

## Nanostructured Metal-Organic Composite Solar Cells

### Investigators

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### Introduction

Organic-based solar cells have high potential to reduce the cost of photovoltaics. Low-cost active materials, high-throughput reel-to-reel deposition technologies, and application versatility makes them very likely to become competitive against inorganic thin-film devices. However the power conversion efficiency of organic photovoltaics (OPV) is still too low. This project aims at realizing a high efficiency organic device using the multijunction concept and metal nanoscale features to enhance the overall cell performance. In particular, transparent high-sheet-conductivity nanopatterned metal films are being developed to be used as transparent conductors allowing parallel subcell connection, and metal nanostructures are being embedded in the active layers to enhance the photon absorption and charge separation efficiency.

### Background

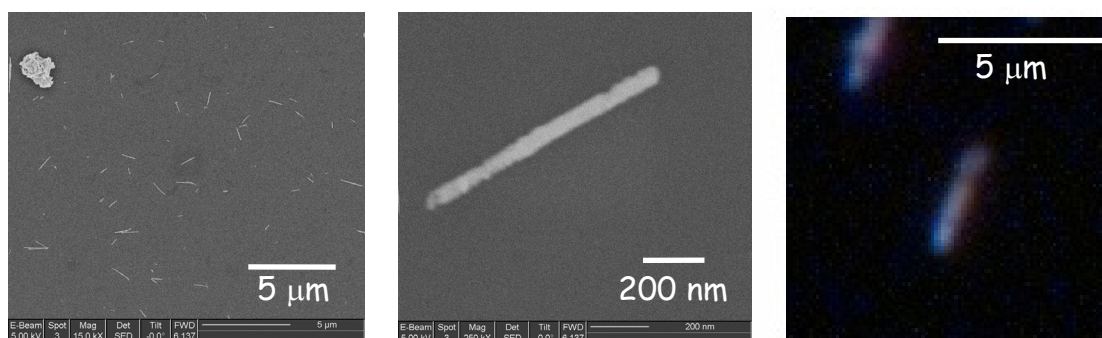
The performance of organic photovoltaics has been improving relatively quickly in the last few years. However this technology is still facing major fundamental limitations towards higher efficiency and stability that need to be overcome for it to be competitive with inorganic thin-film solar cells. This project proposes an innovative cell design to increase the efficiency of organic photovoltaics: a stack of organic/inorganic heterojunctions with embedded nanostructured metal features to improve the overall cell performance. The stack design is a high potential route to increase the light absorption efficiency of photovoltaics. The splitting of the solar spectrum through complementary absorption by different cells with specifically designed bandgaps minimizes thermal losses and increases the overall photon conversion efficiency.

### Results

During the last year, significant progress has been made in two major research directions. In particular, our team has designed and synthesized metallic nano-antenna structures and made progress towards simulation of highly conductive, yet transparent nanopatterned metal film contacts to OPV cells. If successful, both directions will significantly enhance solar cell performance and offer increased competitiveness of OPV for clean energy production compared to routes that ultimately lead to green house gas emissions.

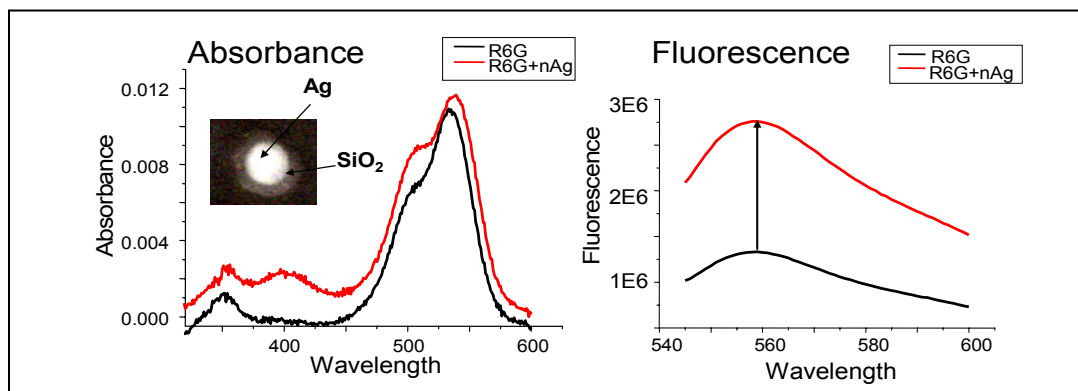
We have synthesized metallic nanowire structures by electrochemical means into porous materials, such as nanoporous anodized alumina or ion track-etched polycarbonate (PC) membranes. As an example, Fig. 1(a) and (b) show scanning electron microscopy images of a bed of 30 nm diameter Ag nanowires and a close-up of a single Ag nanowire. To grow these particular wires, PC membranes were first coated with a

