

## Wet-Chemically Prepared NiO Layers as Hole Transport Layer in the Inverted Organic Solar Cell

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One of the clean alternative energy sources attracting particular attention is solar cells, which can convert the solar light directly to electricity.<sup>1-7</sup> Diverse solar cells have been developed so far, and particularly, organic solar cells (OSCs) have been attracting much attention due to their low cost as well as potential applications in flexible energy conversion devices. OSCs with power conversion efficiency (PCE) of 5-6% have been recently developed by several research groups.<sup>8-10</sup> One of well-known disadvantages of OSCs is its very low stability under atmospheric pressure conditions: the performance of the OSCs can stand only for several days. In order to improve the stability of OSCs, inverted structures of OSCs have been developed.<sup>11-18</sup> In contrast to the conventional structure, in which holes are injected into the transparent conducting electrode (TCE), electrons are directed towards TCE. Inorganic semiconducting materials such as TiO<sub>2</sub> or ZnO deposited on the Indium Tin Oxide (ITO) electrode can be used as buffer layer for accepting electrons, which can also significantly increase the stability of inverted OSCs (IOSCs).

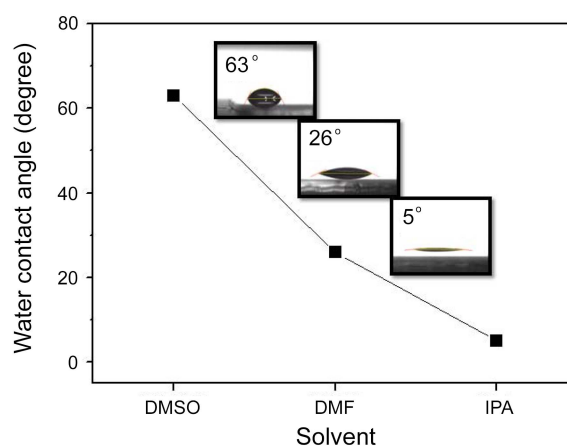
In most of the bulk heterojunction (BHJ) OSCs, poly(4-styrene sulfonate)-doped poly(3,4-ethylenedioxythiophene) (PEDOT:PSS) is widely used as hole transport layers (HTL). PEDOT:PSS can be replaced by *p*-type semiconductors. It has been demonstrated that several metal oxides can show high ability for hole injection in organic light-emitting diodes (OLEDs).<sup>19,20</sup> Recently, *p*-type metal oxide thin film such as V<sub>2</sub>O<sub>5</sub>, MO<sub>3</sub>, and NiO etc. were used as HTL in OSCs.<sup>4,21-27</sup> It should be noted that previous studies mostly used vacuum deposition technique for the fabrication of the metal oxide thin films. In contrast to the previous studies, we aim in obtaining NiO-based IOSCs, with all fabrication step except for the top electrode preparation proceeded under atmospheric conditions and in solutions. Experimental parameters for depositing NiO films using solution-based method have been optimized for obtaining a high efficiency of IOSCs without PEDOT:PSS. We demonstrate that a PCE of 3% can be reached by using solution-based preparation of NiO films, and the photovoltaic performance of this IOSCs is comparable to that of the device consisting of

PEDOT:PSS.

### Experimental Details

IOSCs consisted of a stack of Ag/NiO/P3HT:PCBM/ZnO buffer layer/patterned ITO substrate (10 Ω/cm<sup>2</sup>). For the preparation of ZnO sol-gel solutions zinc acetate [Zn(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O] was dissolved in 2-methoxyethanol solution containing ethanolamine as a stabilizer. Concentration of zinc acetate was 0.75 M. This solution was stirred at 60 °C for 30 min to yield a clear and homogeneous solution, which served as the coating solution. After spin coating of ZnO on ITO-substrate, the films were annealed at 220 °C for 10 minutes.

