

Supplemental Material

The complete fabrication process for the inverted solar cell geometry using a laser ablation processed active layer with its most important parameters is summarized graphically in Fig. 1.

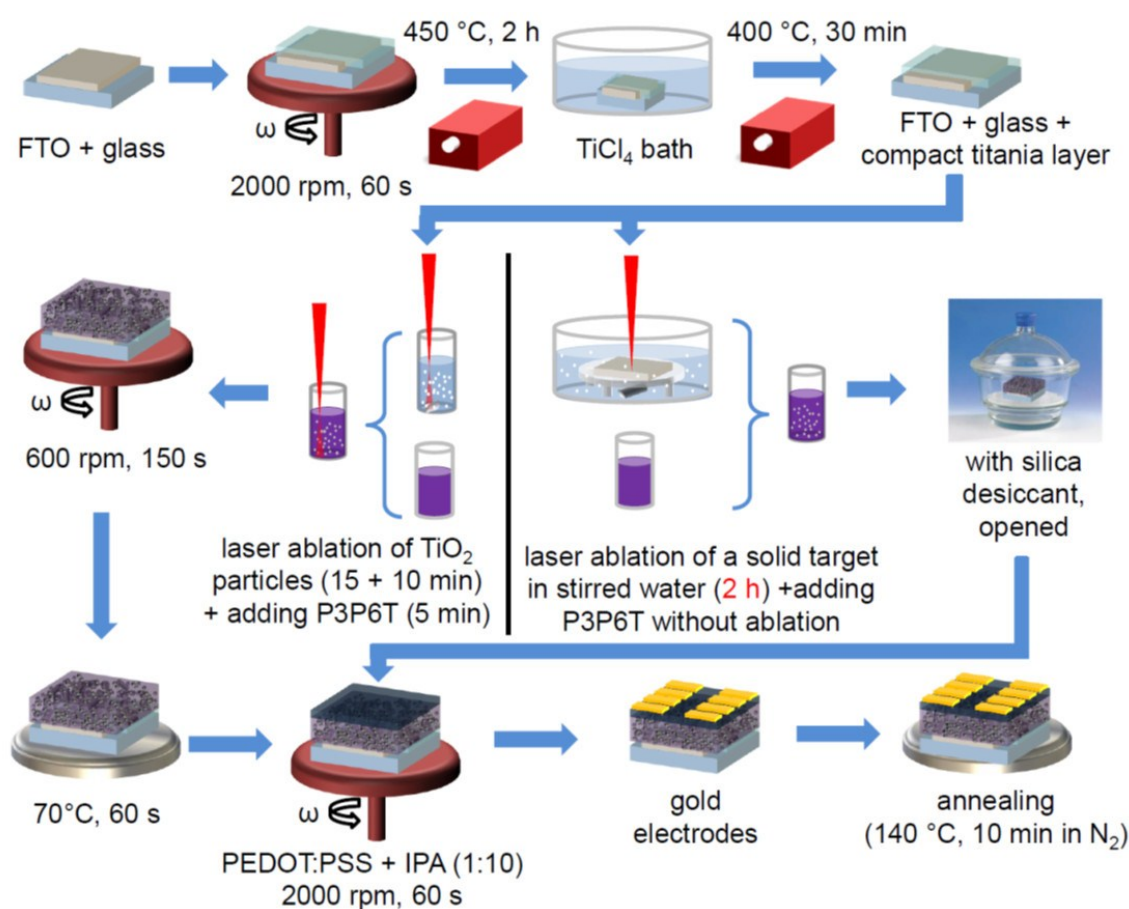


FIG. 1 Fabrication process of solar cells from laser-ablated titania.

As substrates, fluorine doped tin oxide (FTO) covered glasses are used. The FTO layer is partly etched away from the substrate. For that, FTO is covered with an adhesive tape having a width of 12 mm. For the etching purpose, zinc powder is mixed with water and distributed on the non-covered parts of the FTO. A mixture of hydrochloric acid (HCl, 37%) and deionized water (ratio 2:1) is applied on the distributed zinc powder. After completion of the reaction, the remaining parts are rinsed away with deionized water and the tape is removed.

