Interface-Controlled Materials for Solar Energy Conversion:
semiconducting nanocrystal-solids

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Present group topics

surfaces/interfaces (2D)

H$_2$O thin films on metal(-oxide) surfaces
vibrational spectroscopy at solid-liquid interfaces

Lei Yang, Ulrich Biedermann

nanowires (1D)

hybrid organic/inorganic nanowire solar cells
atomic scale surface-supported nanowires

Taufik Adi Nugraha
Abdus Samad Razzaq

quantum dots (0D)
nanocrystal solids for multi-exciton solar cells

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Musa Alaydrus
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Multi-Exciton Generation (MEG)

- Photons with $h\nu > 2E_g$ may create hot excitons that relax by creating additional excitons.
- Quantum confinement enhanced Coulomb interaction in nanoparticles (NPs) may increase MEG rates compared to bulk semiconductors.

[M. Beard, JPCL 2, 1282 (2011)]

[b] $\nu/E_g$

[QY (%)]
MEG in real devices

O. Semonin et al., Science 334, 1530 (2011)

G. Zhai et al., Nanotechnology 23, 405401 (2012)
Need to improve transport => „infilling the vacuum“

- charge carrier diffusion length in NP-ligand films too short
- create NP-solids by embedding NPs in charge transport matrix
- impact of matrix on MEG?
Embedding Si nanoparticles in α-ZnS

Replace spherical region in 4x4x4 ZnS unit cell by Si (d = 1.1, 1.3, 1.6, 1.9 nm) & amorphize matrix by *first principles* molecular dynamics

DFT-LDA (QBox), $E_C = 80$Ry, $\tau = 2$fs, $T=2400$K, Si-atoms free to move for $T<750$K

=> MD estimated to take $>5$ Mio. CPU h, whole group had „only“ 2 Mio. CPU h per year!

Let’s write a grant application for computer time, take a little detour and come back later
Dilemma: *confinement vs. gap size*

- quantum confinement in NPs:
  - enhances Coulomb interaction
  - enlarges electronic gap
  - \( \Rightarrow \) MEG threshold beyond solar spectrum

> Although Si has low [...] critical energy and large [...] figure of merit, its absorption spectrum for small NP sizes does not match the solar spectrum

[A. Zunger et al., Nano Lett. 8, 3174 (2008)]
Silicon allotropes (under pressure)

β-tin (Si-II)

- slow pressure release (~8 GPa)
- fast pressure release (<100ms)

Si-XIII, Si-IX
only incomplete structural information known

BC8 (Si-III)

- fast pressure release (<100ms)
- annealing (470 K)

Eg = 1.1 eV

Si-I

Eg = 0.95 eV

Ibam (Si-IX??)

bct

ST12

Eg = 0.24 eV

hex. diam. (Si-IV)

R8 (Si-XII)

ambient pressure

Eg = 1.1 eV

metal

Si-I

Eg = 0.95 eV

Ibam (Si-IX??)
Silicon NPs with allotrope cores

- $\text{Si}_{34}\text{H}_{36}$ (R8)
- $\text{Si}_{34}\text{H}_{38}$ (BC8)
- $\text{Si}_{42}\text{H}_{48}$ ($Ibam$)
- $\text{Si}_{35}\text{H}_{36}$ (cd)
- $\text{Si}_{39}\text{H}_{40}$ (hd)
- $\text{Si}_{46}\text{H}_{52}$ (ST12)
- $\text{Si}_{44}\text{H}_{48}$ (bct)
Surface reconstructions

$\text{Si}_{102}\text{H}_{56} \,(\text{BC8})$

$E_g = 1.01\,\text{eV}$
BC8 is a semi-metal in the bulk, 0.3 eV direct overlap at the H-point

Quantum confinement opens gap in BC8 nanoparticles

BC8 NPs feature much smaller gaps than Si-I NPs
GW calculations confirm trends observed at single particle level of theory*

