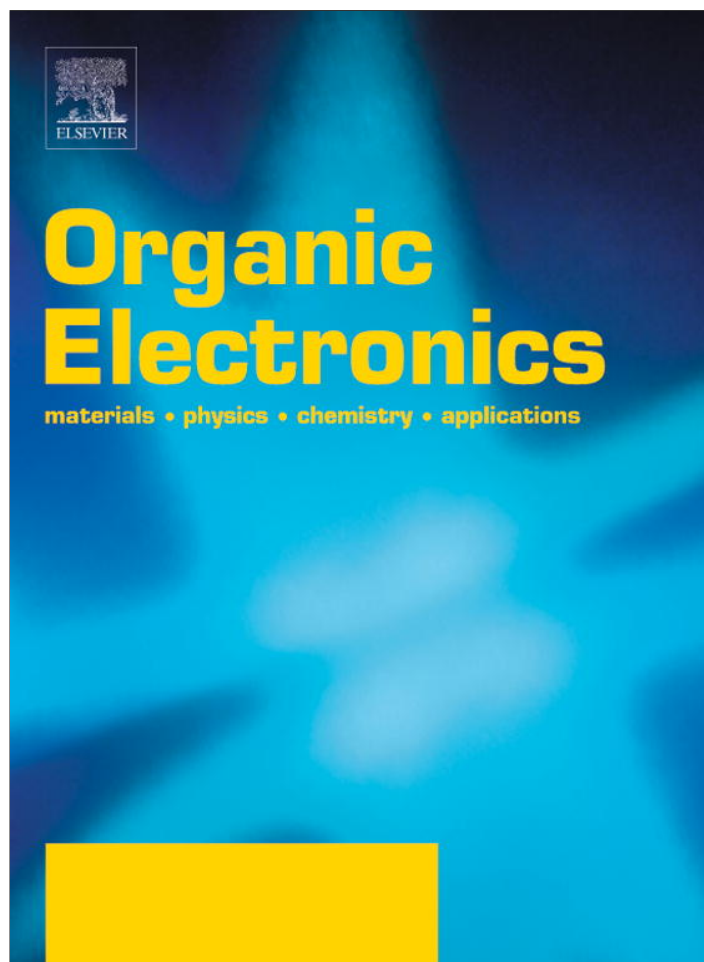




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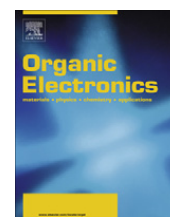
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# Organic Electronics

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## Large-area, high-quality self-assembly electron transport layer for organic optoelectronic devices

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### ABSTRACT

We propose a self-assembly method for forming large-area high-quality solution-processed titanium oxide (TiO<sub>2</sub>) films as efficient electron transport layer for organic solar cells. The self-assembled solution-processed TiO<sub>2</sub> layers are highly ordered and significantly improved in surface morphology over commonly-used spin-coating process resulting in better charge collection and significant material saving. When incorporated into polymer solar cells, the TiO<sub>2</sub> device shows enhanced performance. Furthermore, we demonstrate the TiO<sub>2</sub> can form large-area films, and achieve very uniform and improved device performances. Consequently, the self-assembled TiO<sub>2</sub> films can be efficient and low-cost electron transport layer potentially for large-area organic optoelectronics.

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### 1. Introduction

One of the essential aspects in designing efficient and stable organic optoelectronic devices such as organic light emitting diodes and solar cells is the engineering of interface carrier transport layers between the active layer and electrodes. Among various materials available for interface layers, inorganic transition metal oxides can be used to form good transport layers for organic devices with their wide range of energy-aligning capabilities [1]. They can be used to form low resistive and ohmic contact to improve the power conversion efficiencies (PCEs) of organic solar cells [2]. Metal oxides such as MoO<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, and WO<sub>3</sub> are good hole injection materials [3–6], whereas ones such as TiO<sub>2</sub> and ZnO are good electron injection materials [7,8]. Another attractive merit of transition metal oxides compared to other kinds of carrier transport layers, such as poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) and Ca, are their stability which can improve the lifetime of organic electronics [9–11].

