Spectroelectrochemical characterization of charge injection processes in thin films on ITO: 1) poly(3,4 ethylenedioxythiophene/)/poly(styrenesulfonate) (PEDOT/PSS); 2) tethered CdSe nanoparticles.

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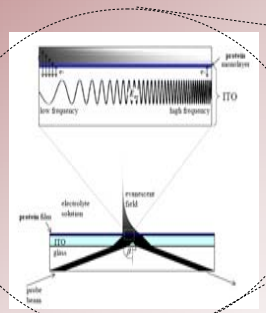
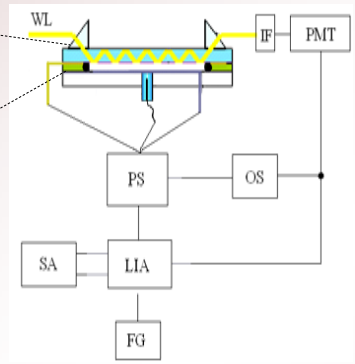
Abstract: The efficiency of charge transfer across interfaces between layers of dissimilar materials is a crucial factor in the performance of several types of organic electronic devices, such as organic photovoltaics (OPVs) and organic light emitting diodes (OLEDs). We are studying the kinetics of charge transfer in different types of conductive films deposited on indium tin oxide (ITO) electrodes using a novel spectroelectrochemical technique, potential modulated attenuated total reflectance (PM-ATR). Poly(3,4-ethylenedioxythiophene/)/poly(styrenesulfonate) (PEDOT/PSS) is frequently used to facilitate hole injection between ITO and the light emitting layer in an OLED. Charge transfer between PEDOT/PSS and ITO cannot be measured electrochemically due to high non-Faradaic background, which is eliminated using the optical method. The charge transfer rate measured using PM-ATR is in the range of 13 – 22 s^{-1}; we are currently evaluating organic monolayers as promoters to enhance this rate. We are also studying semiconductor nanoparticles tethered to ITO. Our recent experiments with CdSe nanoparticle films show that we can easily measure reversible charge injection at submonolayer surface coverage. Our data represent the first reported measurements of charge transfer rates in these types of films on ITO.

Potential-Modulated Attenuated Total Reflectance Spectroscopy



At low frequency of E_{ac} (left), the electroreflectance (ER) response is observed over several monolayers.

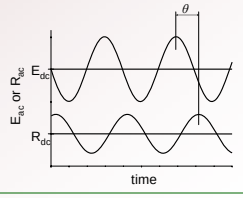
As the frequency of E_{ac} is increased (right), the ER response is increasingly selective toward the fastest electrochromic processes, i.e. the first adsorbed monolayer



The experimental setup for PM-ATR spectroscopy. White light is incoupled, and internally reflected down the length of, an ITO-coated glass microscope slide. The steady-state potential (E_{dc}) is set at the potentiostat (PS). The potential at the ITO electrode is modulated by applying a sinusoidal reference voltage from a lock-in amplifier (LIA) to the external input of the PS. The frequency of the modulation is set at the function generator (FG) which supplies a 5 Vp-p external reference signal to the LIA. The optical signal, i.e. the transmitted intensity of the internally reflected beam, is monitored at a selected wavelength using a bandpass interference filter (IF) and photomultiplier tube (PMT). Both the reference voltage and PMT output are monitored with an oscilloscope (OS). The PMT output is coupled to the LIA input and both the in-phase ($Re(R_{ac})$) and 90° out-of-phase ($Im(R_{ac})$)components are recorded using a LabView signal averaging (SA) program.

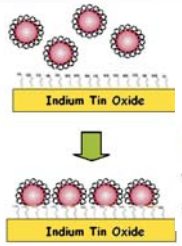
Schematic oscilloscope trace showing the modulation waveform (E_{ac}) centered on the steady-state potential E_{dc}. The resulting electroreflectance waveform (R_{ac}) is shown superimposed on the steady-state ATR reflectance, R_{dc}. The angle θ denotes the phase shift between E_{ac} and R_{ac}.

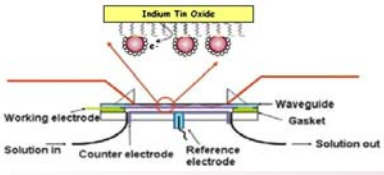
$$E = E_{dc} + E_{ac} \sin \omega t$$
$$R = R_{dc} + R_{ac} \sin(\omega t - \theta)$$



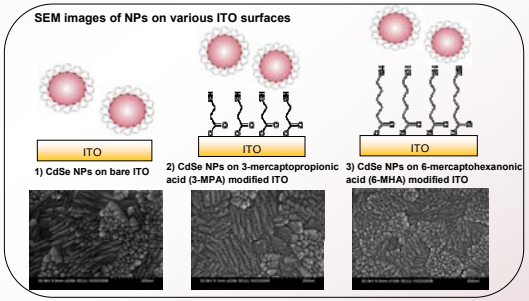
Tethered CdSe Nanoparticles (NPs)

Pyridine capped CdSe NPs d=~4 nm





SEM images of NPs on various ITO surfaces

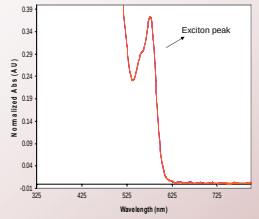


1) CdSe NPs on bare ITO

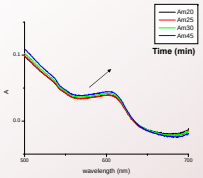
2) CdSe NPs on 3-mercaptopropionic acid (3-MPA) modified ITO

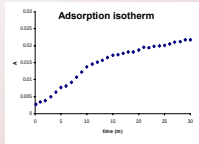
3) CdSe NPs on 6-mercaptohexanonic acid (6-MHA) modified ITO