seed layer of gold on the backside using a metal evaporator. These coated membranes were then immersed in an electroless silver-plating bath. The gold acted as a catalyst for silver precipitation and wires nucleated at the bottom of the pores. Growth continued as the silver was reduced from solution onto the silver precipitates. The porous membrane restricted the growth in one dimension. When wires reached their desired length, the membrane containing the wires was removed from solution and rinsed to remove residual plating solution. The nanowires were finally released into solution by dissolving away the porous membrane in chloroform and spun onto a glass substrate for further analysis. Using this technique large numbers of wires can be generated in an inexpensive fashion. These nanowires act as optical nano-antennas that can concentrate electromagnetic energy into a nanoscale volume. Dark-field optical microscopy studies were performed on these wires and resonantly enhanced light scattering was observed in the visible part of the electromagnetic spectrum. Figure 1(c) shows a representative dark-field optical microscopy of a Ag nanowire. By embedding such structures in OPV devices an improved light absorption, charge separation, and charge collection can be obtained. For example, when placed at the donor-acceptor interface of an organic heterojunction, electrically isolated metal nanoparticles may enhance photon absorption by concentrating the electromagnetic energy of incident radiation close to the junction.



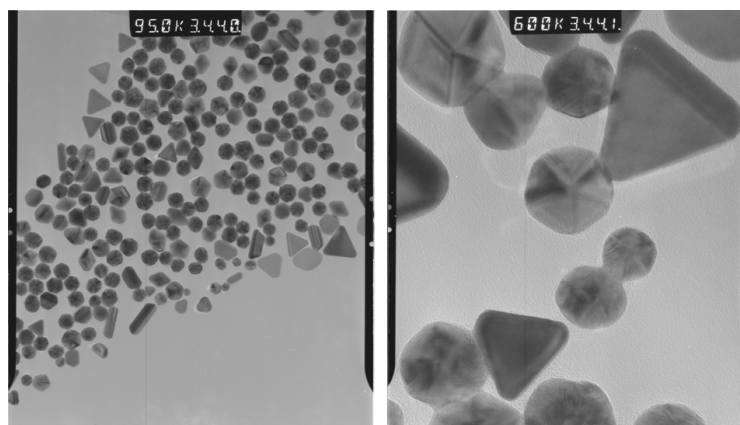
**Figure 1:** (a) Scanning electron microscopy (SEM) image of a bed of 30nm diameter Ag nanowires generated by electroless plating of Ag into a porous polycarbonate membrane. (b) SEM micrograph of a single Ag nanowire. (c) Dark-field optical microscopy image of a 30 nm diameter Ag nanowire.

We have also synthesized 10nm diameter Ag nanoparticles with 3nm thick SiO<sub>2</sub> coatings in solution. These particles were incorporated into organic thin films and their effect on the luminescence and optical absorption was analyzed. We found that, despite the 3 nm thick SiO<sub>2</sub> coating, the Ag nanoparticles still had a strong effect on the optical absorption, as shown in Fig. 2(a). Moreover, we note that the absorption enhancement is broadband. This makes such particles useful in enhancing the conversion efficiency of photovoltaic cells. Finally, we found that, because of the SiO<sub>2</sub> coating, the Ag nanoparticles have no deleterious effect on the luminescence, as shown in Fig. 2(b). This is a major step forward in producing solar cells that use metal nanostructures to enhance photocurrent through photonic effects while not impeding device operation through excitation quenching.