For the preparation of active layer, a mixture of RR-P3HT (30 mg/mL) and PCBM (21 mg/mL) was dissolved in 1,2-dichlorobenzene under vigorous stirring overnight. Then, this solution was spin-coated on ZnO films deposited on ITO under atmospheric pressure at room temperature. NiO powder with a mean diameter of 50 nm (Reagent-grade chemical) was dissolved in solvents. Three different solvents



**Figure 1.** Contact angles of various solvents (DMF, DMSO, and IPA) on NiO films over active layers (P3HT/PCBM) are displayed. For the preparation of each NiO film, spin-coating with the respective solvent was used with a NiO concentration of  $5 \times 10^{-4}$  M.

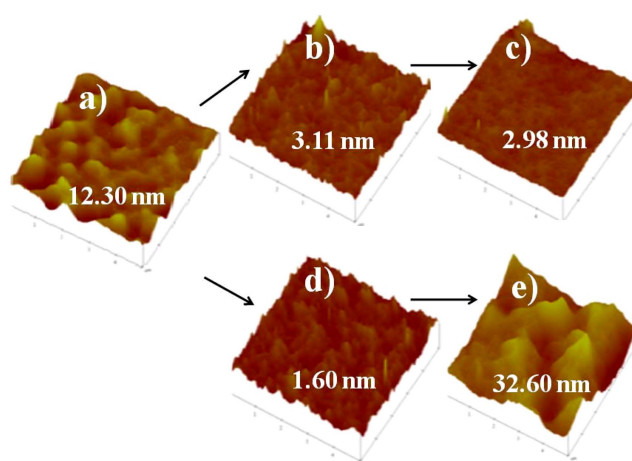
(isopropylalcohol IPA, dimethylsulfoxide DMSO and dimethylformamide DMF) were used for dissolving NiO in the present work as shown in Figure 1. NiO was deposited on top of active layer using spin coating with a rate of 1000 rpm for 1 min. The top electrode (Ag) was deposited by thermal evaporation method with a thickness of 100 nm under  $5 \times 10^{-6}$  torr condition. The active-area of the device with metal mask was  $0.38 \text{ cm}^2$ . The completely fabricated devices were baked at  $150^\circ\text{C}$  for 5 min under air.

The structures of ZnO and NiO films were analyzed by field emission scanning electron microscopy (FE-SEM; JEOL 6000) and atomic force microscopy (AFM, Veeco; MMAFM-2), and their optical properties were measured using UV/Vis transmittance spectrometer (Verian Cary 5000), respectively. The performances of the solar cells were tested using a solar simulator illuminated with a photointensity of AM 1.5,  $100 \text{ mW/cm}^2$ . Contact angle was measured for studying wettability of solvent and NiO.

