Progress & challenges in plasmon-enhanced photocatalysis and photovoltaics

Jen Dionne
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 places plasmons go!

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
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)

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

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Ensemble Measurements:

Single Particle Measurements:

Peng, Schatz PNAS (2010)

Probing very small plasmonic particles: EELS

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
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Surface resonance

Counts (a.u.)

Energy (eV)

2 3 4 5

5 nm
EELS: Classically-sized Particles

Surface resonance

Bulk resonance

Counts (a.u.)

Energy (eV)

2 3.5 5

Counts

Energy (eV)
EELS: Classically-sized Particles

Surface resonance

Bulk resonance

Counts (a.u.)

Energy (eV)

2 3.5 5

Counts (a.u.)

Energy (eV)

2 3.5 5
EELS: Size-dependent spectral response

Counts (a.u.)

Energy (eV)

11 nm
8.5 nm
5.5 nm
3.5 nm
2.5 nm
1.7 nm

EELS: Size-dependent spectral response

Counts (a.u.)

Energy (eV)

Particle Diameter (nm)

Peak Energy (eV)
EELS: Size-dependent spectral response

- Counts (a.u.)
- Energy (eV)
- Particle Diameter (nm)
- Surface
- Bulk

Energy (eV)
- 3.7
- 3.9
- 4.1

Peak Energy (eV)
- 3
- 3.2
- 3.4
- 3.6
- 3.8
- 4

Diameter (nm)
- 5
- 10
- 15
- 20

5 nm
• Classical treatment uses damping term: $\gamma = \gamma_{Bulk} + \frac{Av_F}{R}$
• Accounts for peak broadening but predicts a red shift
Classical treatment uses damping term: $\gamma = \gamma_{Bulk} + \frac{Av_F}{R}$

- Accounts for peak broadening but predicts a red shift

- Instead, use a quantum approach:

J. Garcia de Abajo, Nature 483 (2012)
Quantum Theory Matches Experiment

Incorporating these discrete electron transitions in the electric permittivity of Ag results in the blueshift seen experimentally.
Quantum Theory Matches Experiment

Incorporating these discrete electron transitions in the electric permittivity of Ag results in the blueshift seen experimentally.

<table>
<thead>
<tr>
<th>Particle Diameter (nm)</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>10</td>
<td>3.2</td>
</tr>
<tr>
<td>15</td>
<td>3.4</td>
</tr>
<tr>
<td>20</td>
<td>3.6</td>
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Normalized absorption efficiency

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**Analytic**

**Ab-initio**

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

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

Yes. For particle diameters smaller than ~5nm, quantum-influenced electronic transitions will modify the plasmonic resonance.
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?
Case study: water-splitting photocatalysis

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

Youngblood et al., JACS (2009)
1. Synthesis of well-dispersed Ag@TiO$_2$ nanoparticles

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

Can small plasmonic particles help?
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$_2$

Hg(Ne) lamp

See also: Kamat et al., *JACS* (2005); *ACS Nano* (2011)
UV irradiation of de-aerated Ag@TiO₂

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)
Ensemble Measurements

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

Charge 0 min UV
Single Particle Optical Measurements

Charge
20 min UV

Normalized Scattering

Wavelength (nm)

400 442 500

Normalized Scattering

Wavelength (nm)

400 445 500

Normalized Scattering

Wavelength (nm)

400 440 500
Single Particle Optical Measurements

Charge
40 min UV
Single Particle Optical Measurements

Charge
60 min UV

Normalized Scattering

Wavelength (nm)

400 441 500

Normalized Scattering

Wavelength (nm)

400 443 500

Normalized Scattering

Wavelength (nm)

400 436 500
Single Particle Optical Measurements

![Graphs showing normalized scattering against wavelength in nm for different conditions.]

- **Discharge 0 min O₂**
Single Particle Optical Measurements

Discharge 20 min O₂
Single Particle Optical Measurements
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

1. Can we detect plasmons from particles in the sub-10nm regime?
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Preliminary results are promising. It will be exciting to correlate catalyst size and shape with activity.
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)
Solar upconversion

30-50% of sun’s energy cannot be absorbed

5% Ultraviolet

43% Visible

52% Infrared
30-50% of the sun’s energy cannot be absorbed.

Utilize low-energy transmitted photons.

5% Ultraviolet
43% Visible
52% Infrared
Modeling upconversion (UC) efficiencies

- Peak cell efficiency increases from 30% to 44%
- Ideal cell bandgap blue-shifts from 1.1 eV to 1.8 eV
- Challenges: UC absorption & emission efficiency, UC absorption bandwidths, UC energy levels

The need for efficient upconversion

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

- Effect of UC absorption bandwidth: higher efficiencies with higher bandwidths
Two promising upconverting systems

**Bimolecular systems**

**Lanthanoid-doped nanoparticles**

Photos by Ashwin Atre; See also: Singh-Rachford, et al. *JACS*. 131 (2009)

Photos by Diane Wu; See also: Wang, Nature (2010)
Tunable and Enhanced Upconversion

Conductive upconverting composites

UC Film
Plasmon composite
UC film (as conductive as ITO)

Intensity (a.u.)

Wavelength (nm)

500 550 600 650 700

4.3x 4.1x 4.7x

Diane Wu
Tunable and Enhanced Upconversion

**Conductive upconverting composites**

**Upconverters under pressure**

-Wavelength (nm)
-Pressure (GPa)

Intensity (a.u.)
Tunable and Enhanced Upconversion

Upconverter-doped dielectric core

No nanocrescent

With nanocrescent

Upconverted power towards cell

CL @ 470 nm
Conclusions

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

\textit{Some see things as they are and ask why. Others dream things that never were and ask why not.} – George Bernard Shaw.
Conclusions

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Thanks to you and our funders!!: GCEP, TomKat, DOE
Bimolecular upconversion process

S = sensitizer; E = emitter

Energy Requirements:

Sensitizer

Emitter

hv₁

hv₂
The need for efficient upconversion

- Solar-spectrum matching: don’t want UC energy levels to overlap with AM1.5 absorption lines
  - Burke, McGehee. *In preparation* (2012)

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