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Communication

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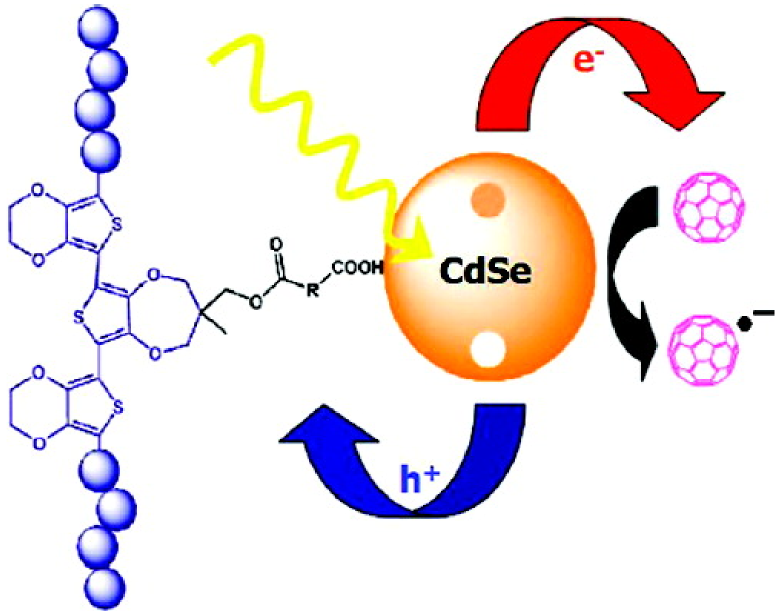

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Poly(3,4-ethylenedioxythiophene)−Semiconductor Nanoparticle Composite Thin Films Tethered to Indium Tin Oxide Substrates via Electropolymerization

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The preparation of organic/inorganic hybrid materials composed of either small molecules or conjugated polymers and semiconductor nanoparticles (SC-NPs) has been pursued as a route to photoelectrocatalytic thin films[1] and thin films with enhanced efficiencies for photovoltaic devices.[2−5] Nanoparticle inclusions (e.g., CdSe) in hole transporting polymers create percolation pathways for electron transport. The efficiency of such hybrid solar cells depends on the morphology of the nanocrystal, the capping ligands surrounding the SC-NP, and processing conditions used to create NP/polymer hybrid films.[2−5] The compatibility of the SC-NP with the polymer host is tailored by choice of surface capping ligand,[2c,d,4] which ultimately controls the morphologies of the two phases, and the efficiencies of charge creation and extraction from the SC-NP and polymer phases.

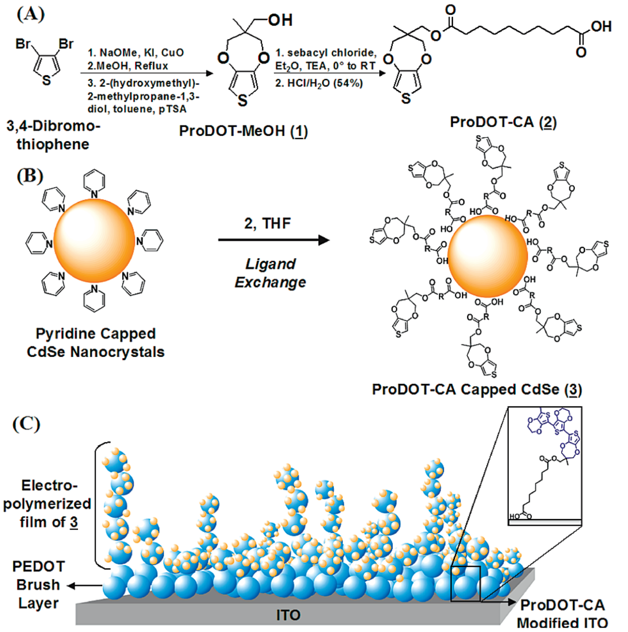
Cadmium sulfide (CdS)-NPs have also been previously chemisorbed to electrode surfaces and their photoelectrochemical properties characterized using solution donor molecules.[1] Vectoral electron transport from the photoexcited NP occurs with high efficiency when sufficient concentrations of the electron donor are present to reduce the photo-oxidized CdS-NP, suppressing nanoparticle corrosion.