Here, we propose a self-assembly and solution-processed method to fabricate an electron transport layer by titanium oxide (TiO<sub>2</sub>) nanoparticles to simultaneously achieve the film features of good uniformity, homogeneity, and electron transport properties as well as capable for large-area applications. Distinguished from conventional spin-coating process, our approach imposes good control on the evaporation rate of the solvent, which allows TiO<sub>2</sub> nanoparticles to undergo a slow self-assembly process, and yet our method can save a lot of materials for film formation. Investigation of surface morphology by scanning electron microscope (SEM) and atomic force microscopy (AFM) indicates that TiO<sub>2</sub> films with ordered and uniform TiO<sub>2</sub> nanocrystals are formed during the self-assembly process. To demonstrate that the self-assembly method are capable of large-area applications, we make self-assembled TiO<sub>2</sub> films with size of 4" × 4" on ITO glass substrates. Device studies with TiO<sub>2</sub> as electron transport layers in inverted polymer solar cells (PSCs) demonstrate that the self-assembly approach can lead to enhanced electron collection compared with films deposited from spin-coating (average PCE improved from 3.65% to 4.03%), while being cost-effective as the deposited material is fully utilized.

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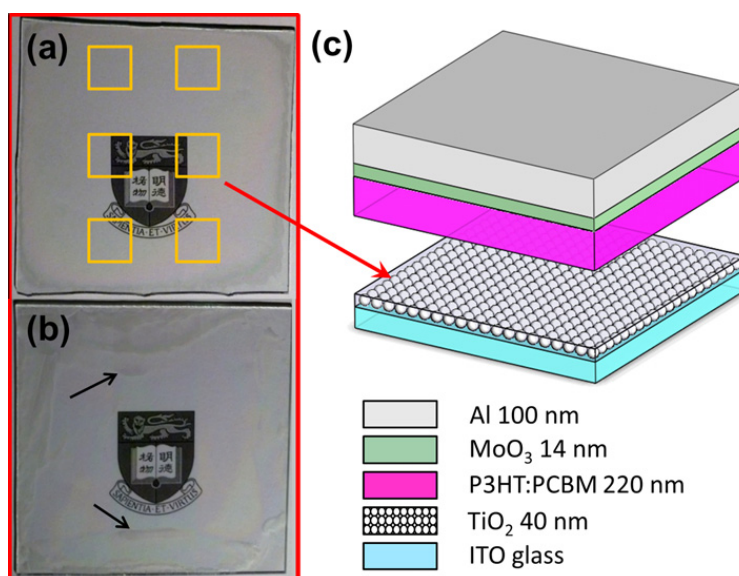


**Fig. 1.** (a) Large-area 4'' × 4'' self-assembled TiO<sub>2</sub> film. The marked regions are extracted and utilized in TiO<sub>2</sub> PSC devices. (b) TiO<sub>2</sub> film of the same size fabricated without controlling the solvent evaporation and defects can be found on the film as indicated by the black arrows. (c) Schematic diagram of inverted PSCs with TiO<sub>2</sub> as electron transport layer.

For the aforementioned large-area 4'' × 4'' self-assembled TiO<sub>2</sub> film, we utilize different regions of the film to fabricate PSC devices. These self-assembled devices are found to have similar improvement in device performance as well, and have good uniformity (average PCE of  $3.91 \pm 0.1\%$ ). The method introduced here is efficient, applicable to large area, and easily controlled and implemented, therefore can be advantageous for low-cost and high-throughput applications.

## 2. Experimental

The ligand free TiO<sub>2</sub> crystals are synthesized by a non-aqueous method [12] (Transmission electron microscopy (TEM) and powder X-ray Diffraction (XRD) images shown in Fig. 2(a) and (b), respectively). The anatase TiO<sub>2</sub> nanoparticles are about 4 nm in size and strategically dispersed in ethanol solution (as described later). For our self-assembly method, TiO<sub>2</sub> solution is cast onto the desired substrate without spin-coating. The substrate is then quickly covered

by a small petri dish. The solution on the substrate then spreads to cover the substrate. The evaporation rate of the solvent is controlled within the petri dish. The whole self-assembly process takes about 30 min. After the self-assembly process, the TiO<sub>2</sub> films are annealed at 150 °C for 10 min on a hot plate in air.

After making large-area 4'' × 4'' self-assembled TiO<sub>2</sub> film on patterned ITO substrate, we cut the substrate into smaller TiO<sub>2</sub> films for our PSC fabrication. Different regions of the large-area self-assembled film are utilized into PSC devices (as indicated in Fig. 1(a)) and characterized for device performance.

