Supporting Information for: Removal of Surface Oxygen Vacancies increases Conductance through TiO$_2$ Thin Films for Perovskite Solar Cells

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1. Preparation of aqueous TiCl₄ solution

TiCl₄ reacts strongly with water. Therefore, TiCl₄ must be added very carefully. We followed the following procedure: We prepared a 2 M stock solution. We cooled down 10 mL of milliQ water in liquid nitrogen until it froze to ice. Over approximately one minute, 2.19 mL of TiCl₄ (Sigma-Aldrich, 99.9% trace metal basis) was slowly added to the ice with a syringe. The vial must be kept in liquid nitrogen, freezing the TiCl₄ almost instantly. Note, we did not use a cannula on the syringe for adding the TiCl₄ to the water because it plugs easily.

The mixture was melt very slowly by removing it from the liquid nitrogen and submerging it in liquid nitrogen repeatedly. Simultaneously, we shook the vial. During this procedure, any potential built up of pressure in the vial should be released. Than the yellowish frozen TiCl₄ dissolves slowly at the water interface until a clear, colorless, precipitation-free solution formed. Finally, the solution was filtered with a PTFE syringe filter and stored at -15 °C. This solution stays liquid at these temperatures.

For the 1 M and the 0.75 M solution, the 2 M stock solution was diluted with the respective amount of milliQ water, without any further cooling. Both the 1 M and the 0.75 M solution were stored at -15 °C. At these temperatures, the solutions became solid.
2. Variation in UV-ozone treatment time

![Graphs A and B]

*Figure S1: A) Influence of treatment time on median current. B) Influence of treatment time on TiO₂ anatase film thickness.*

We conducted three sets of measurements at different weeks, i.e. three different samples. Every sample was exposed subsequently to UV-ozone for 1, 5, 10, 15 and 30 min (Figure S1). Each sample was prepared directly in advance to the UV-ozone treatment. The cSFM measurements were performed directly after treatment. We always used the same tip for each test series. Test series 1 showed a median current increased from 4.6 pA without UV-ozone treatment to 378 pA after 30 min of UV/ozone treatment. For the second and third set, the median current increased from 1.6 pA and 2.2 pA to 101.6 pA and 92.6 pA, respectively. We attribute the difference in absolute values to variations in the tip geometry of the scanning force microscopy probe. The latter results in a variation of tip-sample contact area affecting the absolute current.

For each sample, we calculated the median current value and we plotted the percentage increase of the median current with respect to the previous measurement. For treatment times between 0 and 15 min within a measurement series, the median current varies. We hypothesize that this variation is due to changes in the ambient conditions within our lab. In particular, we use an aqueous TiCl₄ solution, that we spin-coat in air. Presumably, the varying humidity and temperature in our lab play a crucial role in the initial film formation of the film and its further crystallization. The latter can result in slightly different initial electronic properties of the TiO₂ film. Despite these variations, we measured a similar increase in median current by approximately two orders of magnitude after 30 min of UV-ozone treatment for each test series. Therefore, we conclude that 30 min of UV-ozone treatment is the minimum time needed to achieve a reproducible increase of current.
3. Diode characteristics of TiO$_2$ thin films on FTO with and without UV-ozone treatment

The SFM-tip has a PtIr-metal coating with a work function of $\sim$3.9 eV. The semiconducting anatase form of TiO$_2$ has a work function of 5.1 eV. Therefore, we expect a Schottky-diode-characteristic IV behavior with an onset in current at around 1.2 V. To measure an I-V curve, we conducted consecutive cSFM on the same substrate with varying external bias. We plotted the measured median current against the applied bias to generate an I-V-curve (Figure 2S). We measured a new area on the same substrate to avoid any potential influence of previous measurements.

Figure S2: a) Normalized local I-V-curves of an annealed TiO$_2$ film and b) an annealed and UV-ozone treated TiO$_2$ film on FTO. Measurements were conducted starting at an initial bias of +1.5 V, which was increased stepwise to 0 V and then inverted up to -1.5 V (black curve). Subsequently, the bias was reduced stepwise again to 0 V and inverted up to 1.5 V (red curve). Please note that for every image a new area of 256x256 pixels was measured to avoid any potential influence of previous measurements. This set of measurement took approximately 1 h.

