# The Roles of Different NiO Compact Blocking Layers in P-type Sensitized Solar Cells

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**Abstract**— Compact blocking layers made of wide band gap semiconductors, such as $TiO_2$, ZnO, are widely used to suppress recombination at the conductive FTO substrate/electrolyte interface in dye or quantum dot sensitized solar cells, especially in the solid-state devices. Though sharing similar mechanism, blocking layers in p-type sensitized solar cells are rarely studied. Our recent works have demonstrated that the compact NiO films dependent upon the preparation ways play important roles in both p-type dye and quantum dots sensitized solar cells. In p-type dye sensitized NiO solar cell, the compact NiO layer prepared by spin-coating of a sol-gel film, can prevent the recombination at the FTO glass/electrolyte interface and retard the whole cell's recombination kinetics. Therefore, the fill factor and photovoltage can be increased, leading to a 40.77% improved performance of p-type solar cell. In p-type organometal halide perovskite sensitized mesoporous NiO solar cell, it is found that only the spray pyrolysis deposited NiO dense film is effective for selective hole gathering, rather not the sol-gel deposited NiO dense film. The difference may be ascribed to their coverage status on the rough FTO glasses. The existence of such a NiO block layer not only effects on the cell performance but also determines the current flow direction in the p-type perovskite sensitized NiO solar cell.

## 1. INTRODUCTION

Most of the reported dye or quantum dots sensitized solar cells are based on n-type mesoporous semiconductors like nanocrystalline $TiO_2$, which we can call n-type sensitized solar cells. Their efficiency record moves very slowly in recent years [1, 2]. Efforts to make efficient p-type sensitized solar cells as the important supplementary to conventional n-type sensitized solar cells have attracted growing interests, because it provides a possible solution to break through the efficiency bottleneck by combining them to build pn tandem cell [3–5]. To suppress interfacial recombination is important for high efficiency p-type solar cell. One approach is to build an electron barrier at the conductive FTO substrate/electrolyte interface [6]. The cell configuration for such p-type sensitized solar cells is illustrated in Figure 1. NiO thin film is used as blocking layer because of its wide band gap, suitable valance band position and chemical stability [7].

In this paper, we report two methods to prepare compact NiO thin films as the compact blocking layers. One was made by spin-coating (SC) and the other was accomplished by spray pyrolysis (SP). There is a big morphology difference between the two kind NiO films. It's found that the SC deposited NiO blocking layer plays a critical role in p-type dye sensitized solar cell on enhancing open-circuit voltage ($V_{oc}$) and short-circuit current density ($J_{sc}$); while the SP deposited NiO blocking layer plays a critical role on determining the current flow direction of p-type perovskite sensitized NiO solar cell.

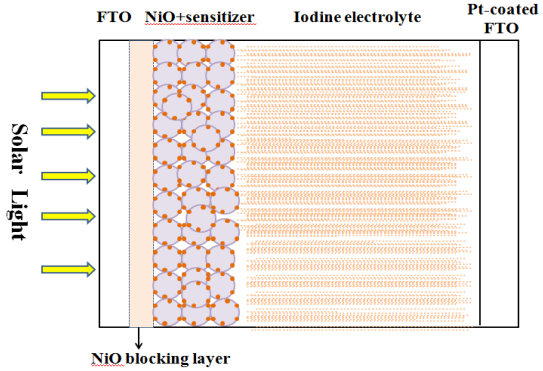


Figure 1: Schematic diagram of the DSSC with a NiO blocking layer.

## 2. EXPERIMENTAL SECTION

Compact NiO thin film preparation.

Compact film 1 made by spin-coating: 0.5 M Nickel acetate tetrahydrate in 2-methoxyethanol was used as the so-gel precursor for deposition, which was subsequent deposited on cleaned FTO glass by spin coating at the speed of 2000 rpm for 30 seconds. Finally, the film was sintered at 550°C for 3 h [8].