## 3. Results and discussion

To demonstrate the capability of the self-assembly solution-processed TiO<sub>2</sub> for large-area applications, we make the TiO<sub>2</sub> film covering a 4 in. by 4 in. ITO glass substrate in our laboratory (Fig. 1(a)). Compared with TiO<sub>2</sub> film of the same size without the self-assembly process (by not

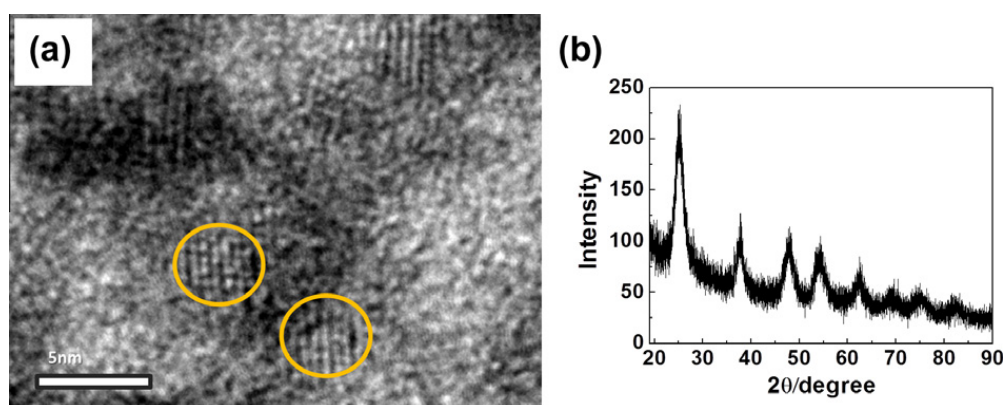


**Fig. 2.** (a) TEM image of TiO<sub>2</sub> nanoparticles; (b) XRD powder pattern of as-synthesized nanocrystalline anatase TiO<sub>2</sub> nanoparticles.

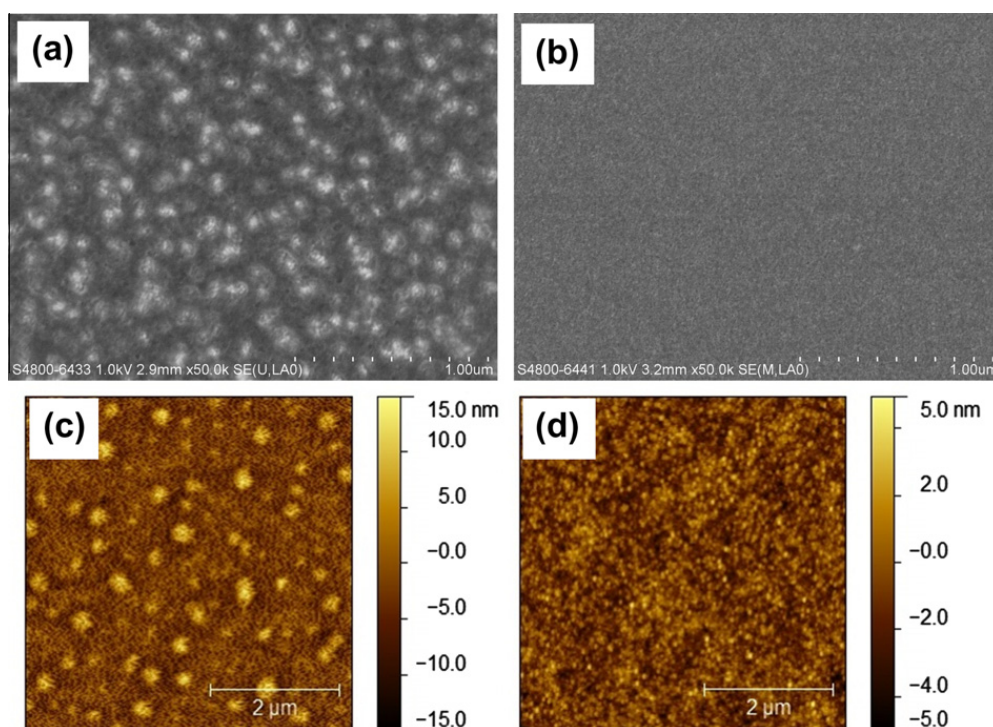


**Fig. 3.** SEM images of (a) spin-coated  $\text{TiO}_2$  and (b) self-assembled  $\text{TiO}_2$  films; (c) AFM image of spin-coated  $\text{TiO}_2$  with RMS roughness of  $\sim 8.1$  nm, (d) AFM image of self-assembled  $\text{TiO}_2$  with RMS roughness of  $\sim 1.8$  nm.