For both the treated and untreated sample, no current above the noise level of 1.5 pA could be measured at a bias voltage < 0.75 V. Therefore, the UV-ozone treatment did not affect the threshold voltage. We noticed a difference of the median current for the backward and forward scan for the sample that was only annealed (Figure 2 a, red curve and black curve). We attributed the decrease in median current to recontamination during the measurement since the whole set was conducted over the time period of 1 h. Interestingly, the UV-ozone treated sample did not show this decrease in median current. There the sample is more stable.
4. Surface erosion

The RMS roughness changed only slightly after 30 nm of UV-ozone measurement. For the first test series, the RMS roughness increased from 6.9 nm to 7.7 nm. For the second test series, the roughness slightly decreased from 9.1 nm to 8.8 nm. The third test series was performed on a different batch of commercial FTO that showed a much higher roughness. Without any UV-ozone treatment a RMS roughness of 19.2 nm was measured. After 30 min of UV-ozone treatment a roughness of 17.0 nm was measured. Thus we exclude changes of roughness as a dominant factor for the increase in median current measured by cSFM.

Furthermore, we measured the TiO₂ film thickness before and after the UV-ozone treatment. First, a glass slide was coated with a 5 nm thick layer of sacrificial gold that has low adhesion to the glass surface. Second, the gold surface was covered with a standard layer of TiO₂ (as described in the Experimental Section). Third, the Au/TiO₂ film was scratched away with a metal cannula. Finally, the resulting step in the film was measured with a profilometer (KLA-Tencor Stylus Profiler Modell P7) at three different spots of each sample. These measurements revealed no change in thickness for the UV-ozone treated samples.
5. Tip erosion

The measured median current can also be affected by tip erosion. Therefore, we measured a second, one day old, untreated sample that already was contaminated and thus should not change its conductance over time. We measured two images of that sample. The first image was recorded with a new cantilever. The second image was measured with the same cantilever after it has been used for 12 h of constant measurement (Figure S2) on other TiO$_2$ substrates. Within this period, over 50 images were recorded, each with a resolution of 256 x 256 pixels. This resulted in over 3 million individual force-distance curves measured with that cantilever.

For the first image, i.e. with the fresh cantilever, we measured a median current of 2.9 pA, which was well above the noise level of 1.5 pA. For the second image, i.e. after 3 million individual force-distance curves, a median current of 3.0 pA was measured. Therefore, we concluded that, tip erosion plays only a minor role and cannot explain the measured increase of median current with UV-ozone treatment. Therefore peak force based cSFM techniques can be used to not only compare current images qualitatively but also quantitatively when using the same cantilever for different samples.

![Figure S3: cSFM image of the same sample with a pristine cantilever (A) and the same cantilever after over 3 million individual force-distance curves.](image)
6. Solar cell parameters of forward and backward scan of I-V-measurements

Table S3: backward- and forward-scan-parameters of treated and untreated perovskite solar cell with a compact SnO$_2$ layer as an ETL

| Device | $J_{sc}$ [mA/cm$^2$] | $V_{oc}$ [mV] | FF [%] | PCE [%] |
|--------|----------------------|---------------|--------|---------|
| annealed and UVO treated | mean value | (21.2±0.3) | (1068±4) | (73.5±1.1 ) | (16.6±0.4) |
| annealed | mean value | (20.4±1.8) | (1059±10) | (69.2±2.4) | (15.0±1.6) |
| annealed and UVO treated | mean value | (21.3±0.2) | (1057±8) | (60.8±2.5 ) | (13.7±0.7) |
| annealed | mean value | (21.4±0.6) | (1030±32) | (51.2±8.7) | (11.4±2.4) |
7. XP spectra of C 1s

We measured the XP C1s signals for a freshly annealed, a freshly annealed and UV-ozone treated and an annealed sample after 24 h. The signal at the C1s binding energy showed not significant changes of neither peak position nor peak shape for samples which were freshly annealed and freshly annealed and UV-ozone treated. This similarity indicates, that the nature of adsorbed carbon species is not altered significantly.

However, both peak shape and position changed strongly for an annealed sample, that was stored at ambient for 24 h. These changes reflect the adsorption of various carbon species on the TiO$_2$ surface.

![Figure 4: Comparison of the different XP spectra of a freshly annealed, a freshly annealed and UV-ozone treated and an annealed sample after 24 h.](image)

In summary, we concluded that changes of the nature of adsorbed carbon species after UV-ozone treatment on freshly annealed TiO$_2$ films are not a dominant factor for the measured increase of conductance.