining the eigenvectors/-values does NOT require explicit knowledge of the matrix; knowledge of the action of the matrix on an arbitrary vector is sufficient!
2. in linear response: \((\epsilon - I) \Delta V_{SCF} = -v_c \Delta n\)
3. charge density response \(\Delta n\) to perturbation of self-consist. field \(\Delta V_{SCF}\) can be evaluated from density functional perturbation theory
4. orthogonal iteration procedure to obtain eigenvectors/-values, using \(\Delta V_{SCF}\) as trial potentials
5. in RPA fast monotonous decay of dielectric eigenvalue spectrum
6. single parameter \(N_{eig}\) to control numerical accuracy

\[ \tilde{\epsilon} = \sum_{i=1}^{N} \tilde{v}_i \lambda_i \tilde{v}_i^H = \sum_{i=1}^{N} \tilde{v}_i (\lambda_i - 1) \tilde{v}_i^H + I \]

[H. Wilson et al., PRB 79, 245106 (2009); D. Rocca et al., J. Chem. Phys. 133, 164109 (2010); H.-V. Nguyen et al., PRB 85, 081101 (2012)]