imposing the solvent evaporation control) as shown in Fig. 1(b), the surface of the self-assembled  $\text{TiO}_2$  layer is much more uniform and smooth as shown in Fig. 1(a). The excellent quality and uniformity of the large-area self-assembled  $\text{TiO}_2$  film is verified by device studies (as discussed later). It should be noted that the thickness of the self-assembled  $\text{TiO}_2$  film can be easily controlled by varying  $\text{TiO}_2$  nanoparticle concentration and casting volume of  $\text{TiO}_2$  solution.  $\text{TiO}_2$  films with thickness ranging from  $\sim 10$  nm to over 100 nm can be readily made.

One key point in the self-assembly process is the selection of solvent. In this process, we choose ethanol as the solvent, which is non-toxic and re-disperses the ligand free  $\text{TiO}_2$  nanocrystals. The weak intermolecular interactions—hydrogen bond in ethanol—are responsible for nanoparticles aligning and arranging orderly. Moreover, the surface tension and viscosity of ethanol is relatively low, indicating that the solution can form good contact with indium tin oxide (ITO) and spread uniformly on the ITO substrate. The vapor pressure of ethanol is low (5.95 kPa at  $20^\circ\text{C}$ ), and the ethanol usually evaporates quickly. Our results suggest that the ITO substrate should be covered quickly after putting the solution on the substrate. The growth time of the film can then be extended longer, giving the nanoparticles sufficient time to self-organize into an ordered film.

For organic device applications, the surface smoothness and compactness of the underneath carrier transport layer is very important. The surface morphology of  $\text{TiO}_2$  nanoparticle films from the spin-coating process and self-assembly approach are examined by SEM and AFM measurements, as shown in Fig. 3(a)–(d), respectively. By comparing the self-assembled and spin-coated  $\text{TiO}_2$  nanoparticle films of the

same thickness ( $\sim 40$  nm), it is observed that spin-coated  $\text{TiO}_2$  nanoparticles tends to accumulate to become heaps and are only moderately dispersed, while the  $\text{TiO}_2$  nanoparticles from self-assembly approach are uniformly distributed and form compact surface (SEM images, Fig. 3(a) and (b)). Results from AFM measurement (Fig. 3(c) and (d)) confirm the improvement in surface morphology in the self-assembly method. The root mean square (RMS) roughness of self-assemble  $\text{TiO}_2$  film is determined to be  $\sim 1.8$  nm, which is significantly smaller than that of spin-coated  $\text{TiO}_2$  ( $\sim 8.1$  nm). For open environment, the  $\text{TiO}_2$  nanoparticle solution evaporates quite rapidly. The fast spinning in spin-coating process may cause uneven evaporation rate of the solvent, hence leaving the nanoparticle layer in an inhomogeneous state. On the other hand, by keeping the substrate in an enclosed environment, the evaporation of the solvent is effectively adjusted to be steadily changing, enabling  $\text{TiO}_2$  nanoparticles to undergo gradual rearrangement and realignment (self-assembly) into ordered and uniform films with improved surface morphology. As observed in the experiment, the self-assembly process initially starts at the center of the substrate. Starting from the center of the substrate to the outer region, the surrounding nanoparticles then gradually align into ordered surface when the solvent slowly evaporates.

We further apply the self-assembled and spin-coated  $\text{TiO}_2$  nanoparticles films into poly(3-hexylthiophene):[6,6]-phenyl C61-butyric acid methyl ester (P3HT:PCBM)-based inverted PSCs as electron transport layer. The device structure is ITO/ $\text{TiO}_2$  (40 nm)/P3HT:PCBM (220 nm)/ $\text{MoO}_3$  (14 nm)/Ag (100 nm) (Fig. 1(c)). In the device fabrication process, we fix all the process parameters except the  $\text{TiO}_2$  deposition methods. In addition, PSC devices

using different regions of the large-area ( $4'' \times 4''$ ) self-assembled  $\text{TiO}_2$  film are also fabricated to study the quality and uniformity of the large-area films (as indicated in Fig. 1(a)). Fig. 4(a) shows  $J$ - $V$  characteristics and performance of a representative set of inverted PSCs with the device structure of ITO/ $\text{TiO}_2$ /P3HT:PCBM/ $\text{MoO}_3$ /Ag.