**Si-BC8 NP GW gaps ideal for solar energy conversion in 4-8nm size range, where MEG is still efficient for Si-I NPs**  [M. Hanna et al., J. Appl. Phys. 100, 074510 (2006)]

GW gaps provide upper estimate: reconstructions, excitonic effects further reduce gaps  

*Fitting performed including known GW bulk gaps; theory: H.-V. Nguyen et al., PRB 85, 081101 (2012)*
Impact ionization (II) is dominating contribution to MEG*; calculate II rates from *ab initio* [M. Vörös et al., PRB 87, 155402 (2013)]

BC8 NPs feature lower activation threshold on absolute energy scale & order of magnitude higher impact ionization rate at same energies and same NP size!

Si BC8 and Ge ST12 NPs can now be synthesized colloidally, but no MEG measurements (yet)
new „exotic“ Si phases continue to be discovered

S. Wippermann et al., Appl. Phys. Rev., invited review article (to be published)
new “exotic” Si phases continue to be discovered

M. Amsler et al., PRB 92, 014101 (2015)

Yuping He et al., EES 7, 2598 (2014)
obtained the 5 Mio. CPU h necessary to 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} MD

Pronounced gap reduction of embedded NPs due to sulfur shell formation

Lone pairs of 3-fold coordinated sulfur at NP-matrix interface introduce new occupied mid-gap states
Si nanocrystals (NCs) in SiO$_2$: type I junction

- Si NCs embedded in SiO$_2$ form a type I junction with their silica host.
- Valence and conduction band edge states localized inside Si NC => no charge transport.
- NC LUMO may be pushed above SiO$_2$ CBM by compressive strain [T. Li, F. Gygi, G. Galli, PRL 2011]
Si nanocrystals (NCs) in ZnS: type II junction

- Si NCs 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 NC LUMO
- ZnS VBM
- Si NC HOMO
Si nanocrystals in ZnS: *band alignment*

Calculate band edge energies as a function of the radial distance from the center of the nanocrystal.

Formation of type II interface between Si NP and a-ZnS matrix, if, and only if, sulfur content is above a certain threshold.
Band alignment from many-body perturbation theory (GW)

Many body corrections in GW approximation introduce mainly a rigid shift

=> confirms type II alignment

impact of embedding on MEG? => embedded systems prohibitively large for our present impact ionization (II) code

recent algorithmic advances in calculating dielectric tensor expected to enable MEG rate calculation

need to work on the II code

NSF grant funding joint experiment-theory collaboration ended in 2014

embedding by ALD not very scalable anyway

fully colloidal approach to both NP synthesis and embedding seems very promising

even more complex systems, strong need to understand surface chemistry and impact on macroscopic properties

collaboration with Dmitri Talapin, choose InAs-NPs and Sn$_2$S$_6$$^4$-ligands as model system

Colloidal approach to synthesis and embedding

Traditional organic hydrocarbon ligands can be exchanged for metal chalcogenide complexes (MCCs), e.g. Sn$_2$S$_6^{4-}$.

MCCs can form conductive glue between NPs.

Gentle heat treatment transforms Sn$_2$S$_6^{4-}$ $\rightarrow$ SnS$_2$.

Interface structure largely unknown.

Sn$_2$S$_6^{4-}$ ligands assumed to adsorb intact as structural units on In-rich surface of InAs-NPs.

\[ (N_2H_5)_4Sn_2S_6 \rightarrow SnS_2 + 4N_2H_4 + 2H_2S \]

[D. Talapin et al.,
Science 324, 1417 (2009),
JACS 134, 18585 (2012),
Nature Mat. 12, 410 (2013)]
Possible structures realized at NP-matrix interface

DFT predicts Sn$_2$S$_6^{4-}$ on bare In-rich InAs-surfaces highly unstable, dissociates without barrier.

