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Organometal trihalide perovskite solar cells arguably represent the most auspicious new photovoltaic technology so far, as they possess an astonishing combination of properties. The impressive and brisk advances achieved so far bring forth highly efficient and solution processable solar cells, holding great promise to grow into a mature technology that is ready to be embedded on a large scale. However, the vast majority of state-of-the-art perovskite solar cells contains a dense TiO₂ electron collection layer that requires a high temperature treatment (>450 °C), which obstructs the road towards roll-to-roll processing on flexible foils that can withstand no more than ~150 °C. Furthermore, this high temperature treatment leads to an overall increased energy payback time and cumulative energy demand for this emerging photovoltaic technology. Here we present the implementation of an alternative TiO₂ layer formed from an easily prepared nanoparticle dispersion, with annealing needs well within reach of roll-to-roll processing, making this technology also appealing from the energy payback aspect. Chemical and morphological analysis allows to understand and optimize the processing conditions of the TiO₂ layer, finally resulting in a maximum obtained efficiency of 13.6% for a planar heterojunction solar cell within an ITO/TiO₂/CH₃NH₃PbI₃₋ₓClₓ/poly(3-hexylthiophene)/Ag architecture. © 2014 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4890245]
matrix in perovskite-based solar cells, even though there are many high efficiencies reported based on mesoporous TiO$_2$.\textsuperscript{6-15} Indeed, several groups pointed out that a simpler device architecture, where a perovskite layer is sandwiched between selective contacts, is able to deliver comparable or even better performance than a mesoporous TiO$_2$/perovskite compound: Efficiencies of around 11\% were obtained for solution-processed planar heterojunction CH$_3$NH$_3$PbI$_3$Cl$_x$-based solar cells, and even up to 15.4\% by vapor deposition.\textsuperscript{16-18} In the latter cases the compact TiO$_2$ layer was deposited by heating a precursor gel at high temperature (\textasciitilde500°C), lacking compatibility with flexible substrates and thus presenting a drawback in view of industrial scale roll-to-roll fabrication. This can in principle be remedied by using poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) as bottom selective contact (thereby inverting the device structure).\textsuperscript{19,20} though the hygroscopic nature of PEDOT:PSS would likely hamper the long-term stability of the moisture-sensitive perovskite.\textsuperscript{21}

It was then shown that the high temperature treatment for TiO$_2$ can be circumvented by using a layer consisting of TiO$_2$ nanoparticles, rather than one that is \textit{in situ} formed by annealing a precursor gel. Two strategies have been demonstrated so far, either the deposition of a nanoparticle dispersion or the direct precipitation of TiO$_2$ nanoparticles from solution onto the substrate.\textsuperscript{22} Both methods use TiCl$_4$ as the titanium source, which produces HCl fumes when in contact with humidity and thus has to be handled with great care. Another method does use titanium isopropoxide (TIP) as titanium source, but requires the addition of graphene flakes to the resulting TiO$_2$ dispersion to obtain optimal performance.\textsuperscript{23} Here we present the chemical and morphological characterization of a TIP-based sub-150°C processed TiO$_2$ electron acceptor layer consisting of nanoparticles, and we investigate the influence of this layer on the morphology of the subsequently deposited perovskite layer. The nanoparticulate TiO$_2$ layer is deposited from an alcoholic dispersion that is very easy to synthesize and the resulting planar heterojunction solar cells outperform previously reported analogs containing high-temperature processed TiO$_2$ layers. The resulting maximum obtained conversion efficiency of 13.6\% is to the authors’ knowledge the highest reported value for a \textit{solution processed} planar heterojunction solar cell based on mixed halide perovskite CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$.