The cleaning process includes four steps, each of them containing a ten minutes ultrasonic bath followed by rinsing of the substrates. First, the substrates are placed in a polytetrafluoroethylene (PTFE) holder and rinsed with deionized water. Thereafter, they are subsequently immersed in Alconox® dissolved in deionized water (16 g/l, Sigma-Aldrich), ethanol (Roth), acetone (Th. Geyer) and isopropyl alcohol (IPA, Roth), in between a ten minutes ultrasonic bath and rinsing of the samples with the appropriate solvent (in case of Alconox®, they are rinsed by deionized water). In the step changing from acetone to IPA cleaning it is taken care that the samples do not dry. After finally rinsing the samples with IPA, they are dried with nitrogen. Right before continuing with the next preparation step, the sample surface is treated in oxygen plasma. This aims to remove all organic traces and to improve the hydrophilicity of the surface. Therefore, the samples are placed in a glass dish in between the electrodes in a plasma etcher (Nano by Diener electronics). The chamber is evacuated to 0.1 mbar before filling with oxygen. At a pressure of 0.4 mbar, the oxygen plasma is started with a power of 250 W for 10 min.

In order to improve the efficiency of solar cells, a hole blocking layer is introduced. The compact titania layer reduces the contact of the hole conductor with the FTO and therefore prevents charge recombination. The layer is prepared according to Yu et al.¹ Solution (1) containing ethanol, titanium(IV) butoxide ($\text{Ti}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4$, TNBT, purchased by Sigma-Aldrich) and diethanolamine ($\text{C}_4\text{H}_{11}\text{NO}_2$, Sigma-Aldrich) is stirred for one hour before solution (2), containing ethanol and deionized water, is added dropwise. After that, the complete solution is stirred for 24 hours, and spin coated on the freshly cleaned FTO substrates with a rotational speed of 2000 rpm for 60 s and an acceleration time of 4.5 s. To prevent the whole FTO being covered by the compact titania layer, one edge is covered with adhesive tape before spin coating, allowing to contact the FTO later on. The compact titanium layer is then calcined in the tube furnace at 450 °C for 2 hours using a heating ramp of 375 °C/h. The thickness of the compact layer is 110 to 140 nm. After calcination, the sample is treated with a bath of TiCl_4 to improve the contact between the different titania layers.² Therefore, 5.5 ml TiCl_4 obtained from Sigma Aldrich are dissolved in 25 ml deionized water in a water bath below 0 °C in order to obtain a clear solution of 2 M TiCl_4 . The samples with the compact titania are immersed in 50 ml deionized water in a water bath at 70 °C and 1 ml of the TiCl_4 solution (2 M) is distributed over the samples. As before, the edge without compact titania is again covered with tape for later contacting. After a bathing time of 45 min, the samples are removed from the TiCl_4 and rinsed with deionized water followed by rinsing with ethanol and thereafter drying with nitrogen. The sample is then again calcined in the tube furnace at 400 °C for 30 minutes using a heating ramp of 1500 °C/h.

The active layer consisting of a P3P6T:TiO₂ compound is prepared as described below. Afterwards it is applied onto the solar cells using two ways, either spin coating or solution casting. The spin coated film is applied with a rotational speed of 600 rpm for 150 s with an acceleration time of 4.5 s. Thereafter, the sample is put on a heating plate at 70 °C to evaporate the remaining solvent. For solution casting the active layer, a desiccator is filled with silica and the plug is removed.

As electron blocking layer, PEDOT:PSS diluted with IPA in the volume ratio 1:10 is used. Thus, PEDOT:PSS is put into the ultrasonic bath for 10 min. The solution is then filtered with a PVDF filter with a pore size of 0.45 µm to remove big clusters. Next, it is diluted with IPA in the volume ratio 1:10. The diluted solution is then sprayed with a hand driven glass sprayer (Test tube sprayer, 6 ml, Lenz) until sufficiently covering the sample. Thereafter, the solution is spin coated with 2000 rpm for 60 s with an acceleration time of 2.0 s.

