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## Solid state p-type dye sensitized NiO–dye–TiO<sub>2</sub> core–shell solar cells†

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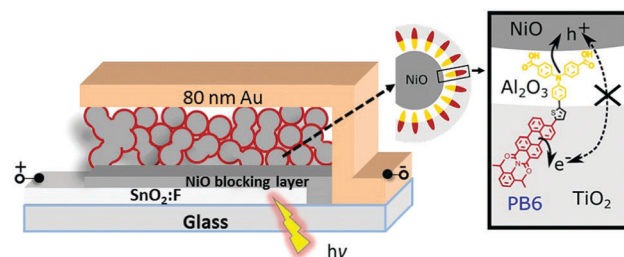
**Solid state p-type dye sensitized NiO–dye–TiO<sub>2</sub> core–shell solar cells with an organic dye PB6 were successfully fabricated for the first time. With Al<sub>2</sub>O<sub>3</sub> as an inner barrier layer, the recombination process between injected holes in NiO and injected electrons in TiO<sub>2</sub> was significantly suppressed and the charge transport time was also improved.**

p-Type dye sensitized solar cells (p-DSCs) have attracted intense interest due to their different charge transfer kinetics with respect to more common studied n-DSCs,<sup>1–3</sup> and the potential application in tandem solar cells<sup>4–6</sup> and solar fuel devices.<sup>7–9</sup> The conventional p-DSCs are based on liquid redox electrolytes. To avoid having a liquid phase in the p-DSCs, we have recently proposed and proven the concept of solid state p-DSCs, in which a solid state phenyl-C61-butyric acid methyl ester (PCBM) was used as an electron transport material (ETM) between the dye sensitized photocathode and the back contact.<sup>10</sup> Optimization of photosensitizer represents one strategy to improve the performance of this kind of solar cells.<sup>11,12</sup> Inspired by the conventional dye sensitized TiO<sub>2</sub> solar cells, we proposed that TiO<sub>2</sub> should be an alternative ETM to PCBM due to the fast electron injection from dyes into TiO<sub>2</sub><sup>13,14</sup> and good electron transport property.<sup>15</sup> Thus, we recently fabricated a dye sensitized NiO–dye–TiO<sub>2</sub> core–shell film and, in contrast to previous work,<sup>16–18</sup> the nanoporous NiO film was first sensitized with the dye and a TiO<sub>2</sub> coating was applied afterwards. This dye sensitized core–shell film showed ultrafast hole ( $t_{1/2} < 120$  fs) and electron injection into NiO and TiO<sub>2</sub> respectively, resulting in ultrafast dye regeneration upon electron injection,  $t_{1/2} \leq 500$  fs.<sup>19</sup> In the present work, we proved that the dye sensitized NiO–dye–TiO<sub>2</sub> core–shell mesoporous film can be used for fabrication of solid

state p-type dye sensitized solar cells. We also show the effect of an Al<sub>2</sub>O<sub>3</sub> inner barrier layer between NiO and TiO<sub>2</sub> on the performance of solar cell.

Fig. 1 shows the configuration and working principle of the proposed p-type dye sensitized NiO–dye–TiO<sub>2</sub> core–shell solar cells. The donor– $\pi$ –acceptor dye PB6 was utilized as photosensitizer since its reduction/oxidation potentials in excited state match with the valence band of NiO and conduction band of TiO<sub>2</sub>.<sup>19</sup>

The fabrication of the photoelectrode used in this study can be described briefly as follows. A compact NiO layer (60 nm) was sputtered onto a FTO substrate, then a mesoporous NiO layer (1.3  $\mu$ m) was prepared by doctor-blading NiCl<sub>2</sub> gel on FTO glass and sintered at 450 °C for 0.5 h.<sup>20</sup> Subsequently, the NiO electrode was immersed into 0.2 mM PB6 dichloromethane (DCM) solution overnight. The dye loading in the film was determined to be 31.6 nmol cm<sup>–2</sup> by desorption experiment (see ESI†). After rinsing with methanol, the dye sensitized NiO film was dried and coated with metal oxides by atomic layer deposition (ALD). For NiO–PB6–TiO<sub>2</sub> photoelectrode, ca. 10 nm TiO<sub>2</sub> layer was coated directly on a dye sensitized NiO film. Because an insulating Al<sub>2</sub>O<sub>3</sub> layer has been proved to be an effective barrier to suppress charge recombination process in DSCs,<sup>21–24</sup> an 1 nm inner Al<sub>2</sub>O<sub>3</sub> layer was introduced by ALD on the dye sensitized NiO film, followed by deposition of ca. 10 nm TiO<sub>2</sub> coating to form NiO–PB6–Al<sub>2</sub>O<sub>3</sub>–TiO<sub>2</sub> photoelectrode.