Compact film 2 prepared by spray pyrolysis: 0.04 M nickel acetylacetonate in acetonitrile was spray pyrolysed on FTO glass at 500°C by using an air nozzle. After that, the film was further sintered at 500°C for 30 minutes [6].

## 3. RESULTS AND DISCUSSION

As the SEM image in Figure 2 clearly shown, the morphology of SC deposited NiO compact film is different from SP deposited NiO compact film. For the SP deposited film, an ultrathin layer of NiO fully covers the turreted FTO microcrystals without changing the FTO surface roughness (Figures 2(a)–(c)). In contrast, the SC deposited film (Figure 2(d)) leads to a flat the NiO capture surface, concaves between the turreted FTO microcrystals have been filled by sol-gel NiO. However, such kind compact layer has a lot of sub-micron pin-holes inside due to volume shrinking during evaporation and sintering procedures.

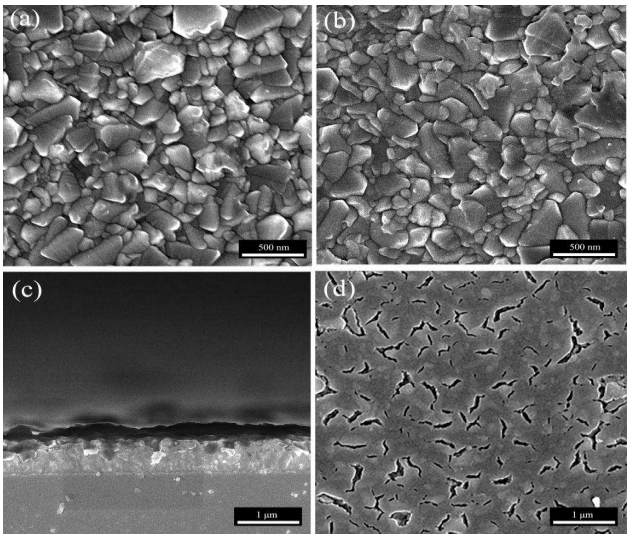


Figure 2: SEM images of (a) bare FTO substrate; (b) NiO film made by SP on FTO surface substrate and (c) its cross cross-section view; (d) NiO film made by SC on FTO substrate.

Figure 3(a) clearly depicts the performance difference between the p-type "P1 dye" sensitized NiO solar cells with and without SC deposited NiO blocking layer. By introducing such a blocking layer, the solar cell's $V_{oc}$, $J_{sc}$ and fill factor (FF) are all improved, which in total results in a 40.77% higher solar conversion efficiency in comparison to the solar cell without blocking layer as clearly shown in Table 1. The inherent reason for such improvements should be ascribed to the recombination suppression at the FTO glass/electrolyte interface. The transient photovoltage decay curves in Figure 3(b) strongly support this point. The lifetimes, quoted as the time taken to reach 1/e of the initial photovoltage, are 8.9 ms and 2.9 ms respectively for the solar cells with and without the blocking layer. The results suggest that the whole solar cell's recombination kinetics is significantly retarded by the FTO surface passivation, which highlights the importance of such blocking layer.

Figure 4 compares the CH3NH3PbI3 perovskite sensitized mesoporous NiO solar cells with and without the SP coated compact NiO blocking layer. We previously found that the SC coated blocking layer cannot work in the perovskite sensitized solar cell system, which might be due to the pin-holes, leading to short circuit contacts between perovskite and FTO. In such a case, the solar cell works as a n-type cell, just like the J-V curve of the solar cell without compact NiO blocking layer (Figure 4(a)). The current flow direction is the same as that of the conventional n-type dye or quantum dots sensitized $TiO_2$ solar cells. What the FTO substrate gathers is the photon-induced

Table 1: Performance of NiO DSSC with and without blocking layer.

