



# Low temperature processed NiO<sub>x</sub> hole transport layers for efficient polymer solar cells



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## ABSTRACT

We here demonstrate the use of solution processed NiO<sub>x</sub> thin films as the hole transport layer (HTL) in a thiophene–quinoxaline copolymer:fullerene solar cell. The NiO<sub>x</sub> films, which are prepared by UV-ozone treating a nickel formate precursor, outperform the solar cells prepared in this study that use PEDOT:PSS as HTL. The power conversion efficiency improves from 5.3% to 6.1% when replacing PEDOT:PSS with NiO<sub>x</sub>. Unlike most conventional ways of fabricating solution processed NiO<sub>x</sub> HTLs, our method does not require high temperature (>300 °C). In fact, we were able to produce high performing NiO<sub>x</sub> HTLs without the use of any thermal annealing. X-ray photoelectron spectroscopy revealed that a mixture of oxides and hydroxides is formed as a result of the UV-ozone treatment, which differs in composition from those formed by high temperature annealing; UV-ozone treatment produces NiOOH, while only the high temperature annealing produces any significant amount of NiO. Contact potential difference (CPD) measurements reveal an increased work function for all UV-ozone treated NiO<sub>x</sub> films, consistent with the presence of NiOOH at the surface. The high work function of the UV-ozone treated NiO<sub>x</sub> films leads to an improved energy level matching between the donor and the HTL, resulting in higher fill factor and hole injection current.

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## 1. Introduction

Polymer solar cells are promising as a technology to produce clean energy from the abundant and freely available solar energy because of their low production cost owing to the compatibility with low temperature deposition processes by roll-to-roll printing for large scale production, the possibility to make flexible, light weight devices and record power conversion efficiencies (PCE) exceeding 10% for single-junction devices [1–6]. To commercialize this technology, it is of paramount importance to further increase the PCE and to insure long term stability, i.e. minimum 5–7 years operation lifetime of the solar cells [7]. One of the ways to improve both the performance and stability of polymer solar cells is to use

metal oxides as hole transport layers (HTL) instead of the commonly used poly (3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) [8,9]. Even though PEDOT:PSS meets all the technical requirements for rapid low cost production of polymer solar cells, its inherent acidic and hygroscopic properties have been proven to be a major cause of degradation in organic photovoltaics (OPV) [10–14].

High work function metal oxides are suitable candidates as HTL materials; MoO<sub>3</sub> [15–19], V<sub>2</sub>O<sub>5</sub> [20,21], CuO<sub>x</sub> [22], WO<sub>3</sub> [23,24], and IrO<sub>x</sub> [25] have all been reportedly used in OPVs. Another metal oxide showing great promise as HTL material is NiO<sub>x</sub>. NiO<sub>x</sub> has been deposited by several different methods, such as pulsed-laser deposition [26,27], thermal evaporation [28], atomic layer deposition [29,30], sputtering [31,32] and solution processing [33–37]. Avoiding deposition techniques that require vacuum is desirable for low cost OPV fabrication and therefore solution-processed NiO<sub>x</sub> is advantageous. However, so far, high performance solar cells using solution processed NiO<sub>x</sub> HTL, often require high annealing temperature [33,35–37]. Stable and efficient polymer solar cells using

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solution processed NiO<sub>x</sub> HTLs have previously been demonstrated by Steirer et al., who thermally annealed a NiO<sub>x</sub> precursor at 300 °C followed by exposure to O<sub>2</sub>-plasma treatment [33]. The study revealed that the O<sub>2</sub>-plasma treatment increased the work function of the NiO<sub>x</sub>, leading to improved device performance compared to solar cells with PEDOT:PSS as HTL. Recently Zhai et al. reported on UV-ozone treatment as a method to produce NiO<sub>x</sub> HTLs at low temperature (<150 °C) [38]. Simultaneous thermal annealing and UV-ozone treatment of a nickel acetate precursor resulted in solar cells that outperformed devices using PEDOT:PSS HTL, mainly due to an increased fill factor (FF). Another way to produce NiO<sub>x</sub> thin films at low temperature or room temperature is to use NiO<sub>x</sub> nanoparticles, as was recently shown by Jiang et al. who achieved improved or comparable performance in polymer solar cells compared to PEDOT:PSS [39].

UV-ozone treatment of oxide surfaces is known to lead to higher work functions [38,40–42]. Here we report on the development of a method to grow NiO<sub>x</sub> films from a nickel formate precursor solution at low temperature (even as low as room temperature) by a post deposition UV-ozone treatment. Using NiO<sub>x</sub> as HTL, improved performance was demonstrated for bulk heterojunction polymer solar cells using poly [2,3-bis-(3-octyloxyphenyl)quinoxaline-5,8-diyl-alt-thiophene-2,5-diyl] (TQ1) [43], mixed with the fullerene derivative [6,6]-phenyl C<sub>71</sub>-butyric acid methyl ester (PC<sub>70</sub>BM).

## 2. Experimental section

### 2.1. Materials

PEDOT:PSS (Clevios P VP Al 4083) was purchased from Heraeus Precious Metals GmbH & Co. KG and filtered through a 0.45 μm nylon filter prior to spin coating. The synthesis of TQ1 is described elsewhere [43]. The number average and weight average molecular weights were M<sub>n</sub> = 34 kg/mol and M<sub>w</sub> = 91 kg/mol, determined by size exclusion chromatography relative to polystyrene standards. PC<sub>70</sub>BM (purity > 99%) was purchased from Solenne BV (The Netherlands). Nickel formate dihydrate (99.9%), anhydrous ethylene glycol (99.8%) and ethylenediamine (>99.5%) were purchased from Alfa Aesar, Sigma-Aldrich and Fluka analytical, respectively. Ortho-dichlorobenzene (oDCB) of analytical grade and 1-chloronaphthalene (CN) of technical grade were purchased from Sigma-Aldrich and used as received.