**Fig. 1** The configuration and working principle of the p-type dye sensitized NiO–dye–TiO<sub>2</sub> core–shell solar cell, NiO–PB6–Al<sub>2</sub>O<sub>3</sub>–TiO<sub>2</sub>, with Al<sub>2</sub>O<sub>3</sub> as an inner barrier layer and PB6 dye as photosensitizer.

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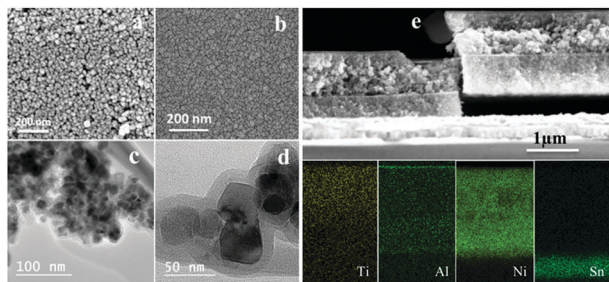


Fig. 2 SEM and TEM figures of the **NiO-PB6-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>** sample. (a and b) SEM surface images before and after ALD; (c and d) TEM images in different magnification; (e) SEM image in the cross section and the corresponding EDX element mapping analysis.

In addition, we prepared two reference samples without dye sensitization, denoted **NiO-TiO<sub>2</sub>** and **NiO-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>**, respectively, to exclude the potential photovoltaic performance from the excitation of the p-n junction formed at the interface of NiO and TiO<sub>2</sub>.

In previous work, we have shown that the TiO<sub>2</sub> layer penetrated into the dye sensitized mesoporous NiO electrode. In order to monitor the penetration of Al<sub>2</sub>O<sub>3</sub> into the dye sensitized mesoporous NiO electrode, as well as TiO<sub>2</sub> into the Al<sub>2</sub>O<sub>3</sub> coated electrode afterwards, the morphology of **NiO-PB6-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>** photoelectrode with 1 nm Al<sub>2</sub>O<sub>3</sub> (calculated from the average ALD deposition rate from multi-cycles) was characterized by SEM and TEM (Fig. 2). A more compact surface (Fig. 2b) was observed after subsequent ALD of Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> compared to the mesoporous dye sensitized NiO film (Fig. 2a). From TEM images in Fig. 2c and d, one can note that NiO nanoparticles are coated by a conformal layer, which is assigned to TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> layers. From EDX elements analysis images of the cross section of the electrode, the presence of Al and Ti inside the NiO mesoporous layer was confirmed, signifying that Al<sub>2</sub>O<sub>3</sub> can penetrate into the mesoporous NiO film and that the thin Al<sub>2</sub>O<sub>3</sub> layer does not block the TiO<sub>2</sub> penetration.

In order to confirm the potential application of these core-shell photocathodes in solar cells, an 80 nm Au layer was thermally evaporated on the top of these electrodes as back contact to complete the solar cell. The performance of such solar cells was characterized under AM 1.5 G illumination with light intensity of 100 mW cm<sup>-2</sup> and the *J-V* curves are shown in Fig. 3a. A short-circuit current density (*J*<sub>sc</sub>) of 12 μA cm<sup>-2</sup> and an open-circuit voltage (*V*<sub>oc</sub>) of 0.40 V were obtained in **NiO-PB6-TiO<sub>2</sub>** solar cell. The device based on **NiO-TiO<sub>2</sub>** film without PB6 dye was also fabricated and showed photovoltaic effect, resulting from the p-n junction of **NiO-TiO<sub>2</sub>** due to the direct contact between NiO and TiO<sub>2</sub>. From Incident Photon-to-Current Efficiency (IPCE) spectra (Fig. 3b), we can note that the PB6 dye in **NiO-PB6-TiO<sub>2</sub>** solar cell has light response in wavelength from 480 nm to 700 nm, which is in agreement with the dye absorption spectrum (Fig. S2, ESI†), proving that the photocurrent is generated by dye. IPCE curve of the **NiO-TiO<sub>2</sub>** solar cell abruptly decreases to zero at wavelengths higher than 500 nm (2.48 eV), and only small part of the visible light can be converted into photocurrent in these solar cells. By using 1 nm Al<sub>2</sub>O<sub>3</sub> to coat NiO, the **NiO-TiO<sub>2</sub>** p-n junction structure in **NiO-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>** was inhibited and the solar cell did

