Characterization of charge injection processes in thin films of tethered semiconductor (CdSe) nanoparticles on transparent conducting oxides: Essential steps in sensitization of new photovoltaic and solar fuel-producing energy conversion systems

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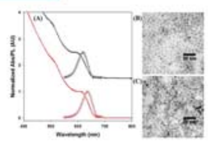
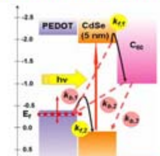
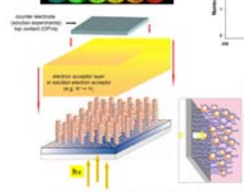
Semiconductor Nanoparticles (3-7 nm diameter) have shown promise as:
a) Light-absorbing, electron transport layers in polymer/nanoparticle hybrid PVs
b) Sensitizers/Photocatalysts for the formation of Solar Fuels (e.g. H_2)

We face significant technical problems in modifying their surfaces to make them compatible with polymer hosts, and to enhance rates of electron transfer to/from the NP upon photoexcitation

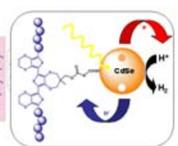
The Problem: What are the frontier orbital energy levels and rates of ET for "tethered" semiconductor nanoparticles?





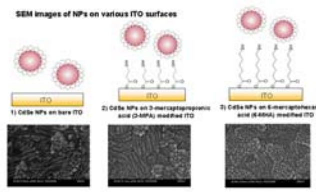


Shallcross et al. J. Amer. Chem. Soc., 2007

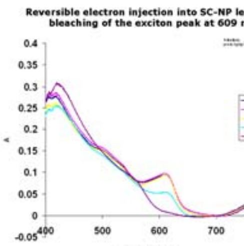


Rates of ET after photoexcitation are controlled by the differences in frontier orbital energies of the NP (E_{CB} and E_{VB}) and those of the surface tether/polymer host and the electron acceptor (e.g. C_{60})

New methods are needed to determine E_{CB} and E_{VB} in environments which are close to those to be used in the energy conversion process

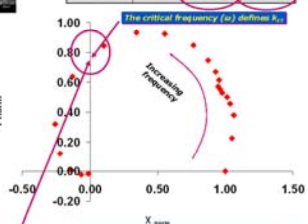


Reversible electron injection into SC-NP leads to bleaching of the exciton peak at 609 nm



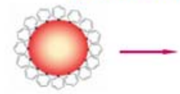
First-ever measurements of k_{ET} for monolayers of semiconductor nanoparticles

	CdSe NPs on bare ITO	CdSe NPs on 3-MPA modified ITO	CdSe NPs on 6-MHA modified ITO
Surface Coverage (mol/cm²)	8.7×10^{-11}	8.3×10^{-11}	5.5×10^{-11}
Uncompensated solution resistance (R_s)	NA	31.3 Ω	25.8 Ω
Double layer capacitance (C_{dl})	NA	3.7×10^{-5} F	4.5×10^{-5} F
Rate constant (k_s)	NA	13.9 s^{-1}	13.2 s^{-1}



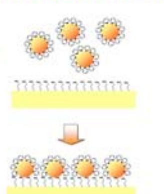
k_{ET} (s^{-1}) = 1/2 ω^2 R_s C_{dl}
k_{ET}: rate constant for charge injection into tethered NP
ω: frequency
R_s: uncompensated
C_{dl}: double layer capacitance

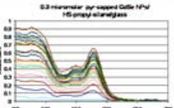
The Approach: Waveguide-Based Spectroelectrochemical Characterization of E_{CB} and k_{ET}

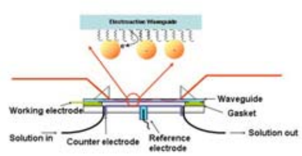


Monodisperse pyridine-capped CdSe NPs (d=~4 nm)

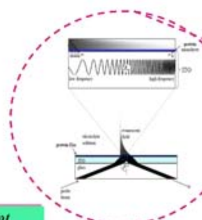
A single monolayer of NPs is captured on an ITO/waveguide surface decorated with tethering molecules ($HS-(CH)_n-COOH$)



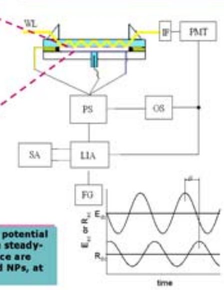




The NP-decorated ITO/waveguide is immersed in a solution which will suppport electron injection into the NP from the ITO substrate, while simultaneously monitoring the excitonic absorbance features in the NP



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



The potential of the NP/ITO interface is modulated (E_{ac}) about a steady-state potential E_{dc} -- the resulting electroreflectance waveform (R_{ac}) is superimposed on the steady-state ATR reflectance, R_{dc}, with a phase-shift θ – only changes in absorbance are observed, allowing a unique approach to the measurement of k_{ET} for tethered NPs, at high ω only ET to the tethered NP is observed.