Our TiO$_2$ nanoparticle dispersion was prepared using a slight modification of a procedure reported by Katoch \textit{et al.}\textsuperscript{24} A 470 \mu l of TIP was added dropwise to a solution of 123 \mu l nitric acid in 2.5 ml ethanol under mild stirring. After stirring for 2 h, 114 \mu l of demineralized water was added for the hydrolysis to proceed and the solution was left stirring for another hour. The result was then diluted with 1-propanol. This transparent dispersion is ready for use, with no need for centrifugation, washing, and redispersing, and is stable for months (Figure 1(a): a 0.127 M dispersion). Fig. 1(b) shows a Dynamic Light Scattering (DLS) measurement of the dispersion, revealing a narrow size distribution with an average particle size of 6 nm. An X-ray diffraction (XRD) measurement of a dried powder sample is shown in Figure 1(c), confirming the anatase phase (thereby inverting the device structure) of the material, and confirming the crystal diameter measured with DLS (via Scherrer equation).

Recently, it was shown by Wojciechowski \textit{et al.}\textsuperscript{25} that the addition of a small amount of titanium diisopropoxide bis(acetylacetonate) (TiAcAc) to a TiO$_2$ dispersion can serve as “electronic glue” between the nanoparticles in the eventual nanoparticulate thin film, enhancing its conductivity and thus improving the resulting solar cell built on it.\textsuperscript{22} In addition, the TiAcAc can also assist in the film formation itself. Figures 1(d)–1(f) show Atomic Force Microscopy (AFM) micrographs of 25–30 nm thick TiO$_2$ films spincoated on indium-tin-oxide (ITO) (3000 rpm; 1000 rpm/s; 30 s) from a 0.127 M dispersion with the addition of 8 mol.\% of TiAcAc (0.08 mole of TiAcAc per mole of TiO$_2$), annealed for different times at 135°C in air. Smooth films are obtained with a low root-mean-square roughness of 1 nm or less on ITO as base layer.

The thermally treated TiO$_2$-covered ITO substrates were then used to build planar heterojunction CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ perovskite solar cells according to a previously published procedure.\textsuperscript{17} In short, a 3:1 methylammonium iodide:PtCl$_2$ solution in dimethylsulfoxide (DMSO) was spincoated (3000 rpm; 800 rpm/s; 540 s) on the TiO$_2$ in a nitrogen-filled glovebox, followed by a thermal treatment at 100°C for 60 min. A layer of poly(3-hexylthiophene) (P3HT) (nominally 60 nm) was then spincoated on top, followed by the evaporation of 200 nm of silver at a pressure of 1 \times 10$^{-6}$ mbar to complete the devices. A key observation is the influence of the thermal treatment of the TiO$_2$ on the performance of otherwise identical solar cells. Devices made from unannealed TiO$_2$ exhibit a reasonable open-circuit voltage ($V_{oc}$) but a negligible short-circuit current ($J_{sc}$) and a very low fill
FIG. 1. (a) Photographic image of a bottle of TiO$_2$ dispersion with a concentration of 0.127 M. (b) DLS measurement of the TiO$_2$ dispersion. (c) XRD spectrum of a TiO$_2$ powder sample. (d)–(f) AFM images of a TiO$_2$ nanoparticulate layer on ITO with the addition of 8 mol.% TiAcAc prior to spincoating (2 $\times$ 2 $\mu$m), annealed in air at 135 $^\circ$C for 10 min (d), 45 min (e), and 90 min (f).

factor (FF), resulting in close to zero photovoltaic output (Fig. 2(a)). The extremely low $J_{sc}$ and FF indicate the presence of a very high series resistance, likely induced by the presence of precursor products. Indeed, when the TiO$_2$ is annealed at 135 $^\circ$C for only 10 min, we already find a reasonable conversion efficiency of around 9%. $J_{sc}$ keeps increasing with a longer TiO$_2$ thermal treatment, finding a maximum at 45 min, leading to an average efficiency of 12.6%. Efficiencies of even up to 13.6% (Fig. 2(b)) were obtained using an adapted annealing treatment as recently described by Saliba et al., where the perovskite is slowly heated to 100 $^\circ$C and then fast to 130 $^\circ$C. Longer TiO$_2$ treatments tend to have a vastly detrimental effect, initially resulting in highly fluctuating performance, and in the case of 90 min annealing even in a breakdown of all cells during the first measurement. It must not be overlooked that the best efficiencies obtained with our new low temperature processed TiO$_2$ layer are considerably higher than those obtained by using a sintered TiO$_2$ layer (500 $^\circ$C) we reported before ($J_{sc} = 20.8 \pm 0.4$ mA/cm$^2$; $V_{oc} = 0.919 \pm 0.006$ V; FF = 0.54 $\pm$ 0.01; $\eta = 10.4 \pm 0.4\%$).$^{17}$

