Progress & challenges in plasmon-enhanced photocatalysis and photovoltaics

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Jon Scholl, Andrea Baldi, Ashwin Atre, Di Wu, Justin Briggs, Michael Wisser, Aitzol Garcia, Ai Leen Koh, Tim Burke, Alberto Salleo, Mike McGehee
Materials Science & Engineering | Stanford University
Oh the places plasmons go!

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Oh, the plasmons go quantum
When particles are small
Their spectra shift blue
Their peaks are less tall
And because they’re sensitive
To their surroundings and charge
Catalytic sensing is easy
On particles small and large.

We’ll coat titania
over a metallic core:
UV light gets absorbed
e\(^-\)/h\(^+\) pairs separate more

But solar photons span
Wavelengths red, green, and blue
For efficient PV
We’ll use upconversion too!
Plasmon resonances of conducting nanoparticles
Plasmon resonances of conducting nanoparticles

Electric field
Plasmon resonances of conducting nanoparticles

\[ \alpha = 4\pi r^3 \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} \]

\[ C_{abs} = k \text{Im}\{\alpha\} \]

\[ C_{sca} = \frac{k^4}{6\pi} |\alpha|^2 \]
Plasmon resonances of conducting nanoparticles

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Plasmon resonances and energy conversion

Near-field enhancement

Thomann, Brongersma, Nano Lett. (2011)

“Hot” electrons

Knight, Halas, Science (2011); see also Mubeen, Moskovits, Nat. Nano. (2013)

Reaction Sensors

Tang, Liu, Dionne, Alivisatos, JACS (2011)

Novo et al., Nature Nanotech 3(10) 2008
Plasmon resonances and energy conversion

1. Can we detect plasmons from particles in the sub-10nm regime?

2. Can we use these plasmons to monitor photocatalytic reactions in-situ?

3. Can we improve below-bandgap absorption of solar photons for photocatalysis & photovoltaics?
Plasmon catalysis into the single-nm regime

- Probing the plasmonic properties of very small particles is challenging: weak optical scattering, particle heterogeneity in ensemble, organic ligands, etc.

Ensemble Measurements:

Peng, Schatz PNAS (2010)
Plasmon catalysis into the single-nm regime

- Probing the plasmonic properties of very small particles is challenging: weak optical scattering, particle heterogeneity in ensemble, organic ligands, etc.

Ensemble Measurements:
- 17.8 nm oleylamine
- 2.2 nm (x420)

Single Particle Measurements:
- $D = 60 \pm 12$ nm
- $D = 10.3 \pm 1.0$ nm
- $D = 5.4 \pm 0.8$ nm

Peng, Schatz PNAS (2010)
Scanning Transmission Electron Microscopy (STEM) EELS has an imaging spatial resolution of ~0.25nm.
Individual, organic-ligand-free nanoparticles

Organic-ligand-free synthesis minimizes organic contamination and the influence of ligand surface damping.
EELS: Classically-sized Particles

Counts (a.u.)

Energy (eV)

2 3.5 5

5 nm
EELS: Classically-sized Particles

Surface resonance

Counts (a.u.)

Energy (eV)

2 3.5 5

5 nm
EELS: Classically-sized Particles

Surface resonance

Counts (a.u.)

Energy (eV)
EELS: Classically-sized Particles

Surface resonance

Bulk resonance

Energy (eV)

Counts (a.u.)

2 3.5 5

i ii

5 nm

2 3.5 5

Energy (eV)
EELS: Classically-sized Particles
EELS: Size-dependent spectral response

Counts (a.u.)

Energy (eV)

2.5  3.5  4.5

5 nm

EELS: Size-dependent spectral response

Counts (a.u.) vs. Energy (eV) for different particle diameters (nm):
- 11 nm
- 8.5 nm
- 5.5 nm
- 3.5 nm
- 2.5 nm
- 1.7 nm

Particle Diameter (nm) vs. Peak Energy (eV) with error bars.

