

# Influence of polymer–metal interface on the photovoltaic properties and long-term stability of nc-TiO<sub>2</sub>-P3HT hybrid solar cells

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## ABSTRACT

The role played by the interface between light harvesting polymer poly(3-hexylthiophene) (P3HT) and thermally evaporated metal electrodes such as Au, Ag, and Cu on the photovoltaic performance and stability of nc-TiO<sub>2</sub>-P3HT (nc refers to nanocrystalline) ordered heterojunction hybrid solar cells has been systematically investigated. These hybrid solar cells with Cu films as positive electrode have been fabricated for the first time, and they exhibit improved open circuit voltage ( $V_{oc}$ ) and fill factor ( $FF$ ) compared to those fabricated with Au and Ag electrodes. More importantly, the Cu-based cells show better stability during continuous operation and ageing in an inert atmosphere. The improved photovoltaic performance and stability of the cells fabricated with the Cu electrodes are attributed to the chemical bonding between Cu and the S atoms of P3HT to give copper–sulfur complex or copper sulfide like species as indicated by the photoelectron spectroscopic (XPS) data. The improvement in stability exhibited by the cells with Cu electrode is interesting in light of the fact that hybrid solar cells based on semiconductor oxides like TiO<sub>2</sub> quickly decay in the absence of oxygen.

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## 1. Introduction

Hybrid solar cells comprise of nanocrystalline inorganic semiconductor oxides (e.g., TiO<sub>2</sub>, ZnO) in direct contact with an organic light harvesting conjugated polymer (e.g., P3HT, MEHPPV). Interaction of incident photons with the polymer generates coulombically bound electron–hole pairs, which dissociate due to a difference in the energy levels of the two components. Once separated, electrons are carried through the network of the inorganic nanocrystals while holes are extracted through the polymer [1–10]. Such hybrid solar cells are attractive as they use inexpensive, environmentally compatible raw materials and can be produced by high throughput manufacturing processes like roll-to-roll printing [11–13]. Despite recent demonstrations of efficient hybrid solar cells, production of solar cells based on semiconductor oxides that exhibit high efficiencies over a long period of time remains a challenge [14–18]. This is mainly because a lot remains to be understood about the complex relationships among the different materials used in such hybrid solar cells, in particular the interfaces among them.

We focus here on the intensively pursued hybrid ordered heterojunction solar cell system consisting of poly(3-hexylthiophene) (P3HT) as the electron donating light absorbing polymer and nanocrystalline titanium dioxide (nc-TiO<sub>2</sub>) as the electron

acceptor [2,6,10]. Such cells normally employ a transparent conducting oxide like fluorine doped tin oxide (FTO) or indium doped tin oxide (ITO) as the negative electrode and a thermally evaporated metal film as the positive electrode. The schematic of such a hybrid solar cell is shown in Fig. 1. The photovoltaic behavior of these hybrid devices has been shown to depend on a delicate equilibrium between TiO<sub>2</sub> and the oxygen present in the cell test environment [14–18]. It appears that oxygen is a prerequisite for proper functioning of these cells as the oxygen vacancies created in TiO<sub>2</sub> can become recombination sites for charge carriers, resulting in a quick decay of the photovoltaic performance in an inert atmosphere. Ironically, oxygen can cause irreparable damage to polymers like P3HT in the long run. The design of an efficient and stable hybrid solar cell based on semiconductor oxides like TiO<sub>2</sub> will become possible only if challenges associated with this complex interaction between TiO<sub>2</sub> and atmospheric oxygen are successfully addressed.

With this perspective, we present here our preliminary data on hybrid solar cells fabricated with Cu films as positive electrodes that exhibit improved stability during continuous operation and ageing in an inert atmosphere, compared to those fabricated with the commonly used Au and Ag electrodes. To the best of our knowledge, this study represents the first report on the use of thermally evaporated Cu thin films as electrodes in hybrid solar cells. A comparison of the performances and stabilities of the solar cells fabricated with the Au, Ag, and Cu electrodes and an understanding of the differences among the cells fabricated with these three electrodes are discussed based on the characterization

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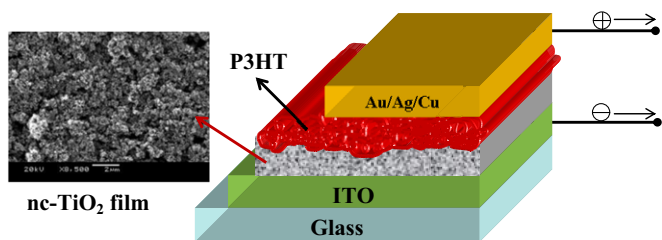


Fig. 1. Schematic of nc-TiO<sub>2</sub>-P3HT hybrid solar cells, with the inset showing a SEM photograph of sintered nc-TiO<sub>2</sub> film.

data obtained with X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM).

## 2. Experimental

### 2.1. Materials

Regioregular poly(3-hexylthiophene) (P3HT) was purchased from Rieke Metals. The nc-TiO<sub>2</sub> (Degussa P-25) sample was a generous gift from Degussa Corporation. Both chemicals were used without further purification. ITO coated glass slides (sheet resistance = 10 Ω/□) were purchased from Nanocs (New York, NY) and cut into 1 in × 1 in square pieces. Al, Au, Ag, and Cu wires used for thermal evaporation were of high purity (99.999%) and were purchased from Alfa Aesar.