- **surface reconstructions**
  - S subsurface substitution
  - S passivation
  - SnS or InS surface layer formation
- **adsorption of ligands on (combinations of) such surface structures**
Calculating free energies: a grand canonical approach

Free energy: \( \Delta G = E_{tot} - E_{ref} - \sum_i n_i \mu_i \)

- \( \mu_{In} \leq \mu_{In} (\text{bulk}) \)
- \( \mu_{As} \leq \mu_{As} (\text{bulk}) \)
- \( \mu_{Sn} \leq \mu_{Sn} (\text{bulk}) \)
- \( \mu_{S} \leq \mu_{S} (\text{bulk}) \)
- \( \mu_N \leq \frac{1}{2} \mu_{N_2} (\text{gas}) \)
- \( \mu_H \leq \frac{1}{2} \mu_{H_2} (\text{gas}) \)

\( \mu \) corresponds to free energy at which reservoir provides particles

Plot phase diagram as function of \( \Delta \mu_{In}, \Delta \mu_{S}, \Delta \mu_H \)

\( \Rightarrow \) relative thermodynamic stability of different structures at specific synthesis conditions
InAs(100)-Sn$_2$S$_6$ surface phase diagram ($\mu_{\text{In}}$)

S-rich & H-rich

Sn @ InAs

InAs surface reconstructions

S + Sn$_2$S$_6$-ligand @ InAs
In-rich & H-rich

S-poor

InAs(100)-Sn$_2$S$_6$ surface phase diagram (μS)
InAs(100)-Sn\textsubscript{2}S\textsubscript{6} surface phase diagram ($\mu_{S}$, $\mu_{In}$)

- **In-rich**
  - (4x4) Sn subsurface
  - $\Delta \mu_{In} = 0$
  - $\Delta \mu_{S}$

- **In-poor**
  - (4x4) Sn on top As
  - $\Delta \mu_{In} = -0.3$

- **S-poor**
  - $\Delta \mu_{S}$

- **S-rich**
  - $\Delta \mu_{S}$

**Tin-induced surface reconstructions**
- (4x2)β2S2

**Sulfur-induced surface reconstructions**
- $2 \text{Sn}_2\text{S}_6$
- $2 \text{Sn}_2\text{S}_6 + \text{S subsurface}$
- $2 \text{Sn}_2\text{S}_6 + \text{S subsurface} + 2 \text{In}$

**Ligand stability regime**
- In-poor
- In-rich

- $\mu_{S}$, $\mu_{In}$
InAs(100)-Sn$_2$S$_6$ surface phase diagram ($\mu_S, \mu_{In}$)

- **S-rich** tin-induced surface reconstructions
- **S-poor** sulfur-induced surface reconstructions

Diagram with axes:
- $\Delta \mu_{In}$ [eV] on the y-axis
- $\Delta \mu_S$ [eV] on the x-axis

Key features:
- (4x4) Sn subsurface
- (4x4) Sn on top As
- (2x1)S-3B

Legend:
- In-rich
- In-poor
- S-poor
- S-rich
InAs(100)-Sn$_2$S$_6$ surface phase diagram ($\mu_S, \mu_{In}$)

tin-induced surface reconstructions

$\Delta \mu_{In}$ [eV]

$\Delta \mu_S$ [eV]

(4x4) Sn on top As

SnS$_4$

(4x4) Sn subsurface

a-SnS$_3$ + S subsurface

In-rich

S-poor

In-poor

S-rich
Subsurface sulfur is a recurring feature in phase diagrams.

Angle-resolved intensity of S 2p XPS peak: nonlinear decay indicates presence of subsurface sulfur also in experiments.