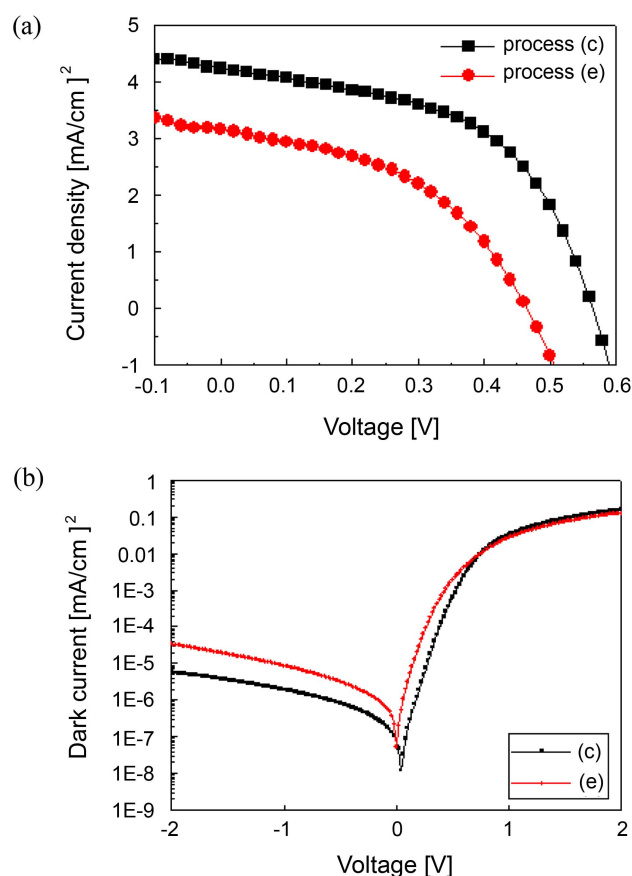
### Results and Discussion

Figures 1 and 2 demonstrate how we have optimized experimental parameters for deposition of NiO films on top of active layers using spin-coating. First, various solvents were used for the preparation of NiO solutions, which were used for spin-coating NiO films, and attempts were made for selecting the best solvent. Figure 1 shows the contact angles of various solvents on NiO films over active layers. NiO films were deposited using spin-coating and for each sample, the respective solvent was used for film deposition. For the NiO film deposition using spin-coating, a NiO-solution of  $5 \times 10^{-4} \text{ M}$  in concentration was used for all three solvents. Among three solvents compared here (DMF, DMSO and IPA), IPA showed the lowest contact angle ( $5^\circ$ ) on NiO, i.e. it is likely that NiO is best dispersed in IPA among three different solvent studied here. Therefore, it is expected that use of IPA should result in the most highly dispersed NiO film structure on active layers. Considering that well-dispersed NiO film on active layers is needed for a better contact between HTL and top electrodes, we suggest that IPA should be used as solvent of NiO. In fact, NiO films prepared using IPA showed a better photovoltaic performance of the IOSC than those with other solvents (DMSO and DMF, data not shown).

Figure 2 shows that annealing temperature can have influence on the surface morphology of NiO films. When active layer was annealed at  $80^\circ\text{C}$ , and NiO was subsequently spin-coated, a relatively smooth surface structure was formed (Fig. 2(b)). In this case, the concentration of NiO-solution using IPA as solvent was  $1 \times 10^{-3} \text{ M}$ . Upon a subsequent annealing of the NiO/active layer structure at  $150^\circ\text{C}$ , the smooth surface structure was still maintained (Fig. 2(c)). When the active layer was annealed at  $150^\circ\text{C}$  prior to NiO deposition, in contrast, post-annealing of NiO film at  $150^\circ\text{C}$  resulted in a higher surface roughness (Fig. 2(e)). In order to prepare highly dispersed NiO films, the active layer should be annealed at  $80^\circ\text{C}$  prior to NiO



**Figure 2.** AFM images of the surfaces of bare active layers and those of NiO on top of the active layers treated under different conditions are compared. For NiO deposition using spin-coating, IPA was used as solvent with a NiO concentration of  $1 \times 10^{-3} \text{ M}$ . (a) The active layers were annealed at  $80^\circ\text{C}$  for 10 min. (b) NiO was deposited on the surface of (a). (c) Sample (b) was annealed at  $150^\circ\text{C}$  for 10 min. (d) Film (a) was annealed at  $150^\circ\text{C}$  for 10 min. (e) Film (d) was annealed at  $80^\circ\text{C}$  for 10 min, and subsequently, NiO film was deposited.



**Figure 3.** (a) The J-V characteristics of devices based on two different NiO films shown in Figure 2(c) and (e) as HTL. (b) Dark currents as a function of voltage are compared for two different devices consisting of NiO layers in Figure 2(c) and (e), respectively.

