# Hybrid inverted bulk heterojunction solar cells with nanoimprinted TiO$_2$ nanopores

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## ARTICLE INFO

## ABSTRACT

Photovoltaic devices with highly ordered nanoporous titanium dioxide (titania; TiO$_2$) were fabricated to improve the photovoltaic performances by increasing TiO$_2$ interface area. The nanoimprinting lithography technique with polymethyl methacrylate (PMMA) mold was used to form titania nanopores. The solar cell with poly(3-hexylthiophene) (P3HT):[6,6]-phenyl C$_{61}$ butyric acid methyl ester (PCBM) active layer on nanoporous titania showed higher power conversion efficiency (PCE) of 1.49% than on flat titania of 1.18%. The improved efficiency using nanoporous titania is interpreted with the enhanced-charge separation and collection by increasing the interface area between TiO$_2$ and active layer.

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## 1. Introduction

Photovoltaic cells based on conjugated polymer and fullerene bulk heterojunction composites have the potential for renewable energy resources due to their lightness, low cost and simple fabrication processing in large area [1–8]. Recent studies have reported remarkably improved performances of the bulk hetero-junction solar cells up to 5% in single-device structure [8,9]. However, there have been reported problems with oxides and organic materials in terms of stability. For example, especially the poly(phenylene vinylene) (PPV) is not stable in the presence of oxides which photo-oxidize the organic materials [10–14]. For the case of poly(3-hexylthiophene) (P3HT) with the oxides, however, the photo-oxidation is not so severe that it can be made air-stable hybrid devices [15,16]. As a consequence, from material point of view, poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) as anodic buffer layer and P3HT with [6,6]-phenyl C$_{61}$ butyric acid methyl ester (PCBM) blend as active layer represent for the state-of-the-art system.

In the conventional bulk heterojunction structure, however, acidic anodic buffer layer PEDOT:PSS has been proved to be deteriorative to the active layer, particularly under humid condition in the case of aluminum electrodes [17–19]. At the same time, it is known to be unstable in air, under illumination or on common electrodes such as indium tin oxide (ITO) from water adsorption by the PEDOT:PSS layer and presence of oxygen throughout the active layers [20–25]. In order to relieve these problems, many studies have been focused on searching alter-native materials to the PEDOT:PSS layer in the inverted bulk heterojunction solar cell structure. These include highly transpar-ent metal oxide [i.e. vanadium oxide (V$_2$O$_5$) and molybdenum oxide (MoO$_3$) [26], gold nanoparticle layer [27], TiO$_2$ nanotube arrays [28] and solution-processed titanium oxide (TiO$_x$) [29], zinc oxide (ZnO) [30] and cesium carbonate (Cs$_2$CO$_3$) [31]. However, the power conversion efficiency (PCE) of inverted solar cell structure is still behind that of conventional structure. Compared to the conventional structure with organic–organic interface (P3HT:PCBM–PEDOT), the inverted structure with organic–inor-ganic (P3HT:PCBM–TiO$_2$) interface leads to worse properties of exciton generation and separation. On the other hand, the inverted structure with TiO$_2$ is expected to achieve stable electron diffusion, electron selective transportation with high hole blocking barrier of TiO$_2$ and additional charge generation of P3HT–TiO$_2$ interface.

In this study, we improve the photovoltaic performances of solar cells fabricated with nanoimprinted nanoporous TiO$_2$ by increasing the interface area in the inverted solar cell structure ITO/TiO$_2$/P3HT:PCBM/Au. It is believed that both P3HT–PCBM and P3HT–TiO$_2$ interfaces result in more efficient charge separations

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and collections with the nanoporous titania interfacing the active layer than with flat titania.

## 2. Experimental

P3HT (Rieke Metals, Inc.) and PCBM (Sigma-Aldrich) were used as active layers without any further purification. The P3HT and PCBM (1:1 weight ratio) were dissolved in chlorobenzene solvent with 3 wt% solution and stirred at 60 °C for 1 h. The titania sol–gel solution was prepared by mixing titanium (IV) ethoxide, HCl and isopropyl alcohol. We previously reported the fabrication technique for highly ordered $TiO_2$ nanopores using anodic aluminum oxide (AAO) which was obtained by two-step anodizing method [32]. The AAO has about 80 nm of diameter and 100 nm of depth. Polymethyl methacrylate (PMMA; Aldrich) with a molecular mass of 350 kg/mol was dissolved in chlorobenzene. Nanopoled PMMA was created by pouring the solution on the AAO and by allowing the solution to percolate within the nanopores with heat treatment at 150 °C for 3 h. The PMMA nanopoles were then separated from the template by a wet etching technique in 1.4% of $FeCl_3$/5 M HCl solution. The Al and alumina residues were completely removed by 10% of NaOH cleaning solution. ITO-coated (15 $\Omega$/$\square$) glass substrate was cleaned in ultrasonic bath with DI water, acetone and isopropyl alcohol for 15 min. Nano-patterned PMMA mold was embossed after spin coating $TiO_2$ solution at 2000 rpm on to ITO substrate. The initial pattern of AAO is replicated to final titania structure by nanoimprinting with PMMA mold. Then $TiO_2$ layer was sintered at 500 °C for 1 h in ambient condition to obtain $TiO_2$ anatase phase. The thickness of flat titania was 100 nm measured by the surface profiler (alpha-step 500). A 200-nm-thick photoactive layer (P3HT:PCBM) was deposited on $TiO_2$ nanopores or PEDOT layer by spin coating. Au (100 nm) anode was thermally evaporated through shadow mask defining active area of 0.1 $cm^2$. Thermal annealing was conducted at 150 °C for 10 min in oven under $N_2$ ambient. The entire fabrication process was conducted in air environment except for thermal annealing of active layer. For a comparison with conventional device performance, solar cells using PEDOT:PSS (Baytron P VP AI 4083; H.C. Stark) and Al were fabricated in the structure of ITO/PEDOT/P3HT:PCBM/Al. The annealing condition and the active layer thickness of conventional devices were same with inverted devices. The current density versus voltage characteristics were measured with Keithley 236 source measurement unit and solar simulator (YSS-E40, Yamashita denso) under AM 1.5 G (100 mW/$cm^2$) irradiation intensity. The total incident light intensity was calibrated with pyranometer (Eko MS-802) and standard reference silicon solar cell. The Brunauer–Emmett–Teller (BET) specific surface areas of the flat and nanoporous titania were measured by analyzing the $N_2$ adsorption–desorption isotherms at 77 K (Micromeritics, ASAP 2020). UV/visible spectrophotometer (Shimadzu UV-1601) was used to study absorption spectra of the P3HT:PCBM films on $TiO_2$ layer. The surface of nanoporous titania was characterized using field-emission scanning electron microscope (FE-SEM; LEO SUPRA 55, Carl Zeiss) and atomic force microscope (AFM; XE-100, Park Systems) in non-contact mode.