### 2.2. Preparation of the hole transport layer

Patterned ITO-coated glass substrates (Kintec Company, China) with a 200 nm thick ITO layer and sheet resistivity of 10 Ω sq<sup>-1</sup> were cleaned in isopropanol in an ultrasonic bath and UV-ozone treated for 20 min. For the samples with PEDOT:PSS as the HTL, 50 nm of PEDOT:PSS was deposited by spin coating followed by thermal annealing at 120 °C in a low vacuum oven for 20 min to remove any remaining water. For the NiO<sub>x</sub> HTL deposition, a 37 mg/ml solution of nickel formate dihydrate was prepared in ethylene glycol and ethylene diamine was added such that a 1:2 (mol/mol) nickel formate dihydrate: ethylene diamine molar ratio was obtained. The solution was stirred on a hot plate at 100 °C overnight and then spin coated onto the cleaned ITO substrates at 7000 rpm for 90 s. The ITO/NiO<sub>x</sub> samples were then either given different heat treatments ranging from 100 to 325 °C in ambient air or were kept at room temperature. Some of the ITO/NiO<sub>x</sub> were subsequently exposed to UV-ozone for 3 h using a PSD-UV cleaner (Novascan technologies, USA). Atomic force microscopy (AFM) images of ITO and ITO/NiO<sub>x</sub> films can be found in Figure S1 of the supplementary material. The difference in surface morphology between the bare ITO and the ITO/NiO<sub>x</sub> is not significant, indicating that the NiO<sub>x</sub>

layer is thin and homogenous. The NiO<sub>x</sub> thickness was estimated by AFM by making a scratch in the NiO<sub>x</sub> film and measuring the step height, and by scanning electron microscopy by cleaving the NiO<sub>x</sub>-covered substrate and imaging the cross section. This way, we find the thickness to be in the range of 5–10 nm.

### 2.3. Device fabrication and J-V-characterization

The solar cell structure is glass/ITO/HTL/TQ1:PC<sub>70</sub>BM/LiF/Al. Blend solutions of TQ1:PC<sub>70</sub>BM in a 1:3 weight/weight ratio, at a total concentration of 29 mg/ml, were prepared in oDCB, with the addition of 5% (vol) of CN. The active layer was deposited on the ITO/HTL substrates by spin coating at 500 rpm for 100 s in a protected N<sub>2</sub> atmosphere (<0.1 ppm O<sub>2</sub>, <0.1 ppm H<sub>2</sub>O) inside a glove box (M. Braun Inertgas-Systeme GmbH). The active layer thickness, 100 ± 5 nm, was measured by scanning across a scratch in the film with the tip of an AFM (Nanoscope IIIa Multimode, Veeco Metrology group, now Bruker Corporation). After spin-coating the active layer, the samples were transferred to the vacuum chamber of the thermal evaporator (Univex 350 G, Oerlikon Leybold Vacuum GmbH) integrated in the glove box, where nominally 0.3 nm LiF and 100 nm Al were deposited with a deposition rate of 0.5 Å s<sup>-1</sup> (LiF) and 1 Å s<sup>-1</sup> (Al) at 10<sup>-6</sup> mbar. The active area of the devices was 8 mm<sup>2</sup>. The ITO is patterned and the HTL material covers the entire area, except for the areas where external contact is made to the ITO. The pixels on each substrate share the same ITO electrode, but have individual Al electrodes. The current-voltage characteristics of the solar cells were measured using a Keithley 2636A SourceMeter under illumination from an AM 1.5 solar simulator (Sol2A, model 94022A, Oriel Instruments, USA), with an intensity of 100 mW cm<sup>-2</sup>, determined by a standard silicon photodiode. The solar cells were protected from air by mounting them in a sealed cell before taking them out of the glove box. As a consequence the solar cells were illuminated through the 2 mm thick poly (methyl methacrylate) (PMMA) cover window of the cell. No spectral correction was made for any UV light absorption by the PMMA. No apertures were used for the JV measurements. However, the EQE integrated over the solar spectrum agrees with the J<sub>sc</sub>. When extracting the photovoltaic parameters, the data points were interpolated using a cubic spline.

EQE measurements were performed using a halogen light source (Müller Elektronik-Optik) in conjunction with a monochromator (Zolix Omni-λ 300). The light beam is split with a Y-fiber and the reference arm fitted to a silicon photodiode of known EQE is measured with a Keithley 237 source meter. The other beam is chopped and hits the device, which is placed in an evacuated cryostat. To avoid detection of residual stray light the photocurrent is measured by a lock-in amplifier (Stanford SR830).

### 2.4. Materials characterization

The composition of the NiO<sub>x</sub> layers was studied by X-ray photoelectron spectroscopy (XPS), performed at beamline D1011 of the MAX-IV National Laboratory for Synchrotron Radiation in Lund, Sweden. The photoelectrons were collected in normal emission using a SCIENTA SES200 electron-energy analyzer. All spectra were energy calibrated with respect to the Fermi level measured on a gold surface that had been cleaned in situ by argon sputtering. Survey scans and Ni 2p spectra were acquired using a photon energy of 1000 eV, O 1s spectra using 590 eV. All spectra were normalized to photon flux and a Shirley background was removed from the core-level spectra. Voigt profiles were used for the fitting.

UV–Vis absorption and reflection spectroscopy were performed using a Cary 5000 UV–Vis–NIR spectrophotometer (Agilent Technologies, USA), equipped with an integrating sphere.

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