Uv-vis Spectrum of 2 uM NP solution in 1:10 pyridine:MeOH

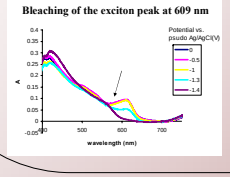


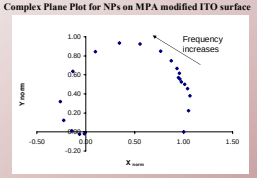
CdSe NPs adsorbed to 3-MPA modified ITO surface





Complex Plane Plot for NPs on MPA modified ITO surface





PM-ATR and Impedance measurements results:

	CdSe NPs on bare ITO	*CdSe NPs on 3-MPA modified ITO*	*CdSe NPs on 6-MHA modified ITO*
Surface Coverage (mol/cm²)	8.7 x 10^{-13}	8.3 x 10^{-12}	6.1 x 10^{-12}
Uncompansated solution resistance (R_u)	NA	29.8 Ω	26.6 Ω
Double layer capacitance (C_{dl})	NA	3.7 x 10^{-5} F	15.3 x 10^{-5} F
Rate constant (k_s)	NA	16.1 s^{-1}	45.2 s^{-1}

Charge transfer rate constant:

$k_s\ (s^{-1}) = 1/2\ \omega_2\ R_u\ C_{dl}$

k_s: rate constant

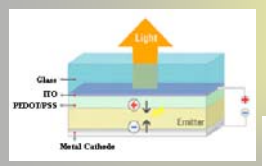
ω: frequency

R_u: uncompensated solution resistance

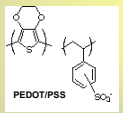
C_{dl}: double layer capacitance

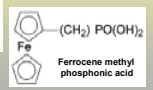
Charge transfer rate determination of PEDOT/PSS films on ITO with and without charge transfer promoters

The interface between an organic layer and an ITO electrode is important in determining the efficiency of organic electronic devices such as organic photovoltaics (OPVs) and organic light emitting diodes (OLEDs). Here PM-ATR was used to measure the charge transfer rate of two differently prepared (adsorbed and spin coated) PEDOT/PSS films on ITO. These measurements cannot be performed electrochemically due to high non-Faradaic background, which is eliminated using the optical method. To our knowledge, these are the first reported measurement of interfacial charge transfer kinetics for PEDOT/PSS on ITO. The effect of depositing a thin film of ferrocene methyl phosphonic acid (FMPA) between the ITO and the PEDOT/PSS film has also been studied. Preliminary results are shown below.



OLED

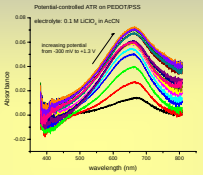




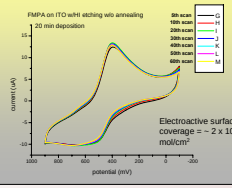
Ferrocene methyl phosphonic acid

Ferrocene derivatives are synthesized in the Marder Lab at Georgia Tech

ATR spectra of PEDOT/PSS under potential control

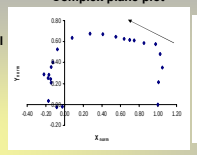


Cyclic Voltammogram of FMPA under similar deposition conditions as PEDOT/PSS

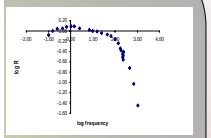


Electroactive surface coverage = ~ 2 x 10^{-10} mol/cm²

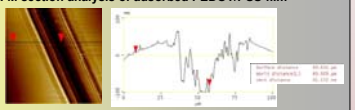
Complex plane plot



Log R vs. log frequency



AFM section analysis of adsorbed PEDOT/PSS film

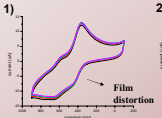


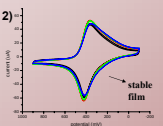
Summary of Results:

	PEDOT/PSS Film (adsorbed)	*PEDOT/PSS film (spin coated)*	*PEDOT/PSS film (spin coated) w/ FMPA*
AFM thickness	~ 50 – 100 nm	~ 50 nm	NA
Time constant ($R_u \times C_{dl}$)	6.7 ms	0.95 ms	3.7 ms
Rate constant (k_s)	13 – 22 s^{-1}	6 – 14 s^{-1}	3 – 10 s^{-1}

Current and Future Directions:

CVs of FMPA on ITO under different deposition conditions:



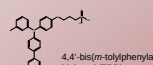


ITO is etched with HI for 10 seconds before FMPA adsorption. After the film deposition, the film is heat annealed under vacuum for 1 h.

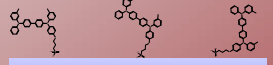
ITO is plasma cleaned before FMPA adsorption. No heat annealing is applied after the film deposition.

The surface treatments are crucial for achieving stable FMPA films on ITO surface. The charge transfer rate is expected to be affected and will be measured under different film treatments.

Some possible orientations for TPD on the ITO surface.



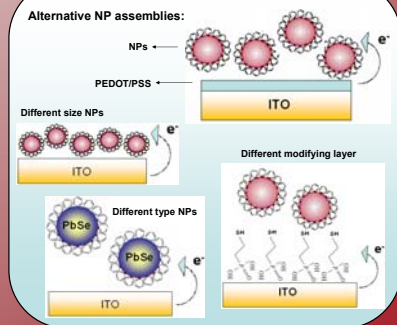
4,4'-bis(*m*-tolylphenylamino) biphenyl (TPD) phosphonic acid



TPD derivatives are synthesized in the Marder Lab at Georgia Tech

Orientation dependent information on the rate of electron transfer between TPD phosphonic acid and the ITO surface is possible using polarized light.

Alternative NP assemblies:



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