We describe here a novel route to prepare nanocomposite thin films of electron-rich poly(3,4-ethylenedioxythiophene) (PEDOT) and 3,4-propylenedioxythiophene-capped CdSe nanocrystals, tethered to ITO electrodes (Scheme 1). Thin films of PEDOT were first grown on ITO electrodes, with a chemisorbed monolayer of 10-((3-methyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepin-3-yl)-methoxy)-10-oxo-decanoic acid (ProDOT-CA (**2**)).[6] ProDOT-CA ligand-capped CdSe-NPs (**3**) and **2** were then cross-linked with thin PEDOT films via electropolymerization. PEDOT/**3** composite films showed significantly greater photoelectrochemical activity with C_{60} as the solution electron acceptor, compared to PEDOT/**2** copolymer control films containing no CdSe-NPs. This approach to nanocomposite films is distinctive from previous studies of solution cast thin films of polymer/nanoparticle composites in that it enables direct wiring of the light-harvesting nanoparticle to the donor polymer and the hole collection electrode (i.e., ITO), leading toward new photoelectrocatalytic and photovoltaic technologies.

ProDOT methanol (**1**) was prepared using reported methods[7] and converted to **2** by esterification and hydrolysis with sebacaoyl chloride. Capping ligands based on ProDOT versus EDOT were explored due to the synthetic accessibility to **1** without compromising the optoelectronic properties of the resultant polymer.[8a,11] The length of the ligand was chosen to optimize both ligand packing and NP solubility. Successive ligand exchange of hexadecylamine (HDA)-capped CdSe-NPs with pyridine, followed by ligand exchange with **2**, afforded the ProDOT-CA-capped CdSe-NP (**3**), primarily soluble in solvents such as THF.[9]

Infrared spectroscopy of the final SC-NP powders suggested nearly complete exchange of the HDA ligands with **2** (Figure S2). Optical spectroscopy of HDA-capped and ProDOT-CA-capped CdSe-NPs and TEM data of both NPs (Figure S1) show size uniformity (ca. 5 nm diameter) and a small blue shift of the absorbance/emission spectra in **3**, attributed to slight etching of the SC-NP as a result of capping with the carboxylic acid ligand.[9]

Scheme 1[a]



[a] Synthesis of ProDOT-CA ligand **2** (A) and ProDOT-CA-capped CdSe-NP **3** (B); (C) sequential electropolymerization of EDOT from acetonitrile solution onto a ProDOT-CA-modified ITO followed by electropolymerization of **3** in the presence of an excess of **2** afforded photoelectrochemically active nanocomposite thin films.

A bottom-up approach was used to prepare **3**/PEDOT hybrid films. Solvent cleaned, O_2-plasma-etched ITO electrodes were incubated in an acetonitrile solution of **2** (1 mM, 30 min) to create a chemisorbed monolayer of electroactive ProDOT.[6,9] Ultrathin films of PEDOT (ca. 10 nm) were next grown from a monomer solution on this chemisorbed monolayer via electro-copolymerization at +0.8 V vs Fc/Fc^+, ensuring kinetic-controlled rates of polymerization.[6,8b] These activation steps and underpotential polymer growth produce PEDOT films that are conformal, with enhanced electrochemical communication between the ITO electrode and tethered SC-NPs.[6] **3** was next incorporated into the light blue PEDOT film at the aforementioned potential, from a stirred, 3.6 μM THF solution of **3** with supporting electrolyte and an excess of **2**.[9] Current versus time plots (Figure S3) showed slow incorporation of **3** from solution into the polymer film, where the majority of the cross-linking occurred in the first 1000 s.[9] Resultant hybrid films were sonicated in THF to remove unattached **3**. Control

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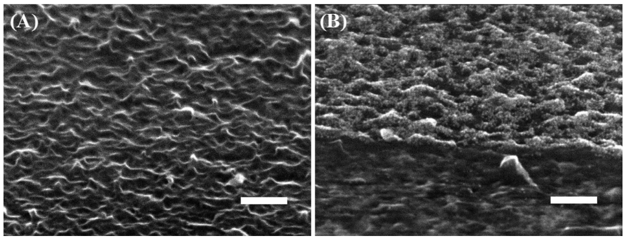

Figure 1. FE-SEM images of electrochemically polymerized (A) PEDOT/**2** copolymer film and (B) PEDOT/**3** nanocomposite thin film near a scratch (scale bars = 100 nm) (for larger images see Figure S5).