Since these two methods of depositing  $\text{TiO}_2$  transport layers (self-assembly and spin-coating) do not alter the composition of the materials, there are not any significant changes in the energy alignment at the interface. It comes naturally that we observe identical open-circuit voltage ( $V_{oc}$ ) in these two types of PSCs. However, the short-circuit current density ( $J_{sc}$ ) is significantly enhanced in self-assembled  $\text{TiO}_2$  film, and an improved fill factor (FF) is also observed, leading to improvement in device PCE from 3.65% to 4.03%. For PSCs using different regions of large-area

( $4'' \times 4''$ ) self-assembled  $\text{TiO}_2$  film as shown in Fig. 1(a), the performance is found to improve similarly, with enhanced FF and  $J_{sc}$ . Moreover, using large-area self-assembled  $\text{TiO}_2$  layer, the devices perform quite uniformly with average PCE of  $3.91 \pm 0.1\%$ .

We attribute the improvement of device performance in self-assembled  $\text{TiO}_2$  over spin-coated  $\text{TiO}_2$  to the capability of self-assembled  $\text{TiO}_2$  nanoparticles to collect charges more efficiently. Owing to the improved surface morphology, there are less traps or defect sites introduced by disorders in the nanoparticle layer or undesired contacts between the transport layer and the active layer from the rough surface. As a result, the electron traps in the  $\text{TiO}_2$  nanoparticle transport layer is effectively reduced. The enhanced charge collection of self-assembled  $\text{TiO}_2$  nanoparticles is evidenced by additional electron-only device with