XPS measurements: D. Talapin (to be published)
Towards NP-superlattices

- complete and refine phase diagrams for relevant surface orientations
- construct NP-ligand superlattices from identified minimum energy structures
- enhance connection to experiment: e.g. Raman spectroscopy
- prepare also embedded NPs by ab initio MD with varying stoichiometries and densities

bare NPs $\Rightarrow$ passivation (e.g. reconstructions, ligand dissociation, thin films) $\Rightarrow$ Sn$_2$S$_6$ adsorption $\Rightarrow$ SnS$_4$ $\Rightarrow$ a-SnS

exact details depend on synthesis conditions / chemical potentials
optimal band gap of 2.4 eV and an IB
- IB should be partially filled
- optical transitions should be bright
- finite width of IB may help reduce non-radiative recombination
- existing realizations:
  - intra-gap impurity states in the bulk epitaxial quantum dots

Proposing to implement IB in colloidal nanoparticle solar cells

A. Martí et al., IEE Trans. 48, 2394 (2001)
Intra-gap state formation in CdSe NPs

- intra-gap state formation due to surface reconstruction
- persistent feature at size range accessible to us (DFT)
- $E_{\text{gap, bulk}} \sim 1.8$ eV, confinement widens gap to 2-2.5 eV range in $d = 4$ nm CdSe NPs

Partial filling of intra-gap state

- Photo-doping: IGS alone can support upconversion through 2-photon absorption
- Chemical doping: $E_0$ (redox potential for a redox couple) > $E_{\text{IGS}}$ of NP

Transitions optically active?

- HOMO localized to one facet, LUMO and IGS on the other
- IGS $\rightarrow$ LUMO transitions significantly brighter than HOMO $\rightarrow$ IGS and HOMO $\rightarrow$ LUMO transitions

likely results in unfavourable steady state filling of intra-gap state
Intermediate band formation in NP-solids

Intermediate band (IB) with finite width forms in simple cubic (SC) and face-centered cubic (FCC) Cd$_{15}$Se$_{15}$ solids. The width of the IB depends on NP separation, might be controlled by appropriately chosen ligands.

M. Vörös et al., ACS Nano 9, 6882 (2015)
Intermediate band formation possible in core/shell-NPs?

- CdSe NPs interesting from conceptual point of view, but low intensity HOMO → IGS transition, IGS due from surface reconstruction probably not very stable
- core/shell systems more promising?
- Klimov group reports high MEG yields in PbSe/CdSe core/shell-NPs

C. Cirlugano et al., Nat. Comm. 5, 4148 (2014)
Multi-exciton generation + intermediate bands?

(a) $E_{\text{abs}} > 2E_{\text{IC}}$
(b) $E_{\text{abs}} > E_{\text{VC}} + E_{\text{IC}}$
(c) $E_{\text{abs}} > 3E_{\text{IC}}$
(d) $E_{\text{abs}} > 2E_{\text{VI}}$
Summary

lower MEG threshold, e.g. in Si & Ge high pressure core NPs

embedding NPs in charge transport matrix, type II junction for Si-NP/ZnS

building realistic NP-matrix interface models from ab initio thermodynamics

dream: simultaneous utilization of low & high energy parts of solar spectrum by IB & MEG in single NP-system

looking for ways to form intermediate bands in colloidal NPs, e.g. surface reconstructions or core/shell

SW et al., PRL 110, 046804 (2013); M. Vörös, SW et al., J Mat Chem A 2, 9820 (2014)

SW et al., PRL 112, 106801 (2014)
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Collaborating Groups

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Dario Rocca
Search for materials to harvest light: Semiconducting Nano-Composites

- Design semiconductor materials with tailored optical & electronic properties
- Nanocrystal superlattices embedded in host matrix
- Grow nanocrystals in solution, shape control by surface-selective ligands
- Exchange ligands by molecular metal chalcogenide complexes (MCCs)

Gentle heat treatment transforms MCCs into amorphous or crystalline metal chalcogenide host matrix

- Applicable to many materials systems
- Synthesis completely by wet chemistry

[Boles, D. Talapin, Science 344, 1340 (2014)]
[W.-L. Ong et al., Nature Mat. 12, 410 (2013)]
[M. V. Kovalenko et al., Science 324, 1417 (2009)]
Multi-Exciton Generation (MEG) in Nano-Composites

Key problems

- Quantum confinement required for efficient MEG, but pushes electronic gap beyond solar spectrum
- Ensure efficient charge transport & extraction and low recombination rates