The last step before characterizing the solar cell is the evaporation of gold contacts followed by annealing. The samples are placed with their topsides showing down on a shadow mask having 8 holes for the later solar cell pixels. The evaporation chamber is evacuated until a pressure of less than $2 \cdot 10^{-5}$ mbar is reached. Then, 140 to 170 mg gold (Heraeus) is evaporated in approximately 2 min at a working pressure of $5 \cdot 10^{-5}$ mbar yielding the solar cell pixels. Since the FTO is etched away at the edges, the gold electrodes and the FTO are not connected. The active area of a solar cell is the overlap of gold contact and FTO, usually with a size of around 0.15 cm². After evaporation of the gold contacts, the solar cells are annealed on a heating plate at 140 °C for 10 min in a closed environment with a constant flow of nitrogen as this shows an improvement in crystallinity of the hole-conducting polymer and thus in the performance of P3HT based solar cells. Before contacting the pixels to characterize the solar cell, a silver paste is applied on the edges of the pixel to improve the contact.

Active layer

The polymer P3P6T is dissolved in deionized water with a concentration of 15 mg/ml and stirred for five hours. The titania powder is weighed and dispersed in deionized water. In order to obtain constant laser parameters, in this case a fixed height of the laser focus with respect to the water surface, 3 ml of deionized water are filled into a glass vial of 5 ml volume (Roth, LC82.1) using the same magnetic stir bar (Roth, 0999.2). The amount of titanium powder is weighed using an analytical balance (Sartorius BP210D) to be 30 mg as exact as possible. Before starting the laser ablation process, the solution is put into an ultrasonic bath for 10 min to disintegrate possible aggregates.

The laser pulses used in the ablation process are provided by a home-built titanium:sapphire laser system. The femtosecond pulses are generated by Kerr-lens mode-locked titanium:sapphire oscillator pumped by a commercial frequency-doubled Nd:YLF laser. The yielded pulses are stretched, amplified in a regenerative titanium:sapphire amplifier and subsequently compressed by a grating compressor to obtain more than 300 μJ at a central wavelength of 810 nm with a pulse duration of 270 fs and a repetition rate of 1 kHz. In order to increase the laser intensity in the interaction area, the laser beam is focused in the sample by a fused silica lens ($f = 100$ mm). The beam diameter in the focal plane (around 31 μm) is determined using a beam profiler. The vial containing the dispersed titanium in water and the stir bar is placed on the stirring plate underneath the focusing lens within a protection chamber. Constant stirring during the laser ablation process allows a well mixture of the titania powder, the avoidance of sedimentation and a constant flow. The focal plane is set to be around 3 to 5 mm below the water surface. In order to protect the optical components of the setup a microscopy glass slide is placed between the sample and the focusing lens. The solution is treated by the laser beam for 15 min, while the laser focus is laterally positioned slightly apart from the vial's center to obtain a faster liquid flow. Subsequently, the fill height is checked using a reference glass with the exact amount of solution as well as the stir bar. Typically, around 0.6 to 0.9 ml of water has to be added in order to ensure a reproducible position of the laser focus with respect to the water surface. The microscopy glass slide is exchanged and the solution is again put into the laser focus for additional 10 min. In order to functionalize the fabricated nanoparticles, the polymer is added. To do so, the titanium powder solution is removed from the laser beam and subsequently, 2 ml of the pre-dissolved P3P6T solution (15 mg/ml) is added to obtain a P3P6T:TiO₂ solution with a weight ratio of around 1:1. After adding the polymer the solution is placed back on the stirring plate to be again in the laser focus for 5 min. This potentially enhances the functionalization process. After finishing the laser ablation process, the vial is wrapped in aluminum foil to protect the solution from light and placed on a stirring plate until application for further experiments.