**Figure 2:** (a) Effect of Ag-core (10nm)/SiO<sub>2</sub> shell (3nm) nanoparticles embedded in an organic thin film in the absorbance (a) and photoluminescence (b). Both absorbance and photoluminescence are enhanced by the presence of the Ag-core/SiO<sub>2</sub>-shell nanoparticles.

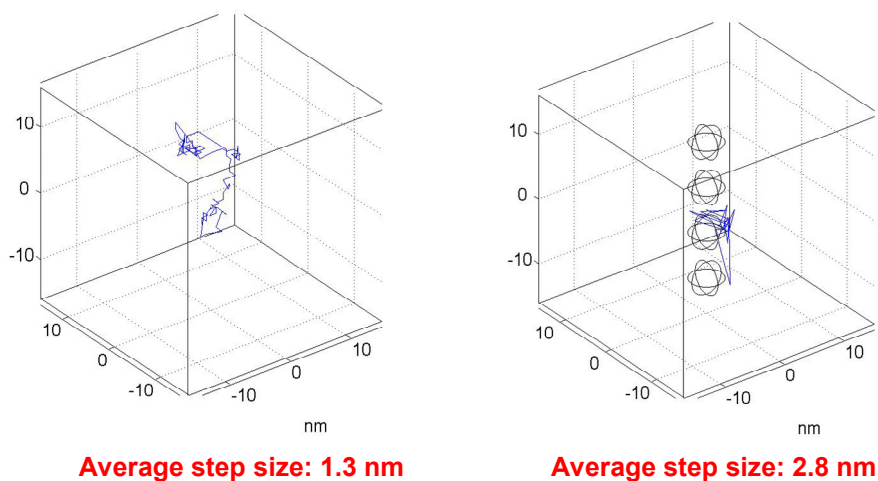
We are also exploring the effect of the metal nanoparticle shape on the absorption and fluorescence enhancement. Figure 3 shows a transmission electron micrograph of Au nanoparticles of various shapes synthesized in solution. Furthermore, these nanoparticles have been incorporated into organic thin films using our newly developed aerosol deposition process, yielding, for the first time, precisely controlled multilayer organic-metal nanostructures.



**Figure 3.** Transmission electron micrograph of solution synthesized Au nanocrystals. The average particle diameter is 10nm.

In order to study the effect of metal nanostructures on the migration of energy in organic thin films, we have constructed a computer model that calculates the hopping probability of excitons by Förster transfer. The model is based on the discrete dipole approximation and it is the first model that simulates energy transport in organic-metal hybrid systems on the nanometer scale. We find that, in the presence of metal nanostructures, energy (excitons) migrate further due to field enhancement. Figure 4

shows a representative trace of an exciton through a pristine organic material and through a material with Ag nanoparticles. In the presence of Ag nanoparticles, the average exciton hopping distance increases from 1.3nm to 2.8nm. Initial experimental results confirm our computer simulations.



**Figure 4:** Effect of the presence of metal nanostructures on the migration of energy (excitons) in organic thin films.

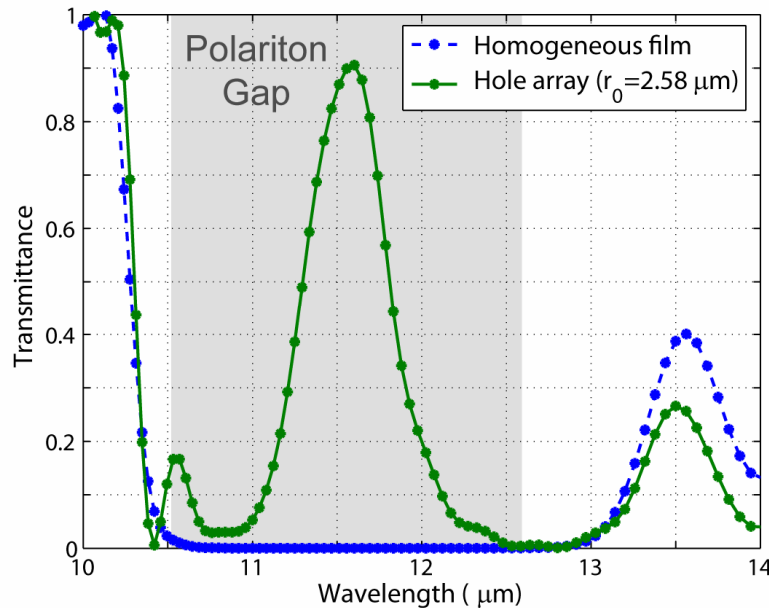
Our second major research direction is focused on the realization of transparent metallic electrodes for OPVs. Careful design of sub-wavelength aperture arrays in metallic thin films offer a particularly interesting approach towards this goal. In the past few years, there has been great progress increasing the transmission through nano-patterned metal films [1]. In most reported cases, enhanced transmission is associated with the excitation of surface wave resonances (surface plasmon polaritons) on the front and back surfaces of the metallic film and their evanescent tunneling through subwavelength holes [2, 3]. Under appropriate conditions, propagating modes inside the cylindrical hole can also play a substantial role [4]. Surface resonances and propagating modes provide complementary pathways for the transmission of light and are expected to enable transparent nano-patterned metal film contacts.