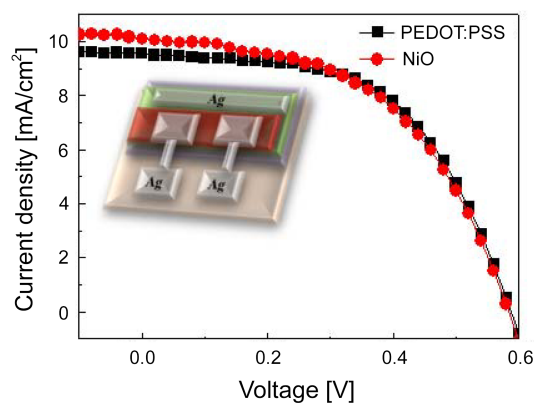
**Table 1.** Photovoltaic performances (PCE, FF,  $V_{oc}$ ,  $J_{sc}$  and  $R_s$ ) for two different devices in Figure 3 are compared.

	PCE (%)	FF (%)	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	$R_s$ (W cm <sup>2</sup> )
(c)	1.24	0.52	0.56	4.24	7.56
(e)	0.66	0.45	0.46	3.16	8.94

deposition.

We constructed IOSCs based on two different NiO films shown in Figure 2(c) and (e) (Fig. 3, Table 1). These two NiO films show much different surface structures with root mean square (RMS) roughness values of 2.98 and 32.60 nm, respectively, which were determined by AFM. For the devices shown in Figure 3, the thickness of active layers (P3HT/PCBM) was 370 nm. When the smoother NiO surface was used for constructing the IOSC, PCE of 1.24% could be reached, whereas the rougher NiO film resulted in a PCE value of only 0.66%. This result implies that a lower roughness of NiO is essential for obtaining a better photovoltaic performance. Fill-factor (FF), open-circuit voltage ( $V_{oc}$ ), short-circuit current ( $J_{sc}$ ) of the device with a lower roughness of NiO were all higher than the respective values of the device consisting of a NiO film with a higher surface roughness. In Figure 3(b), and Table 1, it is also shown that the dark current and series resistance of the IOSC with a smoother NiO are lower than those of the device with a rougher NiO film surface, leading to increase in FF and  $V_{oc}$  values.

We have made efforts for improving the device efficiency using NiO as HTL by varying thickness of active layers. When the thickness of active layers was 500 nm, a PCE of 3.01% could be obtained. Increase in the active layer thickness can enhance the absorption of photon, resulting in increased  $J_{sc}$  value. For this device, FF,  $V_{oc}$ , and  $J_{sc}$  were 51%, 0.58 V, and 10.07 mA/cm<sup>2</sup>, respectively. It is worth mentioning that further increase in the active layer thickness can decrease the PCE, since for example, the diffusion length of the exciton is limited. Since photon absorption of active layers is dependent of electrode materials, the thickness of the active layer should be optimized for each device.

**Figure 4.** The J-V characteristics of inverted organic solar cells using PEDOT:PSS and NiO as hole transporting layers, respectively, are compared.**Table 2.** Photovoltaic performances (PCE, FF,  $V_{oc}$ ,  $J_{sc}$  and  $R_s$ ) for two different IOSCs with PEDOT:PSS and NiO as HTL in Figure 4 are compared

	PCE (%)	FF (%)	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )
PEDOT:PSS	3.11	55	0.58	9.54
NiO	3.01	51	0.58	10.07

The photovoltaic performance of the NiO-based device was shown to be comparable to the IOSC using PEDOT:PSS, as shown in Figure 4 and Table 2. The PCE of the NiO-based device was lower than that of the device using PEDOT:PSS only by 0.1%, and regarding the  $J_{sc}$  value, the NiO-based solar cell was superior to the conventional solar cell consisting of PEDOT:PSS.

### Summary

We have demonstrated that solution-based fabrication of NiO films as HTL can be used for the construction of IOSCs. Type of solvent of NiO-solution, and annealing procedure of the active layers were optimized for obtaining a PCE of 3% of IOSC. The photovoltaic performance of NiO-based device is comparable to that of the same type of solar cell using PEDOT:PSS instead of NiO. These solution-based processes can be a promising method for a mass production OSCs under ambient condition.

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