Scale bar = 5 nm.
EELS: Size-dependent spectral response

Counts (a.u.) vs. Energy (eV) for different Particle Diameters (nm):
- 11 nm
- 8.5 nm
- 5.5 nm
- 3.5 nm
- 2.5 nm
- 1.7 nm

Surface vs. Bulk Peak Energy (eV) vs. Diameter (nm):

- Surface Energy (eV) range: 3.7 to 4.1
- Bulk Diameter (nm) range: 5 to 20
Modeling the size-dependence

- Classical treatment uses damping term: \( \gamma = \gamma_{\text{Bulk}} + \frac{A v_F}{R} \)
- Accounts for peak broadening, predicts a red shift in noble metals
- Instead, use a quantum approach:

J. Garcia de Abajo, Nature 483 (2012)
Quantum theory matches experiment

Modeling the impact of these discrete electron transitions on particle spectra results in a blue shift comparable to experiments.
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Analytic

Ab-initio

DFT permittivity functions based on He & Zeng, JPCC. 2010

Plasmon resonances and energy conversion

1. Can we detect plasmons from particles in the sub-10nm regime?

   Yes!

   • Localized plasmons become ‘quantum confined’ around 5 nm
   • Single electron transitions can significantly impact the collective response of a “sea” of electrons
Plasmon resonances and energy conversion

1. Can we detect plasmons from particles in the sub-10nm regime?
2. Can we use these plasmons to monitor photocatalytic reactions in-situ?

Norskov, NanoToday, 2007
Case study: water-splitting photocatalysis

Porous TiO$_2$

Youngblood et al., JACS (2009)
Case study: water-splitting photocatalysis

Youngblood et al., JACS (2009)
Can small plasmonic particles help?

1. Synthesis of well-dispersed Ag@TiO$_2$ nanoparticles

2. Characterization of their photocatalytic activity in:
   - Ensemble measurements
   - Single particle measurements

Andrea Baldi
Synthesis of Ag@TiO$_2$ nanoparticles
Synthesis of Ag@TiO$_2$ nanoparticles
Synthesis of Ag@TiO$_2$ nanoparticles
Synthesis of Ag@TiO$_2$ nanoparticles
UV irradiation of de-aerated Ag@TiO$_2$
UV irradiation of de-aerated Ag@TiO$_2$

See also: Kamat et al., *JACS* (2005); *ACS Nano* (2011)
Ensemble Measurements

Discharge in $O_2$

See also: Kamat et al., JACS (2005); ACS Nano (2011)
Single Particle Optical Measurements
Single Particle Optical Measurements
Single Particle Optical Measurements
Single Particle Optical Measurements

Charge
20 min UV

Normalized Scattering vs. Wavelength (nm)
Single Particle Optical Measurements

Charge
40 min UV
Single Particle Optical Measurements

Charge 60 min UV
Single Particle Optical Measurements
Single Particle Optical Measurements

Discharge 20 min O₂
Single Particle Optical Measurements

Discharge 40 min O₂
Single Particle Optical Measurements

Discharge
60 min O₂
Single Particle Optical Measurements

Discharge 80 min $O_2$
Single Particle Optical Measurements

- Bars denote peak full-width at half maximum
- On-going: correlate single particle structure with catalytic activity
Plasmon resonances and energy conversion

Preliminary results are promising. It will be exciting to correlate catalyst size and shape with activity.

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3. Can we improve below-bandgap absorption of solar photons for photocatalysis & photovoltaics?
Solar upconversion

- Photons with an energy less than the bandgap ($E_g$) of a solar cell are unused
- Photons with energy just above $E_g$ are poorly absorbed
A potential solution: upconversion

- A process where light is emitted with photon energies higher than those of the light generating the excitation
- Implementation: Solar cell and upconverter are electrically isolated
  1) No additional recombination in cell
  2) Separate optimization of cell & upconverter
Upconverting cells exceed the Shockley-Queisser limit

- Peak cell efficiency increases from 30% to 44%
- Ideal cell bandgap blue-shifts from 1.1 eV to 1.8 eV
- Solar concentration is not necessary

How does non-ideal upconversion impact a cell?

- Effect of UC absorption/recombination efficiency: need high quantum efficiencies

- Effect of UC absorption bandwidth: higher efficiencies with higher bandwidths


Additional design considerations

- Solar-spectrum matching: don’t want UC energy levels to overlap with AM1.5 absorption lines

- UC absorption peak positions: usually in the near-infrared (811nm and 1200nm for a 1.7eV cell)

T. Burke, M. McGehee

Two promising upconverting systems, part 1

Photos by Ashwin Atre; and Diane Wu
See also: Singh-Rachford, et al. JACS. 131 (2009)
Two promising upconverting systems, part 2

Lanthanoid-doped nanoparticles

Photos by Diane Wu
What are the predicted improvements?

Bimolecular systems

Lanthanide systems

Towards Enhanced Upconversion

Conductive upconverting composites

Ag NW

5 μm

Intensity (a.u.)