To find the origin of the performance dependence on the thermal history of the TiO$_2$ layer, chemical analysis of the layers was performed using X-ray photoelectron Spectroscopy (XPS). No other elements than the ones expected from the starting products (C, N, O, Ti) were found in the TiO$_2$ layers, confirming their chemical purity. To probe more into detail, high-resolution core level spectra were taken of relevant elements. Fig. 3(a) shows N1s spectra of TiO$_2$ layers that were annealed at 135 $^\circ$C for times from 0 to 90 min. In the pristine case there are two clear components: a higher binding energy component that represents nitrates (407.5 eV) and a low binding energy component that corresponds with nitrogen in a carbonated environment (400.5 eV), resulting from nitric acid, and both TIP and TiAcAc, respectively.$^{27}$ As the TiO$_2$ layer is annealed, the nitrate component
shrinks, which is logical since the annealing temperature of 135 °C is well above the boiling point of nitric acid (83 °C). However, the nitrite component vanishes in favor of the component at lower binding energy, indicating that the nitric acid is disintegrated and its nitrogen being incorporated in the organic matrix of TiAcAc and TIP residue. This is seconded by the corresponding C1s core level spectra (Fig. 3(b)), as will be clarified in the following. The C1s comprises three components: one at 284.6 eV (C–C bonds), one at 286.8 eV (C–N and C–O bonds), and one at 289 eV (carboxyl). We observe that the C–N/C–O component at 286.8 eV decreases upon annealing, while the carboxylic component at 289 eV increases; these are the organic moieties from the TIP and TiAcAc that oxidize due to the annealing being executed in air. The small remainder of the peak at 286.8 eV must therefore be a C–N contribution, corresponding with the nitrogen peak at 400.5 eV. Notice that the complete disappearance of nitric acid at 45 min of annealing coincides with the maximum obtained efficiency of the corresponding solar cells (Fig. 2(a)), indicating that the presence of residual nitric acid induces a parasitic series resistance in the device and could possibly cause interfacial recombination.

We turn our attention now to the Ti2p spectra in Fig. 3(c), comparing a pristine versus a 45 min annealed layer. It is immediately obvious that there is no elemental Ti present in either case (454 eV); all Ti is in the 4+ oxidation state (459 eV). It has previously been speculated that TiAcAc might decompose upon heating, forming TiOx that acts as mortar between TiO2 particles, thus increasing the resulting layer’s conductivity.
should be corroborated by additional peaks appearing at the low binding energy side of the main line. In contrast, our measured Ti2p3/2 signal comprising only a Ti4+ component that is unchanged upon annealing at 135 °C, reveals the absence of any Ti3+ or Ti2+ contributions to the spectrum. In fact, when analyzing the Ti2p3/2 photoemission peak using a physically motivated line shape, a single symmetric line turns out to be sufficient to describe the experimental data, thus ruling out the presence of any additional components with oxidation state other than 4+.

At this point one might speculate that a degraded form of TiAcAc with 4+ oxidation state for Ti is capable of bridging the voids between TiO2 nanoparticles such that the resulting layer has a better conductivity. The source of an improved conductivity can indeed be traced back by comparing the Ti2p3/2 core level region for a layer after annealing at 135 °C with that of a conventional TiO2 sol-gel film sintered at 500 °C,31 both measured under identical experimental conditions (Fig. 3(c)). Clearly, the low-temperature deposition induces a significant line broadening as compared to the sintered film. As the line shape of the latter represents the combined effects of (i) line broadening due to the finite life time of the photoionized states of the probed Ti ions and (ii) the broadening induced by the finite energy resolution of the spectrometer, the increased line width in case of the low-temperature sample clearly points to an additional broadening effect. This additional line broadening most likely arises from small fluctuations/deviations in stoichiometry around the probed Ti ions, which can best be expressed as TiO2±δ, reflecting a distribution of different “chemically shifted” components that superimpose to form the measured photoemission line. Consequently, a significant density of, e.g., defects acting as dopants must be present in the low-temperature deposited titania films, which can most probably be assigned to the “mortar” material, easily explaining their improved conductivity.