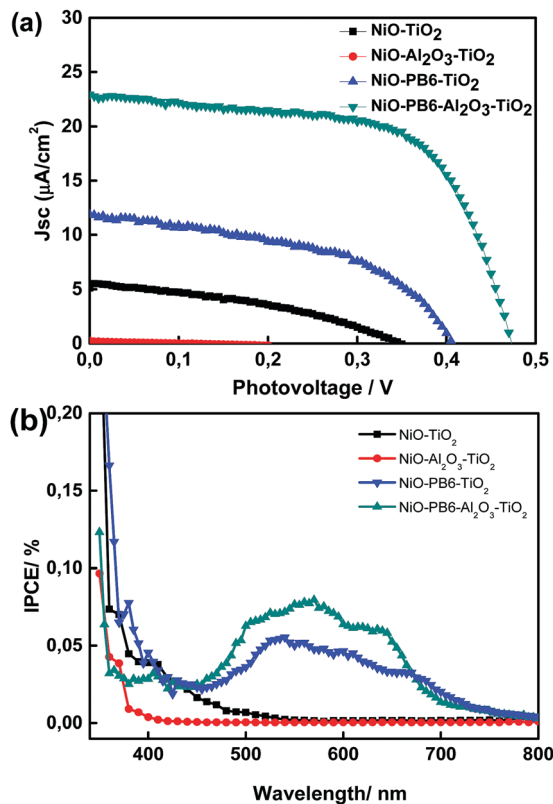


Fig. 3 *J-V* curves and IPCE of different dye sensitized p-type core-shell solar cells and reference solar cells.

not render any distinguishable photocurrent from *J-V* and IPCE characterization (see Fig. 3a and b). The same strategy was adopted in a **NiO-PB6-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>** solar cell, in which Al<sub>2</sub>O<sub>3</sub> could also act as a blocking layer to suppress the charge recombination between injected holes from dye in NiO and injected electrons from dye in TiO<sub>2</sub>. As the molecular extension of the PB6 dye was estimated to be *ca.* 2.5 nm, a 1 nm Al<sub>2</sub>O<sub>3</sub> layer should not completely cover the electron donor unit of the PB6 dye, assuming the standing dye configuration on the metal oxide surface. It should provide an opportunity for the TiO<sub>2</sub> layer to fully cover the dye acceptor unit and collect the electrons. Noticeably, the photovoltaic performance of the **NiO-PB6-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>** solar cell was significantly improved compared to the device without Al<sub>2</sub>O<sub>3</sub>, showing a *J*<sub>sc</sub> of 23 μA cm<sup>-2</sup> and a *V*<sub>oc</sub> of 0.48 V, and higher IPCE values in visible region. Meanwhile, a fill factor (FF) of 66% was achieved in the **NiO-PB6-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>** solar cell, which is the highest FF reported<sup>3</sup> in p-type DSCs to our best knowledge (Table S1, ESI†).

To further elucidate the electron and hole injection in **NiO-PB6-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>** electrode, femtosecond transient absorption spectroscopy was carried out (Fig. S3, ESI†). A pronounced Stark effect was observed upon light excitation, resulting from dye regeneration after hole and electron injection from dye into NiO and TiO<sub>2</sub> respectively. The dye regeneration time in **NiO-PB6-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>** is *t*<sub>1/2</sub> ≤ 500 fs. These are consistent with our previous study of **NiO-PB6-TiO<sub>2</sub>**,<sup>19</sup> signifying that the Al<sub>2</sub>O<sub>3</sub> layer essentially did not affect the dye regeneration rate. Meanwhile, the same kinetic behaviour as **NiO-PB6** reported



