Nanostructured Metal-Organic Composite Solar Cells

PIs: Mark Brongersma (MSE), Peter Peumans (EE) and Shanhui Fan (EE)

The Science

Flexible Solar Cell

Stacked subcells

Organic heterojunction

Ag

Subcell composition

Transparent, nanopatterned electrodes

Metallic nanostructures

The Team

- Brongersma group (Material Science and Engineering): *Plasmon optics; Near-Field Characterization.*
- Peumans group (Electrical Engineering): *Organic Photovoltaics; Nanofabrication*
- Fan group (Electrical Engineering): *Theory and simulations of nanophotonic devices.*
Combining Photovoltaics with “Plasmonics”

**Silicon and Compound Semiconductor Cells**
- High efficiency (~24-36%)
- High cost.

**Organic Solar Cells**
- Low efficiency (~5%)
- Low cost

**Plasmonics**
- Metals enable manipulation of light at the nanoscale!

**Exciting New Opportunity!**
- Combine the fields of plasmonics and photovoltaics
- Organics and metals exhibit a good materials & processing compatibility
- Organic cells offer a very high possible increase in efficiency

*Photos from DOE and B. Kippelen, Georgia Tech*
Understanding the operation of a solar cell is key to designing improvements.

- A typical cell operation
  1. Photon absorption
  2. Exciton diffusion
  3. Charge transfer
  4. Charge separation
  5. Carrier collection

- Band diagram

Diagram showing the operational principle of an organic solar cell.
Operational Principle of Organic Solar Cells

Two key problems:

- Short exciton diffusion length (~ 5-10 nm)

  Solution: Create excitons near the D\A interface

- Transparent contacts need to be high conductivity and low cost

  High quality (conductivity) ITO is expensive and typically a lower grade is used

  Solution: Realize virtually transparent metal contacts with the conductivity of metals and the transparency of glass or ITO
Metal (Plasmonic) Nanostructures offer Solutions!

- Metals can be used in unexpected ways…….
The unique optical properties of metals have been exploited for centuries!

- Colorful Czech glass vase
- Ag nanoparticles cause yellow coloration
- Au nanoparticles cause red coloration
Excitation of a Single Metallic Nanoparticle

Properties of a single metallic nanoparticle

**Particle**
- Volume = $V_0$
- $\varepsilon_M = \varepsilon'_M + i\varepsilon''_M$

**Host matrix**
- $\varepsilon_H = \varepsilon'_H = n_H^2$

\[
\sigma_{\text{ext}}(\omega) = 9 \frac{\omega}{c} \varepsilon'_H^{3/2} V_0 \frac{\varepsilon'_M(\omega)}{\left[ \varepsilon'_M(\omega) + 2\varepsilon'_H \right]^2 + \varepsilon''_M(\omega)^2}
\]
Poynting vector

Energy flux (Poynting vector) for a plane wave incident on a metallic nanoparticle

C. F. Bohren, D. R. Huffman, Absorption and Scattering of Light by Small Particles, Wiley, New York 1983
Ag nanoclusters enhance absorption of organic thin films

- Reason: field concentration and energy storage by the Ag particles
- This effect can be exploited to preferentially create excitons near the D/A interface

*Reason: field concentration and energy storage by the Ag particles*
*This effect can be exploited to preferentially create excitons near the D/A interface*

Metal Nanostructure Enhanced Solar Cell

- Finite-element models for electromagnetic waves + exciton diffusion
- Zig-zag configuration concentrates electromagnetic power at active junction

Peumans group
Metal Nanostructure Enhanced Solar Cell

Metal antenna effects

![Graph showing generated photocurrent vs. wavelength for different materials and conditions.](image)

- CuPc
- PTCBI
- Ag cylinders
- No metal
- Air cylinders

Wavelength [nm]

Generated Photocurrent [arbs.]
Metal Nanostructure Enable Spectral Tuning

Selection of metal allows for spectral tuning of organic solar cell

- Spectral tuning can be employed in multi-junction stacked cells
Importance of Coating the Metallic Particles

Charge transfer and separation should only occur at the D/A interface

- Ag/SiO₂ particles embedded in organic thin films enhance absorption
- SiO₂ shell is essential (bare Ag particles cause exciton recombination as seen in PL)

![Graph showing photoluminescence with and without Ag/SiO₂ particles.](image)
Spectral Tuning by structure

20nm Au spheres

Au nanorods

Absorption (a.u.)