FIG. 3. (a) High-resolution N1s core level spectra of TiO2 layers annealed for 0–90 min. (b) High-resolution C1s core level spectra of TiO2 layers annealed for 0–90 min. (c) High resolution Ti2p3/2 core level spectra of a TiO2 layer before (diamonds) and after (blue line) annealing for 45 min at 135 °C together with a spectrum acquired on a TiO2 layer sintered for 60 min at 500 °C (red line). For comparison, characteristic line positions of different oxidation states have been added.
FIG. 4. SEM images of perovskite layers deposited on TiO₂ base layer that were annealed at 135 °C in air for different times from 0 to 90 min.

Based on the analysis of the N1s and C1s spectra it is clear why the TiO₂ layer needs a thermal treatment of 45 min to obtain optimally functioning solar cells (decomposition of NO₃), though it is still obscure why a longer annealing step results in much less performance and in worst-case even shunting cells. To shed more light onto the negative effect of prolonged annealing, we now examine the perovskite layer. Scanning Electron Microscopy (SEM) images were recorded to investigate
whether the annealing time could have an influence on the consecutively deposited perovskite. The series of images in Fig. 4 reveal that there is indeed a correlation between the thermal history of the TiO$_2$ and the morphology of the eventual perovskite layer. The smoothest layer is obtained for a pristine TiO$_2$ layer, however the photovoltaic properties are, as mentioned, overshadowed in this case by the detrimental presence of HNO$_3$. An intermediate annealing time of the TiO$_2$ (10–45 min) returns grainy to needle-like perovskite morphologies that closely resemble those we previously reported, accompanied by decent photovoltaic performance. Those films do show a number of pinholes but, contrary to foregoing hypotheses, this does not need to degrade the resulting performance significantly. A treatment beyond 45 min appears to induce a considerably coarser perovskite morphology that shows much larger holes of several square micrometers. This is the likely cause why corresponding solar cells shunt easily; at such holes there is only a thin layer of P3HT (nominally 60 nm) that separates the TiO$_2$ from the top silver contact, so the occurrence of occasional short circuits is conceivable. It also deserves to be mentioned that the gradual change in morphology seen in the SEM results is paralleled by a decrease in peak height of the $\text{h}_0$ peaks in XRD (not shown), indicating a reduced preferential orientation of the perovskite crystals. This might lead to inferior charge transport and could be an additional reason for the low performance of solar cells containing overly annealed TiO$_2$ layers.

The origin of the perovskite morphology dependence on the thermal history of the TiO$_2$ layer can be explained by the presented chemical analysis. The observed increased presence of carboxyl moieties on the TiO$_2$ surface as function of annealing time points to an enhanced wettability of the surface for the DMSO-based perovskite precursor, intuitively implying better film formation. In spite of that, the eventual perovskite layers show an opposite trend, becoming rougher when deposited on longer annealed TiO$_2$. This can be rationalized by considering that the actual perovskite is formed only when the precursor film is heated, i.e., the initial solvent wetting properties are subordinate to the subsequent crystallization mechanism of the dried film. As has been shown before, a high quality perovskite film is often more easily formed when a preformed matrix or a textured surface is available, functioning as a kind of seed layer. Therefore, we propose that the organic residue from the starting products (at 286.8 eV in the C1s spectra in Fig. 3(b)) assists in the formation of smoother perovskite films. Upon the conversion into carboxylic compounds (at 289 eV), there are fewer seeding options for the perovskite crystals, causing them to form more rough and discrete structures, rather than an uninterrupted film.