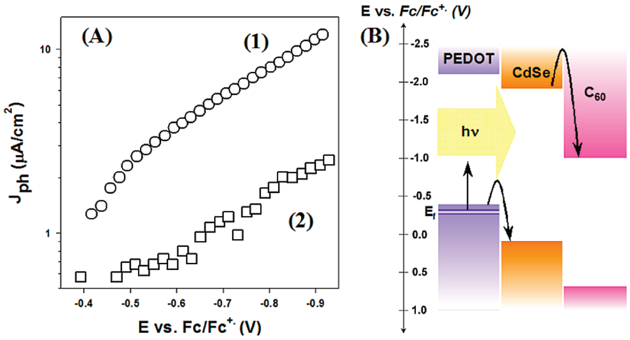

Figure 2. (A) Background-corrected[9] photocurrent as a function of applied potential for (1) **3** electrochemically cross-linked into a thin PEDOT film and (2) a control PEDOT/**2** copolymer film. (B) Energy level diagram showing concerted hole capture and electron transfer to C_{60} by de-doped PEDOT and CdSe SC-NPs, respectively. The first reduction potential for C_{60} and the onset of electrochemical oxidation, along with their optical gaps, were used to estimate the energy levels for C_{60} and PEDOT, respectively. The relevant CB energy for **3** was estimated from solution electrochemical measurements.[13]

PEDOT/**2** copolymer films were prepared by electropolymerization of **2** onto similar PEDOT films.

X-ray photoelectron spectroscopy (XPS) confirmed the incorporation of **3** into PEDOT films (Figure S4). The Cd(3d)/Se(3d) intensity ratio was ca. 1.2−1.4, ca. 25−40% of the surface Se existed in the SeO_x form, some of which was formed during ligand capping, as verified from XPS characterization of spin-cast films of **3**.[10] Field-emission SEM and tapping-mode AFM images of PEDOT/**2** copolymer films and PEDOT films cross-linked with **3** are shown in Figures 1, S5, and S6. PEDOT/**2** copolymer films show a continuous surface structure, while images taken after incorporation of **3** into the PEDOT film show a clear added nanoscale texturing of the surface region, with ca. 5 nm closely packed roughness features and larger features that can extend 100 nm in height (see Figures S5 and S6).

Background-corrected photoelectrochemical responses of PEDOT/**3** composite films and control PEDOT/**2** copolymer films, using C_{60} (0.8 mM) as the solution electron acceptor under visible light excitation, are shown in Figure 2A.[9] Photocurrents corresponding to NP-sensitized reduction of C_{60} by the PEDOT/**3** film began at ca. −0.4 V (vs Fc/Fc^{+}), well positive of the $E°$ for $C_{60}/C_{60}^{-\bullet}$ (ca. −1.0 V vs Fc/Fc^{+}),[9] and increased exponentially with increasing negative potential (Tafel-like behavior). These potentials are sufficient to fully reduce (de-dope) PEDOT and allow electron injection into photoexcited CdSe-NPs. Copolymer films of **2** and PEDOT showed much smaller photocurrents, even though it has been recently demonstrated that photoinduced charge injection from a ProDOT polymer to C_{60} is possible.[11] Anodic photocurrents were observed at more positive potentials, which were avoided here to avoid NP corrosion.[9]

Figure 2B shows the estimated energy levels controlling charge transfer.[9] The "Fermi energy" for the PEDOT layer is controlled by the degree of electrochemical de-doping of this polymer, which occurs negative of −0.4 V vs Fc/Fc^{+}. The electron affinity of C_{60} is estimated from its first reduction potential (ca. −1.0 V vs Fc/Fc^{+}).[9] The CB energy for **3** cross-linked into the PEDOT layer is estimated from solution electrochemical experiments,[5,12] and the band gap energy of the NP is used to estimate the VB energy.[9] Energy levels for the NP are expected to be strongly ligand dependent and further altered in the condensed phase;[1−3,5,12] however, electron injection from photoexcited CdSe-NPs into crystalline C_{60} has been recently shown to be energy sufficient.[13]

In conclusion, we have demonstrated that electropolymerized PEDOT films with cross-linked CdSe SC-NPs offer an enabling technology for nanometer-scale control of the blending of functionalized NPs with donor (hole transporting) polymer hosts. Further optimization of ligand chain length, structure, and head group, type of thiophene polymer, and the size and type of NP will be necessary to fabricate solar cells with improved energy conversion efficiencies.

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Supporting Information Available: Experimental procedures for the preparation of polymers and nanoparticles, and additional imaging, XPS, and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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