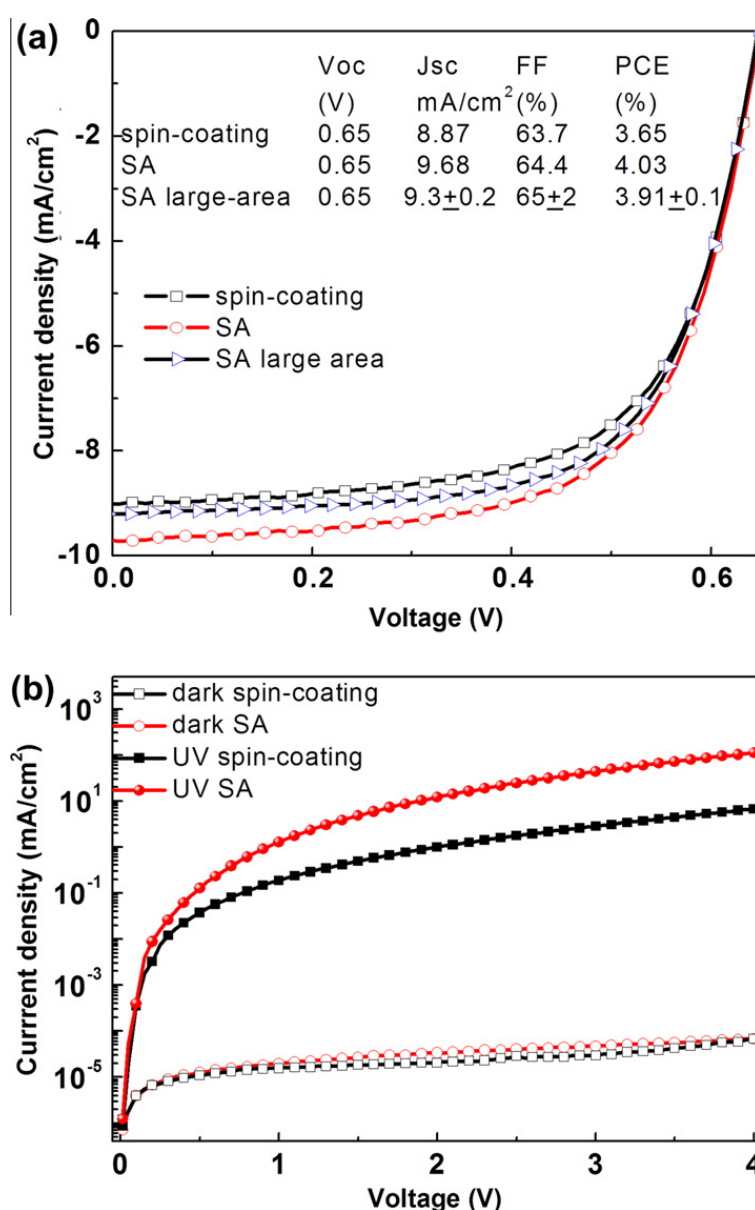


**Fig. 4.** (a)  $J$ - $V$  characteristics of inverted PSCs with  $\text{TiO}_2$  films as electron transport layer by spin-coating and self-assembly (SA) methods, under AM 1.5G  $100 \text{ mW}/\text{cm}^2$  illumination. The device performances including average device performance of large-area SA  $\text{TiO}_2$  films are summarized in the inset table. (b)  $J$ - $V$  characteristics of electron-only devices with spin-coated and self-assembled  $\text{TiO}_2$  films.

spin-coated and self-assembled TiO<sub>2</sub> nanoparticle layers of the same thickness. We fabricate the electron-only device with the structure of ITO/TiO<sub>2</sub> (spin-coated and self-assembled, 40 nm)/P3HT:PCBM (220 nm)/Ca (20 nm)/Al (100 nm), which can characterize the electron transport abilities [13]. When the electron-only devices are measured without ultraviolet (UV) light, both the self-assembled and spin-coated TiO<sub>2</sub> layers show identically low electron current densities in the dark *J*–*V* characteristics, indicating poor electron collection properties when electrons are injected into TiO<sub>2</sub>, as shown in Fig. 4(b). When excited by UV light shortly before measuring the dark *J*–*V* characteristics, electrons generate in TiO<sub>2</sub> layers and fill the shallow electron traps in titania [14], leading to decreased work function of TiO<sub>2</sub> and the forming of better energy alignment between TiO<sub>2</sub> and organic materials [15]. While both the self-assembled and spin-coated TiO<sub>2</sub> devices exhibit enhanced electron current after UV excitation, we find that in this case the electron current density is significantly larger for excited self-assembled TiO<sub>2</sub> device than for excited spin-coated TiO<sub>2</sub> device, indicating better electron collection properties for the self-assembled TiO<sub>2</sub> films (Fig. 4(b)). Therefore, the electron-only device characterization, combined with the SEM results, suggest that the improvements in device performance by using self-assembly approach is due to the more efficient charge collection in the device, owing to the enhanced film morphology of the self-assembled TiO<sub>2</sub> transport layer.

It is very important to note that while TiO<sub>2</sub> transport layers are known to require certain durations (such as 10–25 min or longer) of UV light exposure before they can transport electrons efficiently (otherwise the *J*–*V* curve shows characteristic S-shape) [14], all of our PSCs with TiO<sub>2</sub> layers are usually turned “on” by illumination instantly by using the ligand free anatase TiO<sub>2</sub> nanoparticles and remain relatively stable afterwards.

In addition, it should be mentioned that compared with spin-coating, our approach uses much less material for the same thickness of films (our method typically only uses less than 10% of the amount needed for spin-coating). The significant saving in our approach is done by utilizing most of the material deposited, as opposed to spin-coating spinning off much of the material in the process to ensure complete coating of the substrate. The effective saving of material can potentially pave the way for large-scale, high-throughput production for even less cost.

#### 4. Conclusions

In conclusion, we have presented a feasible and controllable self-assembly method for forming solution-processed titanium oxide (TiO<sub>2</sub>) nanoparticle films of high quality. Independent of the spin-coating method, the self-assembly process can produce films with highly ordered and uniform surface, as verified by SEM characterization. Furthermore, inverted PSCs fabricated with self-assembled TiO<sub>2</sub> as electron transport layers demonstrate enhanced device performance. Owing to the improved surface morphology, the enhancement can be further explained by the improved charge collection in the self-assembled TiO<sub>2</sub> as observed

from electron-only device. Meanwhile, due to the complete utilization of the deposited material, the self-assembly method can potentially have even lower cost compared with spin-coating. The proposed self-assembly method has simultaneously achieved the features of being efficient, capable of forming large-area and uniform films, highly feasible and cost-effective, which can be desirable for low-cost and high-throughput organic device applications.

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