## 3. Results and discussion

Fig. 1 shows schematic diagram of the hybrid bulk heterojunction solar cell and its energy band structure. Since the conduction band of $TiO_2$ is similar to that of PCBM, electrons can transport to ITO electrode through $TiO_2$ with ease. Moreover, the valance band of $TiO_2$ is efficient to prevent back electron or hole transfer with its high-energy barrier.
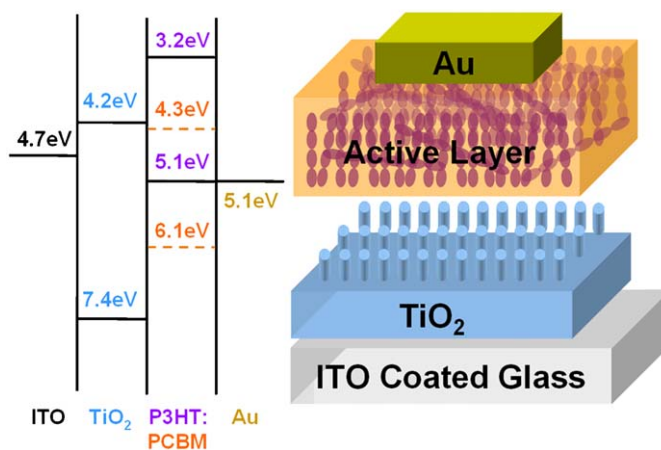


**Fig. 1.** Schematic diagram of the hybrid inverted bulk heterojunction solar cell and its energy band structure.

Fig. 2 shows FE-SEM and AFM images of nanoporous $TiO_2$. It shows that nanoporous titania was successfully fabricated using nanoimprinting lithography with PMMA nanopoles as a stamp. The initial film thickness of flat $TiO_2$ was 100 nm. The rms roughness extracted from AFM images of flat and nanoporous $TiO_2$ were ~1 and ~10 nm, respectively. The surface area is not always the function of roughness. BET analysis was conducted for both $TiO_2$ films. As the samples used for BET analysis were thin-film-coated ITO glass substrate, both thickness and weight of film significantly affect the surface area. Thereby, it is difficult to obtain exact number of surface area. We compared the results by preparing the samples to have same size and thickness. When we assume that the $TiO_2$ nanopores are perfect cylinder structures, the calculated increase of nanoporous $TiO_2$ surface area was about 60% than flat $TiO_2$. However, the measured surface area of nanoporous $TiO_2$ was increased about 40% than flat $TiO_2$. The mismatch was due to the defects resulted from various process steps to fabricate the nanoporous $TiO_2$. The increased rms roughness and surface area using nanoporous $TiO_2$ were expected to provide large interface between $TiO_2$ and active layer that would benefit for exciton generation and separation. The final titania nanopores have lager diameter (100 nm) and lower depth (30–40 nm) than AAO (80 nm of diameter and 100 nm of depth). The larger diameter of pores is thought to result from the lateral volume shrinkage of pore wall during sintering titania deposited from sol–gel solution. Also imprinting titania with PMMA mold compresses titania, thereby leaving shallower depth of pores. The pores with a size smaller than 20 nm would enhance the charge separation most effectively because a typical range of exciton diffusion length in polymers is 4–20 nm [33]. On the other hand, it is difficult to make polymer materials to self-organize and form close-chain packing structure inside such a small pore [34]. A relatively large size of nanopores in our structure is thought to enhance phase separation and allow the chain packing in active layer.

We previously observed that both the flat and nanoporous $TiO_2$ formed anatase phase with (1 0 1) preferred orientation on ITO substrate measured by X-ray diffraction (XRD) analysis [32]. The conduction band edge of $TiO_2$ anatase phase is about 0.2 eV higher than that of rutile $TiO_2$. Also, anatase phase facilitates electron transfer more than rutile and the higher energy barrier of anatase phase suppresses hole transfer or back electron transfer more effectively [35].

UV/visible absorption spectra in Fig. 3 shows that absorption of active layer coated on nanoporous $TiO_2$ was almost similar but slightly higher than that on flat $TiO_2$. Vibronic features of P3HT