| | $V_{oc}$ (mv) | $J_{sc}$ (mA/cm$^2$) | FF | $\eta$ |
|---|---|---|---|---|
| NiO blocking layer | 81.54 | 4.16 | 32.36 | 0.107 |
| Without blocking layer | 65.37 | 3.82 | 31.24 | 0.076 |

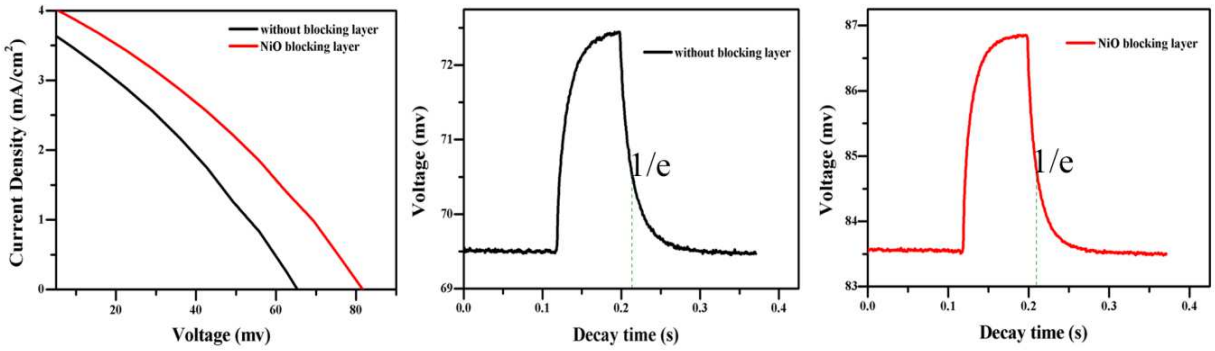


Figure 3: (a) J-V curve of NiO DSSC with and without blocking layer; (b) and (c) open-circuit voltage decay curves of DSSC fabricated with and without blocking layer.

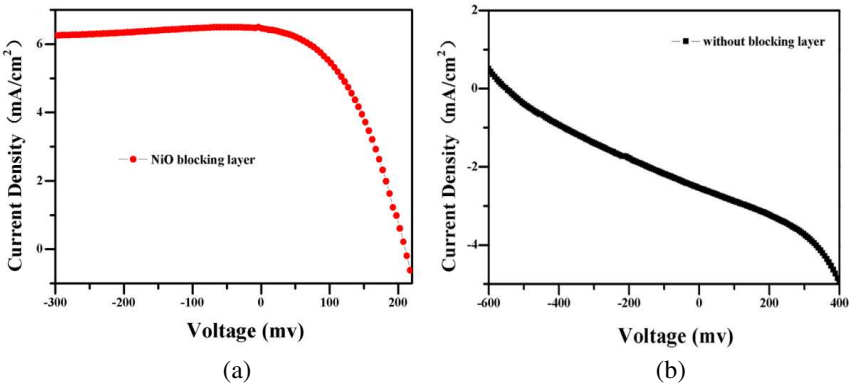


Figure 4: *J-V* curves of the perovskite sensitized NiO solar cells with (a) and (b) without a SP coated NiO blocking layer.

electrons transfer though the perovskites not the holes transfer from the mesoporous NiO network. If a SP coated NiO blocking layer is added, the current flow will be p-type like, namely, the front FTO glass will collect the photoinjected holes. This comparison strongly highlights the important role of the SP coated blocking layer in determining the current flow direction in perovskite sensitized NiO solar cell. The morphology of the NiO compact layer is very important for the blocking effect.

## 4. CONCLUSIONS

Compact nickel oxide thin films on FTO glass have been successfully fabricated by spray pyrolysis and spin coating methods. SEM characterizaiton shows that the morphologies are different between SP and SC coated compact films. Compact NiO blocking layers are essential for p-type dye or perovskite sensitized solar cells. Not only do they play the roles as electron barriers but also boost the cell performance.

## ACKNOWLEDGMENT

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