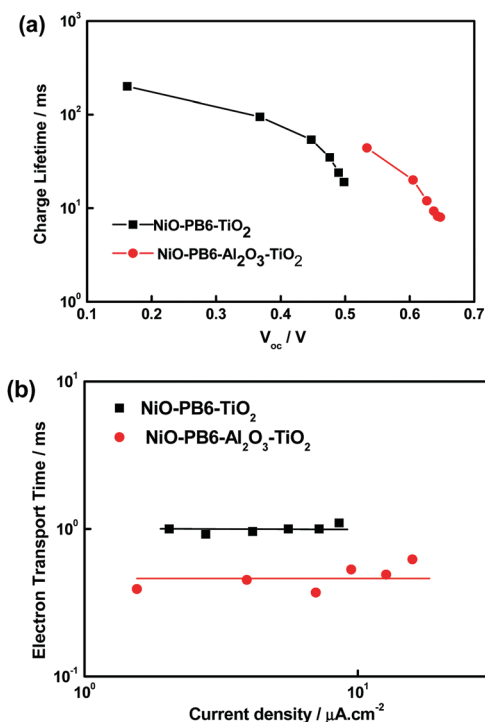


Fig. 4 Electron lifetime as a function of  $V_{oc}$  and transport time as a function of photocurrent density of **NiO-PB6-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>** and **NiO-PB6-TiO<sub>2</sub>**.

in our previous study<sup>19</sup> was found in **NiO-PB6-Al<sub>2</sub>O<sub>3</sub>** (Fig. S4, ESI<sup>†</sup>), further confirming that the Al<sub>2</sub>O<sub>3</sub> layer did not significantly influence hole injection.

In order to gain insight into the effect of the Al<sub>2</sub>O<sub>3</sub> layer on the charge recombination process in solar cells, charge lifetimes as a function of  $V_{oc}$  of the solar cells were measured (Fig. 4a). It shows that **NiO-PB6-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>** solar cell has longer charge lifetime than **NiO-PB6-TiO<sub>2</sub>** solar cell at a given  $V_{oc}$  value. From charge extraction experiments (Fig. S5, ESI<sup>†</sup>), two types of solar cells show almost identical extracted charges at a specific  $V_{oc}$ , implying that the Al<sub>2</sub>O<sub>3</sub> layer does not influence the energy band position in either NiO or ALD TiO<sub>2</sub>. These results suggest that the Al<sub>2</sub>O<sub>3</sub> layer indeed plays the role of an inner barrier layer in suppressing charge recombination between NiO and TiO<sub>2</sub>, thus contributing to the enhanced  $V_{oc}$  and increased  $J_{sc}$ .

Interestingly, the charge transport time (Fig. 4b) of the **NiO-PB6-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>** solar cell is shorter than that of the **NiO-PB6-TiO<sub>2</sub>** solar cell. We suggest that the TiO<sub>2</sub> formed in the presence of Al<sub>2</sub>O<sub>3</sub> is more compact due to the more hydrophilic properties after ALD Al<sub>2</sub>O<sub>3</sub> (the existence of -OH units on the ALD Al<sub>2</sub>O<sub>3</sub> surface). TiO<sub>2</sub> of better quality is expected to be grown on the more hydrophilic surface during ALD in contrast to the NiO surface sensitized with an organic dye,<sup>25</sup> although the amorphous structure in both samples is confirmed by TEM. The shorter charge transport time in **NiO-PB6-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>** solar cell should be responsible for higher  $J_{sc}$  and higher fill factor as compared to the **NiO-PB6-TiO<sub>2</sub>** solar cell. Notably, the charge transport times of both types of solar cells are almost independent of the photocurrent (light intensity), which is unusual for the conventional n-type and p-type DSCs.<sup>26,27</sup>

One possible explanation is that the TiO<sub>2</sub> phase is not continuous inside the mesoporous NiO film (1.3 μm), resulting in that only a very thin NiO film coated by ALD TiO<sub>2</sub> works for the charge collection. Another explanation would be that holes and/or electrons transferred *via* the semiconductor surfaces.<sup>28</sup> The former one can also be applied to explain why the photocurrent is much lower than the conventional p-DSCs, although the dye regeneration in the core-shell solar cell is much faster<sup>19</sup> and the charge lifetime is comparable to those p-DSCs.<sup>26,29</sup> Therefore, making continuous TiO<sub>2</sub> layer or increasing the pore-filling of TiO<sub>2</sub> inside mesoporous NiO could be a reasonable strategy to significantly improve the efficiency of such solar cells.