IV characterization

Current-voltage curves of the solar cells are recorded under dark and illuminated conditions. For simulating the solar spectrum a Solar-Constant 1200 (K. H. Steuernagel Lichttechnik GmbH) solar simulator is used. For generating the spectrum a halogenide lamp with rare earth metals combined with a reflector system and a borsilicate filter for homogeneous sample illumination are used. The solar simulator is calibrated to 1000 Wm^{-2} via a silicon based reference solar cell (WPVS Reference Solar Cell Typ RS-ID-3 by Fraunhofer ISE).

SEM

N-Vision 40 SEM (Zeiss) 1 is used, where secondary electrons are detected using an in-lens detector. Measurements are performed with an acceleration voltage of 5.0 kV at a working distance between the electron gun and the sample of 0.7 to 3.9 mm.

XRD

XRD measurements are performed using a D8 by Bruker, which is controlled with the software XRDcommander combined with XRDwizard. The X-ray radiation is produced by a copper X-ray tube with a wavelength of $\lambda_{\text{Cu}} = 0.1541$ nm. The X-ray beam impinges the sample under an angle θ and the detector is set to the same angle θ with respect to the sample to use the Bragg-Brentano setup. XRD measurements are performed for $20^\circ < 2\theta < 60^\circ$ for titanium dioxide, and $3^\circ < 2\theta < 40^\circ$ for polymers with a step size of 0.001° to 0.01° in the areas of interest. In regions with no expected peak, the step size is increased in order to accelerate the measurement. The counting time per step is $3 \text{ s} < t < 15 \text{ s}$ depending on the scattering volume which is low for thin films. The width of the measured peaks depends on the crystallite size in the sample. The crystallite size d_{hkl} is calculated from the fitted peaks using the Scherrer equation $d_{\text{hkl}} = 2\pi/\Delta q_{\text{hkl}}$ where Δq_{hkl} is the integral line width, defined as the ratio of the Bragg peak area to its amplitude.

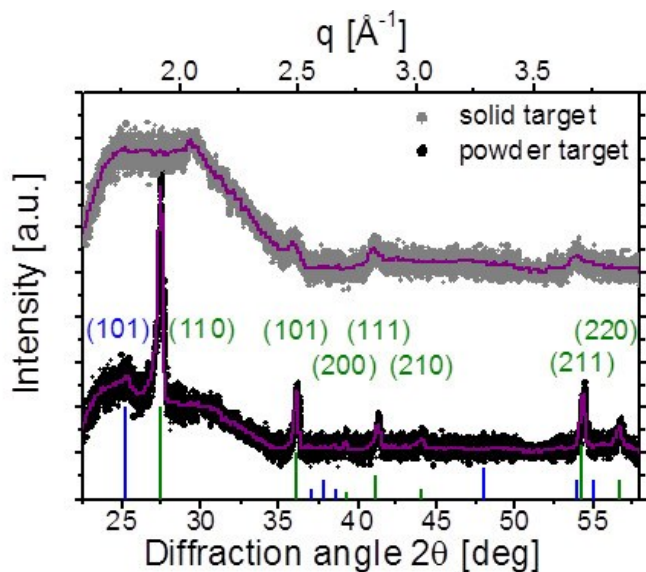


FIG. 2 XRD pattern of laser ablated TiO₂ from solid titanium and titania powder target. Theoretical positions of TiO₂ in anatase and rutile phase are plotted in green and blue, respectively.