=> Identify nano-composites with suitable electronic & optical properties, made from earth-abundant & non-toxic materials

Quantum confinement in nanocrystals enables efficient multi-exciton generation

[A. Nozik, Physica E 14, 115 (2002)]

MEG: hot excitons relax by creating additional electron hole pairs
Allotropes of Si and Ge

- **Cubic diamond**, semiconductor
- **BC8**, semimetal
- **$X_{34}H_{38}$**, ($X=$Si,Ge)
- **$X_{35}H_{36}$**, ($X=$Si,Ge)
- **ST12**

[S. Ganguly et al., J. Am. Chem. Soc. 136, 1296 (2014)]

[S. J. Kim et al., J. Mater. Chem. 20, 331 (2010)]
Density Functional Theory (DFT) calculations predict reduced electronic gaps for nanocrystals with BC8 and ST12 core structures. Trends confirmed by many-body perturbation theory calculations ($G_0W_0$) for diameters up to $d = 1.7$ nm => extrapolation predicts optimum gap range for MEG-based solar energy conversion for Si BC8 at $d = 4 - 8$ nm ($E_{\text{Gap}} = 1.1 - 0.5$ eV)
Multiple Exciton Generation in Si & Ge allotrope nanocrystals

Impact ionization (II) is dominating contribution to MEG; calculate II rates from first principles [M. Vörös et al., PRB 87, 155402 (2013)]

Lower electronic gaps of nanocrystals with Si BC8 and Ge ST12 core structures translate indeed into lower MEG activation energy and up to order of magnitude higher MEG rates at same NP size and photon energy!

Density functional theory (DFT):

**Hohenberg-Kohn theorem:**

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

\[ E_{XC}[n] \approx E_{XC}^{LDA}[n] = \int n(r)\varepsilon_{XC}^{hom}(n(r)) d\mathbf{r} \]

[Starting point: initial geometry]

**Atomic positions**

**External potential**

**Interatomic forces**

\[ \left\{ -\frac{\nabla^2}{2} + \int \frac{n(r')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + V(\mathbf{r}) + \frac{\delta E_{XC}^{LDA}}{\delta n(\mathbf{r})} \right\} \psi_j(\mathbf{r}) = \epsilon_j \psi_j(\mathbf{r}) \]

**Structurally relaxed ground-state**

**Vibrational and thermal properties**

**Electronic properties**

**Spectroscopic and transport properties**

[Walter Kohn, Nobel Prize for chemistry in 1998]
**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

\[
\frac{id\rho(t)}{dt} = \left[ \hat{H}(t), \hat{\rho}(t) \right]
\]

\[
\rho(r, r', t) = \sum_v \phi_v^*(r, t) \phi_v(r', t)
\]

- single particle occ. orbitals

\[
\int \hat{H}(r, r', t) \phi(r', t) dr' = \left( -\frac{1}{2} \nabla^2 + \nu_H(r, t) + \nu_{ext}(r, t) \right) \phi(r, t)
\]

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

- time-dep. perturbation, i.e. electromagn. field

- self-energy

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

\[
\Sigma_{SEX}(r, r', t) = -\sum_v \phi_v(r, t) \phi_v^*(r', t) W(r, r')
\]

- 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

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

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

\[ W(\mathbf{r}, \mathbf{r'}) = \int \epsilon^{-1}(\mathbf{r}, \mathbf{r''})v_c(\mathbf{r''}, \mathbf{r'}) d\mathbf{r''} \]

- **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

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

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

- 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!

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

- Charge density response \(\Delta n\) to perturbation of self-consist. field \(\Delta V_{SCF}\) can be evaluated from density functional perturbation theory

- Orthogonal iteration procedure to obtain eigenvectors/-values, using \(\Delta V_{SCF}\) as trial potentials

- In RPA fast monotonous decay of dielectric eigenvalue spectrum

- Single parameter \(N_{eig}\) to control numerical accuracy

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