### 2.2. Solar cell fabrication

ITO coated glass substrates were masked using polyimide tape and patterned by slow etching in a mixture of 75% de-ionized water, 20% HCl, and 5% HNO<sub>3</sub>. The substrates were then rinsed with de-ionized water and cleaned by successive sonication in aqueous detergent, de-ionized water, acetone, and isopropanol. The cleaned substrates were dried in flowing nitrogen and finally treated with oxygen plasma for 15 min in a plasma cleaner (Harrick PDC-32G). A suspension containing 10 wt. % nc-TiO<sub>2</sub> was prepared using Degussa P-25 and ethanol. This suspension was sonicated for an hour and then stirred vigorously till a smooth flowing paste was obtained. The paste was again sonicated for 15 min. Finally, 65 μL of the paste was applied onto a cleaned ITO coated glass substrate and cast by doctor blading using a glass rod [19,20]. After slow drying in air, the substrates were sintered in air at 450 °C for 30 min to evaporate the residual solvent and improve electrical contact between particles, and cooled slowly to room temperature. The sintered nc-TiO<sub>2</sub> films were transparent with a thickness of around 2 μm, as measured using a Dektak 3 surface profilometer and a scanning electron microscope (SEM, JEOL LSM-5610). To avoid possible shorting of the solar cell in the absence of a TiO<sub>2</sub> blocking (compact) layer, the Degussa P-25 TiO<sub>2</sub> film thickness was carefully varied till a thickness was attained at which none of the cells on a single ITO substrate showed shorting behavior.

10 mg of P3HT was dissolved in 1 mL of chlorobenzene and stirred for 2 h in an oil bath (at 50 °C under nitrogen atmosphere) to increase the solubility of P3HT. The P3HT solution was then filtered through a 0.20 μm pore size PTFE membrane syringe filter (Pall Life sciences). P3HT films of varying thicknesses (50–200 nm) as confirmed by profilometer and scanning electron microscopy (SEM) were deposited by spin coating. Thin (~50 nm) films were obtained by coating at a speed of 1500 rpm for 60 s, while thicker (~200 nm) films were obtained by letting the solutions remain on the substrate for 60 s before spinning at a

lower speed of 500 rpm for 20 s. After slowly drying the films in a petri-dish, P3HT was cleaned from the ITO contact areas with chlorobenzene and a lint-free cotton swab. Finally, the device was completed by thermally evaporating a 2 × 3 matrix of 85 nm thick, square metal (Au, Ag, or Cu) electrodes each measuring 3 mm × 3 mm onto the P3HT coated nc-TiO<sub>2</sub>. An additional 100 nm thick aluminum (Al) layer was then deposited both for protecting the underlying layer and for attaching electrical measurement probes. The metal films were deposited at 10<sup>-7</sup> Torr using a JEOL thermal evaporator. Although some of the cell fabrication steps were carried out under ambient conditions, care was taken to ensure that the exposure times were limited to short periods of less than 10 min.

### 2.3. Characterization techniques

Tapping mode atomic force microscopy (AFM) imaging was carried out with a Nanoscope IIIa Dimension 3100. Scanning electron microscopy (SEM) images were collected on a Hitachi S-5500 SEM. X-ray photoelectron spectroscopic (XPS) studies of the P3HT–metal interface were conducted with a Kratos analytical spectrometer using monochromatic Al Kα X-ray source. The charging effect was corrected by using the binding energy of C 1s signal at 285 eV. A Shirley type nonlinear background was subtracted and peak deconvolution was performed using Gaussian–Lorentzian curves. Samples for XPS analysis comprised of 200 nm thick P3HT film on silicon substrate covered with ~1–3 nm of the positive electrode metal (Au, Ag, or Cu) films. Solar cell current density–voltage (*J*–*V*) characteristics were measured under inert (argon) atmosphere in a glove box (H<sub>2</sub>O and O<sub>2</sub> < 0.1 ppm) using a Keithley 2400 source measurement unit. The solar cells were illuminated through the ITO side of the substrate using an Oriel 91160 300 W solar simulator as the excitation source (100 mW/cm<sup>2</sup> white light illumination under AM 1.5G conditions). Solar cell ageing was carried out by storing the devices inside sealed dark containers in the glove box.

## 3. Results

### 3.1. *J*–*V* characteristics

We first tested the photovoltaic performances of the nc-TiO<sub>2</sub>-P3HT hybrid solar cells fabricated with different metal (Au, Ag, and Cu) electrodes inside an argon filled glovebox. All devices had a P3HT layer thickness of ~200 nm. Dark *J*–*V* characteristics of the devices measured before illumination are depicted in Fig. 2(a). Devices with the Au electrode displayed diode characteristics with a turn-on voltage of 0.2 V. The use of Ag and Cu electrodes resulted in devices, which initially behaved like ohmic conductors in the dark. This behavior is especially pronounced in the case of Ag. This is possibly because of the close work functions of the Ag (~4.7 eV) and ITO electrodes (~4.5 eV). It must be noted that Ag electrodes are partially oxidized even at the low oxygen partial pressures encountered during evaporative deposition, which increases their work function [21,22]. Furthermore, the thermal evaporation equipment used to deposit the metal films in this work was situated outside the glove box. On illumination, devices based on all three metals exhibited photovoltaic behavior, as depicted in Fig. 2(b). Devices made with Au electrode showed higher *J*<sub>sc</sub> values (0.32 mA/cm<sup>2</sup>) than those made with Ag (0.13 mA/cm<sup>2</sup>) and Cu (0.06 mA/cm<sup>2</sup>). However, the Cu-based devices displayed higher values for both *V*<sub>oc</sub> (0.41 V) and *FF* (38%). These photovoltaic parameters summarized in Table 1 were measured for a series of cells and the values were found to be

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