Wavelength (nm)

UC Film

Composite UC film (as conductive as ITO)

Diane Wu
Nanowires are promising, but have a strong polarization and angle-dependent response. Further, need UC in near-field of wire.
Upconverting metamaterials in solar cells

Solar cell
Insulator
Upconverter

Ag shell, upconverter-doped core

Intensity ($E^2$) enhancement of ~100x throughout the entire upconverting volume

Upconverting metamaterials in solar cells

- Solar cell
- Insulator
- Upconverter

Ag shell, upconverter-doped core

Graphs showing the field intensity for different angles and wavelengths.
Upconverting metamaterials in solar cells

- Solar cell
- Insulator
- Upconverter
- Ag shell, upconverter-doped core
Upconverting metamaterials in solar cells

Enhancement of power into cell

Wavelength (nm)

Crescent Orientation

No nanocrescent

With nanocrescent

Solar cell

Distance from tip (nm)

Total Field Intensity

Wavelength (nm)

0° 45° 90°
Nanocrescent array: a tunable index ‘metamaterial’

- The refractive index of the upconverting “metamaterial” can be matched to the solar cell above it.

Nanocrescent fabrication
Nanocrescent fabrication

![Diagram of nanocrescent fabrication with Ag on a substrate.](image1)

![Image of nanocrescent structures.](image2)

- Scale: 100 nm (left)
- Scale: 1 μm (right)
Nanocrescent characterization

In collaboration with A. Polman, FOM-Institute AMOLF (Amsterdam)
Coming soon: upconverting crescents

**Bimolecular systems**

<table>
<thead>
<tr>
<th>Organic</th>
<th>Aqueous</th>
<th>Upconverting Dyes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexadecane</td>
<td>Styrene</td>
<td></td>
</tr>
</tbody>
</table>

Upconversion at 445 nm

**Lanthanoid systems**

Synthesis based on Wohnhass, Macromol. Biosci 11, 772 (2011)
Summary

1. Can we detect plasmons from particles in the sub-10nm regime?
2. Can we use these plasmons to monitor photocatalytic reactions in-situ?
3. Can we improve below-bandgap absorption of solar photons for photocatalysis & photovoltaics?

Some see things as they are and ask ‘why?’. Others dream things that never were and ask, ‘why not?’.
– George Bernard Shaw.

Thanks to our funders: Stanford, AFOSR, NSF, SLAC/SIMES, DOE, GCEP, Intel!
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Bimolecular upconversion process

S = sensitizer; E = emitter

Energy Requirements:

$S^*$ + $hv_1$ → $1S^*$

$1S^*$ → ISC → $3S^*$

$3S^*$ → TET → $1E^*$

$1E^*$ → TTA → $2E^*$

$2E^*$ + $hv_2$ → $1E^*$ + $1E$
The need for efficient upconversion

- Solar-spectrum matching: don’t want UC energy levels to overlap with AM1.5 absorption lines

- UC absorption peak positions: usually in the near-infrared (811nm and 1200nm for a 1.7eV cell)

Burke, McGehee. *In preparation* (2012)

Tackling low UC efficiencies

1. The ‘electronic’ approach: modify dipole transition moments
   - consider Yb$^{3+}$/Er$^{3+}$
   - all UC transitions are between f levels $\rightarrow$ LaPorte forbidden or spin-forbidden
   - Can we modify the optical transition rates by changing the crystal field?

\[ \begin{align*}
\text{Yb}^{3+} & : 2F_{5/2} \rightarrow 2F_{7/2} \rightarrow 2F_{5/2} \\
& \text{980 nm} \\
\text{Er}^{3+} & : 4I_{11/2} \rightarrow 4I_{15/2} \rightarrow 4I_{11/2} \\
& \text{654 nm} \\
& \text{542 nm} \\
& \text{520 nm}
\end{align*} \]
Ln$^{3+}$ upconverters under pressure

$\text{Yb}^{3+}/\text{Er}^{3+}$ in hexagonal $\text{NaYF}_4$

Electromagnetic Radiation

Screws

Intensity (a.u.)

Wavelength (nm)

100 nm

1.15 GPa
6.97 GPa
12.9 GPa
19.6 GPa
28.3 GPa

Ruby
Sample
Ln$^3+$ upconversion & PL under pressure

- Intensities are affected by pressure: changes to interionic separations and Yb$^3+/Er^3+$ energy level resonance
Peak shifts are also pressure-dependent: peaks “spread apart” as pressure is increased, suggesting a distortion in the crystal field.