Wavelength (nm)

AuNPs

AuNRs
Synthesis of metallic nano-antennas

Porous Polycarbonate Membrane

Evaporated Gold Seed layer

Sonication removes gold

Electroless silver growth solution

Polycarbonate dissolved in chloroform

Many free wires

Ethanol
Characterization of the Nanorod Antennas

Goal: fabricate rods of about $\lambda/2$ with a strong light-matter interaction

- Nanorods with a few 10s of nm diameter and up to several $\mu$m have been synthesized
- Darkfield microscopy shows resonant light matter interaction

A spectrometer is currently built onto the microscope to allow measurement of scattering spectra on single particles

Ed Bernard, Brongersma Group
What is a surface plasmon (polariton)?

- Compare electron gas in a metal to real gas of molecules
- Metals are expected to allow for electron density waves: plasmons
- This resembles a light wave propagating along a metal surface!

![Diagram of surface plasmons at a metal-dielectric interface]

Potential to have a strong interaction of light with adjacent organic layers!
Photon Scanning Tunneling Microscope (PSTM)

- **Light Detector**
- **Cantilever**
- **Au film**
- **High NA objective**
- **λ/2 Waveplate**
- **LASER**
- **CCD**

More info: www.WITec.de
Strong Analogy between Light and Surface Plasmons

Young’s double slit experiment for surface plasmons

- Diffraction limit for lateral confinement in metal stripe waveguides!

Paper submitted
Enhanced Transmission through Sub-\(\lambda\) Apertures

Work we were inspired by…

- Ag film with a 440 nm diameter hole surrounded by circular grooves
- Transmission enhancement of 10 x compared to a bare hole
- 3x more light than directly impinging on hole!
- Reason: Excitation of surface plasmons

Nano-patterned Transparent Metal Contacts

Fabrication and analysis of transparent electrical contacts

R. Pala, M. L. Brongersma et al (unpublished)

Exciting Surface Plasmons Inside an Organic Cell

Surface Plasmon excitation can be exploited to further improve efficiency

- Trick: surface plasmons increase interaction length!

Transparent contact

Patterned metal contact

Light propagates normal to A/D interface

SPs propagate along the A/D interface

- Can we demonstrate plasmons increase absorption?
Grating Transmission and Plasmon Excitation

- Determine the propagation length $l$
- Investigated the change in $l$
- Fits the theory

PMMA with R6G dye
Measuring Grating Transmission in the Near-field

Determination of the near-field intensity is key!

- The near-field intensity determines the actual absorption near the A/D interface.
- What do we measure with our near-field optical microscope (PSTM):

  We have started investigating a number of calibration samples.

Rashid Zia
Near-field Image Resembles $H_z$!
Initial simulations of the entire system indicate possible improvements

- Finite-element models for electromagnetic waves + exciton diffusion

- Higher improvements can be obtained for a carefully engineered grating
Summary and Outlook

- The realization of highly conductive, yet transparent, nanopatterned metal film contacts.
- The use of metal nanostructures as efficient antennas for capturing and concentrating solar energy.
- Future idea: Integration of various organic photovoltaic subcells into highly efficient multi-junction stacks (pull current out the side).
Never underestimate the Power of Plasmonics!

- Great potential of enhancing efficiency of organic photovoltaic cell through plasmonics.
- We are beginning to understand the complex interplay between metallic nanostructures and organic photovoltaic cells.

Thanks to GCEP for the Support!
D: CuPc (Copper Phthalocyanine)

A: PTCBI (3,4,9,10 perylenetetracarboxylic bisbenzimidazole)