In order to understand the interaction of these two pathways, we have undertaken a study of a closely-related system based upon surface phonon polaritons. Surface phonon polaritons are the infrared counterpart to surface plasmon polaritons and feature weaker damping, thus offering the advantage of stronger and sharper optical resonances, which in turn lead to more distinct signatures. These more distinct and easy to interpret features allow us to better understand the physics behind the resonances, after which we will apply them to metallic films. In particular, we have studied the transmission properties of a SiC film with a two-dimensional periodic arrangement of subwavelength cylindrical holes.

Ionic crystals, such as SiC, allow transverse phonon polariton excitations in the infrared wavelength regime. At resonance, a transverse optical phonon and a transverse

electromagnetic wave can couple to create a frequency range (the polariton gap) in which the propagation of electromagnetic waves is prohibited. In the polariton gap, the propagation of electromagnetic waves (light) is prohibited for bulk SiC. By careful drilling of holes, it is possible to open up a transparent region in the spectrum of this otherwise opaque material. This is possible because the holes, although subwavelength, support a propagating mode. The propagating mode lies completely within the polariton gap. As the radius of the hole is reduced, the mode cutoff frequency asymptotically approaches the surface phonon polariton frequency inside the hole. This means that subwavelength holes have the peculiar property of always supporting propagating modes near the surface phonon frequency, regardless of how small the holes are.

Figure 5 shows the transmission spectrum (normal incidence) of a SiC film perforated with a two-dimensional periodic arrangement of subwavelength cylindrical holes with radius  $2.58 \mu\text{m}$  (period =  $7.5 \mu\text{m}$ , thickness =  $5 \mu\text{m}$ ). It is obtained by performing a three-dimensional finite-difference time-domain calculation. The spectrum of the perforated film features a near-perfect transmission peak exactly where a propagating mode is predicted by the dispersion diagram. In comparison, the transmission of a homogeneous SiC film of the same thickness is zero inside the polariton gap between  $10.53 \mu\text{m}$  and  $12.59 \mu\text{m}$ .