Finally, it is interesting to remark that our extremely smooth anatase TiO$_2$ layers, having “minimal” contact area with the perovskite (i.e., a rather sharp bilayer interface), still allow for very high photocurrents. This is in contrast with a recent report from Yella et al., who observe that rather rutile TiO$_2$ layers, having a more intimate contact with the perovskite, are more efficient at extracting electrons. An explanation for this apparent inconsistency might be offered by their use of the triiodide-based perovskite (that generally has lower charge carrier diffusion lengths) as opposed to the mixed halide variety in our case (typically with higher diffusion length). In the former case a rougher TiO$_2$ film may assist in compensating for the slightly inferior charge carrier diffusion length of the triiodide perovskite by creating an ersatz bulk heterojunction, whereas in the latter case any additional roughness would be redundant.

In conclusion, we introduced a low-temperature processable TiO$_2$ electron collection layer, customized for planar heterojunction perovskite solar cells. The layer is deposited from an easy one-pot synthesis nanoparticle dispersion and requires a thermal treatment at only 135 °C, in contrast with the typical 450 °C–500 °C baking steps for conventional TiO$_2$ base layers, making it compatible with roll-to-roll fabrication on plastic foils. Even slightly lower temperatures could deliver the same outcome, provided longer annealing times and/or lower pressure. In addition, the resulting planar heterojunction devices significantly outperform their otherwise identical counterparts containing a high temperature processed TiO$_2$ layer. From this initial set of experiments, an efficiency of 13.6% is achieved, which is at the time of writing the highest value for solution-processed planar heterojunction mixed halide perovskite solar cells so far, and the highest value for a perovskite solar cell using P3HT as hole transporting layer. The results also show that the chemical composition and thermal history of the nanoparticulate TiO$_2$ film have a consequential impact on the device
performance. Finally, it cannot go unnoticed that the observed high photocurrents and fill factors are obtained even with films exhibiting a significant amount of pinholes, illustrating that the interplay between the selective contact and the perovskite is probably an even more important consideration than the smoothness of the perovskite itself.