As mentioned above, the length of PB6 dye is *ca.* 2.5 nm, which provides us an opportunity to study the effect of the thickness of Al<sub>2</sub>O<sub>3</sub> on the performance of the solar cells. In principle, a too thin Al<sub>2</sub>O<sub>3</sub> layer cannot effectively suppress charge recombination loss and render unsatisfactory performance. Conversely, a too thick Al<sub>2</sub>O<sub>3</sub> layer could completely bury the dye and the TiO<sub>2</sub> cannot sufficiently contact with the acceptor of the dye, which will induce unsatisfactory performance as well due to low regeneration efficiencies. There should be an optimal thickness of Al<sub>2</sub>O<sub>3</sub> giving an optimized performance. Different thicknesses of Al<sub>2</sub>O<sub>3</sub> (0.08, 0.5, 1, 2 and 10 nm) were therefore investigated in **NiO-PB6-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>** solar cells. From Fig. 5, *ca.* 1 nm of Al<sub>2</sub>O<sub>3</sub> was proven to be the optimal thickness, because it only covers the entire electron donating unit, triphenylamine (TPA) of PB6, and allows the whole electron acceptor part (perylene monoimide (PMI)) buried inside TiO<sub>2</sub>, which is expected to be the optimal configuration for charge separation between dye and semiconductors.

With the Al<sub>2</sub>O<sub>3</sub> layer thinner than 1 nm, less photocurrent and photovoltage was observed, implying more extensive recombination in these devices. With 2 nm Al<sub>2</sub>O<sub>3</sub> film, the photocurrent from the corresponding device also significantly decreased, suggesting that the charge separation probably is inefficient. The hypothesis can be further supported from the results utilizing a 10 nm Al<sub>2</sub>O<sub>3</sub> layer, resulting in solar cells without any obvious photocurrent likely to be caused by the absence of contact between dye and TiO<sub>2</sub>.

In summary, solid state p-type dye-sensitized NiO-dye-TiO<sub>2</sub> core-shell solar cells have been proposed and fabricated for the first time, in which the NiO is sensitized by the organic PB6 dye, after which a TiO<sub>2</sub> layer is deposited by ALD to form the dye sensitized NiO-dye-TiO<sub>2</sub> core-shell structure. By inserting a thin insulating Al<sub>2</sub>O<sub>3</sub> layer, the charge recombination between NiO and TiO<sub>2</sub> after charge injection from dye was significantly retarded. On the basis of the molecular extension of dye, the effect of Al<sub>2</sub>O<sub>3</sub> layer thickness on the solar cell performance was further investigated, showing an optimal thickness of *ca.* 1 nm for the PB6-based devices. The optimal Al<sub>2</sub>O<sub>3</sub> thickness should be different from different dyes, which encourages us to apply the strategy on other dye systems in future study. Furthermore, other n-type metal oxides can be considered as electron transport materials instead of TiO<sub>2</sub> in the core-shell solar cells. This type of solar cell holds the potential to rival conventional liquid p-type dye sensitized solar cells after systematic studies and



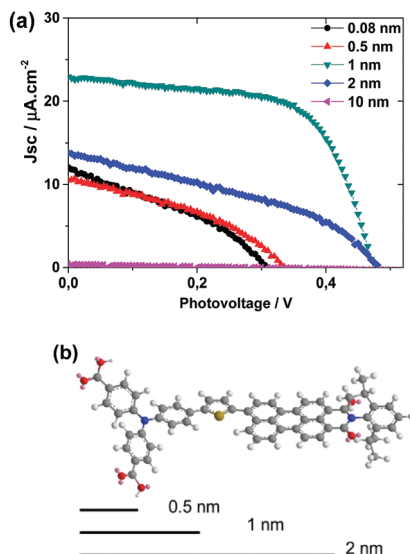


Fig. 5 (a)  $J$ - $V$  curves for  $\text{NiO-PB6-Al}_2\text{O}_3\text{-TiO}_2$  solar cells with different  $\text{Al}_2\text{O}_3$  thickness layers; (b) the 3-D molecular structure of PB6 with 0.5 nm, 1 nm and 2 nm length scales for comparison.

optimization of different components, and may show potential for application in solar fuel devices as well.

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## Conflicts of interest

The authors declare no competing financial interests.

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