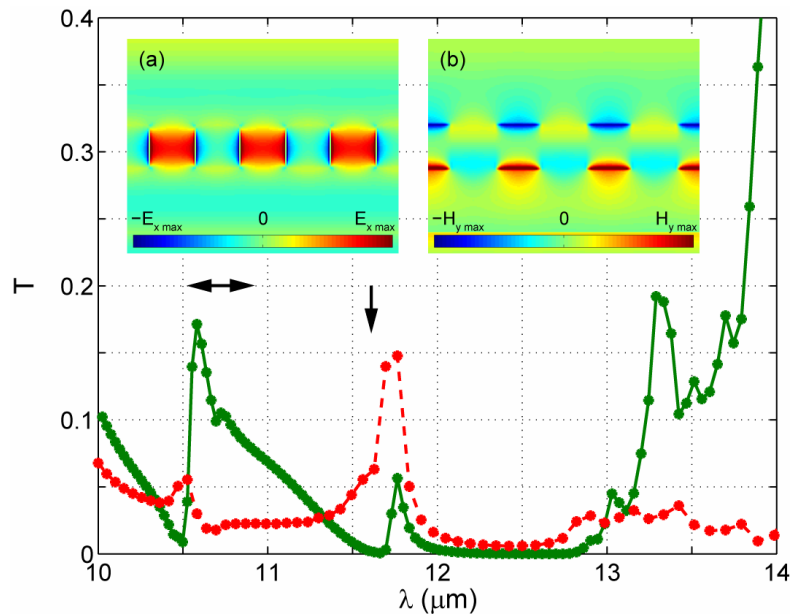


**Figure 5:** Transmission spectrum at normal incidence of a SiC film with a two-dimensional periodic arrangement of subwavelength cylindrical holes (solid green curve). The transmission spectrum of a homogeneous SiC film (dashed blue curve) clearly shows the polariton gap (gray region).

We demonstrated the presence of high transmission through SiC films when a two-dimensional periodic arrangement of subwavelength holes is made. Moreover, we showed that, due to the unique dispersion properties of surface phonon polaritons, such

high transmission is largely associated with propagating modes inside the subwavelength holes.

Figure 6 shows the transmission spectrum at normal incidence for a coated SiC film with a two-dimensional periodic arrangement of subwavelength cylindrical holes (solid green curve). The hole radius is  $1.6 \mu\text{m}$ , the periodicity of the array is  $6.4 \mu\text{m}$  in both transverse direction and the thickness of the SiC film is  $4 \mu\text{m}$ . The coating has a real, frequency-independent dielectric constant of 16 and is 200 nm thick.



**Figure 6:** Transmission spectrum at normal incidence for a coated SiC film with a two-dimensional periodic arrangement of subwavelength cylindrical holes (solid green curve). The vertical arrow shows the location of the first zero-crossing in the folded dispersion diagram for modes in a asymmetric air-dielectric-SiC waveguide. The dashed red curve shows the normalized spectrum of the surface resonance and results from an FDTD simulation in which the excitation is a dipole source near the surface. The insets show (a) the electric field at the first peak and (b) the magnetic field at the second peak in the transmission spectrum, respectively.

We also showed that the presence of two transmission mechanisms can lead to distinctly different transmission spectra and that the optical properties of the structure can only be understood by taking both pathways into account. If the two mechanisms are spectrally separated, they each lead to transmission peaks (Figure 5). This result is expected to shed some new light a similar pathway in metallic systems with subwavelength holes. For example, by proper design it should be possible to take advantage of both mechanisms in the transmission through metallic thin film contacts, which should greatly broaden the transmission bandwidth of such systems rendering them more transparent.

### Future Plans

In the coming year, we will perform measurements of the electromagnetic field enhancements that can be obtained near carefully designed metallic nano-antennas. This will be done using local Raman and fluorescence measurements in a confocal fluorescence microscope. In a second stage, the fabricated metal nanostructures (electrochemically grown, nanopatterned, and shape-engineered metal nanoparticles) will be incorporated into thin-film organic solar cell structures. The effect of the presence of electrically insulated nanoscale antennas on the performance of these devices will be analyzed. We will also investigate non-linear effects such as photon upconversion and downconversion in metal nanostructure-organic composites. Furthermore, our aerosol thin-film deposition process will be modified to allow us to modify the metal nanoparticles while in transit toward the substrate. This will allow us to precisely tune the interaction between molecules and metal nanostructures.

Based upon the simulations on transparent electrodes, we will now specifically design plasmonic thin film structures in which both the surface resonances and the propagating modes inside the holes are located in different spectral region. This will open up broad a band transmission over the solar spectrum through sub-wavelength aperture arrays. The optimum metallic electrodes will be fabricated and their electronic transport and optical transmission properties will be investigated experimentally.

### Publications

1. P. B. Catrysse and S. Fan. Conference on Lasers and Electro-Optics/International Quantum Electronics Conference, QCM4 (2006)
2. J.-Y. Lee and P. Peumans. "Organic photovoltaic cells incorporating metal nanoparticles," Materials Research Society Fall Meeting, Boston, 2005.

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3. T. W. Ebbesen, H. J. Lezec, H. F. Ghaemi, T. Thio, and P. A. Wolff, *Nature* **391**(6668), 667-669 (1998).
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