GIWAXS

Experiments are performed at the P03 beamline at the Petra III ring of the Deutsches Elektronen-Synchrotron DESY in Hamburg.³ The GIWAXS measurements are performed at a wavelength of $\lambda = 0.954 \text{ \AA}$ at a sample to detector distance SDD of $(153.25 \pm 0.44) \text{ mm}$. The two-dimensional detector is a Pilatus 300K (Dectris). Each pixel has a size of $172 \times 172 \text{ \mu m}^2$. In order to avoid oversaturated areas as well as to protect the detector from damage, beam stops are used for shielding the direct beam. In order to probe as much volume as possible the incident angle is set to $\alpha_i = 0.13^\circ$. The cake cuts are done in horizontal ($1^\circ - 10^\circ$) and in vertical ($85^\circ - 95^\circ$) direction using the software DPDAK v0.3.2.⁴ The vertical cake cut leads to information on the crystal orientation perpendicular to the substrate, the horizontal cake cut on the crystal orientation parallel to the substrate. The background scattering is accounted for by measuring the bare substrate.

UV-vis

The spectra are recorded using Lambda 650S of PerkinElmer providing the possibility to measure the transmission using an integrating sphere (Spectralon R highly reflective 150 mm spherical chamber). The combination of a deuterium and a halogen lamp provides a wavelength range of $190 < \lambda < 900 \text{ nm}$ by switching the light source at around 320 nm. The slits are set to 2 nm and the scan speed is 265 nm min^{-1} . UV-vis spectroscopy is used to determine the bandgap of the probed material.⁵ The optical band gap energy E_{gap} is related to the absorption coefficient α via the Tauc equation $(\alpha E)^n = B(E - E_{\text{gap}})$ with the constant B for different transitions, the energy $E = (h \cdot c) / \lambda$, $n = 1/2$ for allowed indirect transitions and $n = 2$ for allowed direct transitions. In order to obtain the optical band gap E_{gap} , $\sqrt{\alpha E}$ is plotted against the photon energy E and linearly extrapolated to obtain E_{gap} .

FTIR

A Spectrum Two of Perkin Elmer Inc. with a range of $4000 - 400 \text{ cm}^{-1}$ equipped with a diamond attenuated total reflectance (ATR) is used. The spectrometer is located in an argon filled glove box. With ATR the light is at least once totally reflected at the interface to the sample and therefore forms an evanescent wave which extends into the sample having a small penetration depth. The data are then further processed using the software Spectrum of PerkinElmer, Inc.

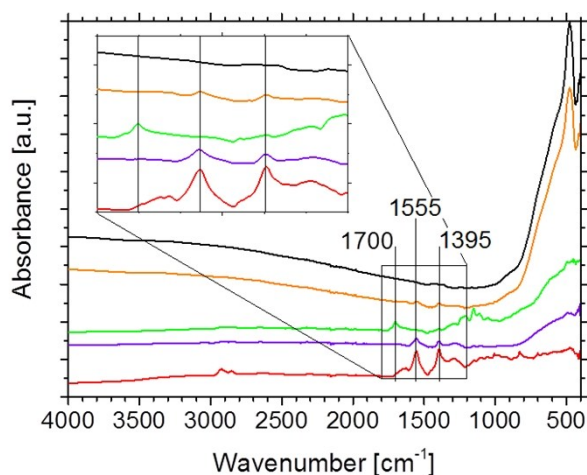


FIG. 3 Infrared spectra of P3P6T and laser ablated TiO_2 . The red curve represents pure P3P6T and the black one pure TiO_2 by laser ablation from titania powder. A blend of TiO_2 laser-ablated from suspension and P3P6T powder (orange), and the corresponding compound of P3P6T: TiO_2 (purple) are shown. Additionally the compound with TiO_2 ablated from a titanium target, denoted P3P6T: TiO_2^* (green) is shown. Data are shifted along the y-axis for clarity.

Table 1 Attribution of IR bands

Observed band	Mode assignment	Reference number
1395 cm^{-1}	$\nu_s(\text{CO}_2)$; symmetric carboxylate stretching	[6]
1555 cm^{-1}	$\nu_a(\text{CO}_2)$; asymmetric carboxylate stretching	[6]
1620 cm^{-1}	bending vibration of coordinated H_2O & Ti-OH	[7, 8]
1700 cm^{-1}	1680 cm^{-1} : C-O stretching; appears just for functionalization	[8]

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