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1 N.-G. Park, J. Phys. Chem. Lett. 4, 2423–2429 (2013).
2 H. J. Snaith, J. Phys. Chem. Lett. 4(21), 3623–3630 (2013).
3 NREL, see http://www.nrel.gov/ncpv/images/efficiency_chart.jpg, 2014.
4 A. Kojima, K. Teshima, Y. Shirai, and T. Miyasaka, J. Am. Chem. Soc. 131(17), 6050–6051 (2009).
5 J.-H. Im, C.-R. Lee, J.-W. Lee, S.-W. Park, and N.-G. Park, Nanoscale 3(10), 4088–4093 (2011).
6 J. H. Heo, S. H. Im, J. H. Noh, T. N. Mandal, C.-S. Lim, J. A. Chang, Y. H. Lee, H.-J. Kim, A. Sarkar, Md. K. Nazeeruddin, M. Gratzel, and S. I. Seok, Nat. Photonics 7(6), 486–491 (2013).
7 S. D. Stranks, G. E. Eperon, G. Grancini, C. Menelaou, M. J. P. Alcoccer, T. Leijtens, L. M. Herz, A. Petrozza, and H. J. Snaith, Science 342(6156), 341–344 (2013).
8 G. Xing, N. Mathews, S. Sun, S. S. Lim, M. Grätzel, S. Mhaisalkar, and T. C. Sum, Science 342(6156), 344–347 (2013).
9 C. Wehtrefenning, G. E. Eperon, M. B. Johnston, H. J. Snaith, and L. M. Herz, Adv. Mater. 26(10), 1584–1589 (2014).
10 V. D’Innocenzo, G. Grancini, M. J. P. Alcoccer, A. R. S. Kandada, S. D. Stranks, M. M. Lee, G. Lanzani, H. J. Snaith, and A. Petrozza, Nat. Commun. 5, 3586 (2014).
11 J. M. Ball, M. M. Lee, A. Hey, and H. J. Snaith, Energy Environ. Sci. 6(6), 1739–1743 (2013).
12 J. Burschka, N. Pellet, S.-J. Moon, R. Humphry-Baker, P. Gao, M. K. Nazeeruddin, and M. Gratzel, Nature (London) 499(7458), 316–319 (2013).
13 A. Abrusci, S. D. Stranks, P. Docampo, H.-L. Yip, A. K. Y. Jen, and H. J. Snaith, Nano Lett. 13(7), 3124–3128 (2013).
14 J. H. Noh, S. H. Im, J. H. Heo, T. N. Mandal, and S. I. Seok, Nano Lett. 13(4), 1764–1769 (2013).
15 N. J. Jeon, J. Lee, J. H. Noh, M. K. Nazeeruddin, M. Grätzel, and S. I. Seok, J. Am. Chem. Soc. 135(51), 19087–19090 (2013).
16 G. E. Eperon, V. M. Burlakov, P. Docampo, A. Goreiely, and H. J. Snaith, Adv. Funct. Mater. 24(1), 151–157 (2014).
17 B. Conings, L. Baeten, C. De Dobbeleare, J. D’Haen, J. Manca, and H.-G. Boyen, Adv. Mater. 26(13), 2041–2046 (2014).
18 M. Liu, M. B. Johnston, and H. J. Snaith, Nature (London) 501(7467), 395–398 (2013).
19 P. Docampo, J. M. Ball, M. Darwich, G. E. Eperon, and H. J. Snaith, Nat. Commun. 4, 2761 (2013).
20 J. You, Z. Hong, Y. Yang, Q. Chen, M. Cai, T.-B. Song, C.-C. Chen, S. Lu, Y. Liu, H. Zhou, and Y. Yang, ACS Nano 8(2), 1674–1680 (2014).
21 K. Kawano, R. Pacios, D. Poplavskyy, J. Nelson, D. D. C. Bradley, and J. R. Durrant, Sol. Energy. Mater. Sol. Cells 90(20), 3520–3530 (2006).
22 K. Wojciechowski, M. Saliba, T. Leijtens, A. Abate, and H. J. Snaith, Energy Environ. Sci. 7(3), 1142–1147 (2014).
23 A. Youla, L.-P. Heininger, P. Gao, M. K. Nazeeruddin, and M. Grätz, Nano Lett. 14(5), 2591–2596 (2014).
24 J. T.-W. Wang, J. M. Ball, E. M. Barea, A. Abate, J. A. Alexander-Webber, J. Huang, M. Saliba, I. Mora-Seró, J. Bisquert, H. J. Snaith, and R. J. Nicholas, Nano Lett. 14(2), 724–730 (2014).
25 A. Katoh, H. Kim, T. Hwang, and S. Kim, J. Sol-Gel Sci. Technol. 61(1), 77–82 (2012).
26 M. Saliba, K. W. Tan, H. Sai, D. T. Moore, T. Scott, W. Zhang, L. A. Estroff, U. Wiesner, and H. J. Snaith, "Influence of Thermal Processing Protocol upon the Crystalization and Photovoltaic Performance of Organic-Inorganic Lead Trihalide Perovskites," J. Phys. Chem. C (published online).
27 J. F. Moulder, W. F. Stickle, P. E. Sobol, and K. D. Bomben, Handbook of X-ray Photoelectron Spectroscopy (Physical Electronics, Inc., Minnesota, USA, 1995).
28 F. Werfel and O. Brummer, Phys. Scr. 28(1), 92–96 (1983).
29 NIST X-ray Photoelectron Spectroscopy Database, Version 4.1, http://srdata.nist.gov/xps/
30 G. K. Wertheim and S. B. Dicenzo, J. Electron Spectrosc. 37(1), 57–67 (1985).
31 C. De Dobbeleare, J. Mullens, A. Hardy, and M. K. Van Bael, Thermochim. Acta 520(1–2), 121–133 (2011).
32 D. Liu and T. L. Kelly, Nat. Photon. 8(2), 133–138 (2014).