RESEARCH ARTICLE

Extreme sensitivity of dye solar cells to UV-induced degradation

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Abstract
Present practice to avoid harmful effects of UV light on dye solar cells (DSC) is to use a UV filter. However, we show here that a standard 400 nm UV cutoff filter offers inadequate protection from UV-induced degradation. DSCs that were exposed to only visible light by LED lamps maintained 100% of their initial efficiency after 3000 hours of exposure, whereas the efficiency of DSCs subjected to full light spectrum (Xenon arc lamp) with an efficient UV filter dropped down to 10% of their initial performance already after 1500 hours. Optical analysis of the UV filter confirmed that the amount of light transmitted below 400 nm was negligible. These observations indicate that (a) DSCs can be very sensitive to even minor amount of UV and (b) eliminating the effects of UV light on DSC stability cannot easily be avoided by a UV filter on top of the cell. A detailed analysis of the degradation mechanisms revealed that the culprit to loss of performance was accelerated loss of charge carriers in the electrolyte of the DSCs—a typical symptom of UV exposure. These results suggest that commonly used stability tests under LED illumination are insufficient in predicting the lifetime of DSCs in outdoor conditions. Instead, for such purpose, we recommend solar cell stability to be tested with a full light spectrum and with a suitable UV filter.

1 | INTRODUCTION

Nanostructured third-generation solar cells have long attracted interest in the research community. They are expected to enter the market as low-cost alternatives to complement silicon solar cells, which currently dominate the solar energy production.[1] A common issue preventing large-scale commercialization of emerging solar technologies is their inadequate stability in real-world conditions, when compared to more established technologies. Therefore, a better understanding of the causes and methods for reducing the rate of degradation is crucial. For dye solar cells (DSC),[2] the lowered performance is commonly caused by the degradation of charge carriers in their electrolyte.[3] This process is called bleaching due to

the changes it causes in the electrolyte color, turning conventional iodine-based electrolyte from yellow to transparent, and it has been shown to be greatly accelerated by exposure to UV illumination.[3–5] Therefore, DSCs require UV protection to improve stability,[5] which is often accomplished with a UV cutoff filter, that is, a film that is placed between the light source and the photoactive area of the DSC.[6–8]

An important question that follows is if the present UV protection practices are adequate when the cells are placed outdoors. Outdoor tests are rare, and even the welcome exceptions[9,10] have not been focusing on long-term stability but demonstrated few weeks or months of exposure.[9] One very long test (2.5 years) has been reported, and the devices survived the aging test.[10] The cells were kept under a 1 cm

thick cover, inevitably absorbing large proportion of UV. The results indicated long-term stability under such a cover, but did not provide evidence on stability with a normal thin UV filter. Thus, accelerated aging tests would be highly relevant to verify the UV stability of DSCs.

Accelerated aging tests are often done without UV light (under LED lights), and the results are extrapolated to assess long-term stability in outdoor conditions. This is done assuming that UV degradation could be omitted altogether when using UV filters. As only a few studies have reported details on the intensity and spectral shape of the UV illumination the cells were exposed to, it is difficult to determine the exact impact of UV.[11] One reason for this is the lack of standardized procedures for DSC aging tests. A further complication is that most solar simulator spectral standards are defined for wavelengths above 400 nm, thus overlooking the UV part of the solar spectrum.[11]

Lack of standardized procedures is one cause of discrepancies between aging studies as noted by our previous studies and by others.[11–13] One critical area where studies give vastly varying results is the effect of water to the stability of DSCs: Some studies report that the even small amounts of water are detrimental,[14–16] while others claim that having a substantial amount of water in the device can even improve the performance both initially and in long-term.[17,18] It has also been reported that the UV light-induced degradation could be connected to water in the devices.[13] This may indicate that the different light sources used in different studies lead to varying, even contradicting results on how water affects the stability of DSCs. The present contribution aims provide new information on these discrepancies.

In this paper, the ability of a high-performance UV cut-off filter to protect DSCs from UV radiation is investigated. Subsequently, the effectiveness of the most commonly used UV protection methods for DSCs is assessed. We prepared a large number of DSC devices and followed their degradation for 3000 hours, which is three times longer compared to usual light soaking tests. Half of the cells were aged under a Xenon arc lamp, which emits light in the UV, while protected by a 400 nm cutoff filter. The other half of the cells was illuminated by white LEDs, which emit no UV light. The performance of the cells was constantly monitored during the aging process, and changes in electrolyte charge transport were analyzed with electrochemical impedance spectroscopy and color analysis.

2 | METHODS

Twenty-three identical DSC samples were prepared for the aging test. The samples were randomly split into two groups: 11 to degradation under UV-filtered full spectrum and 12 to degrade while illuminated only by visible light.

The structure of the cells was a sandwiched configuration between two substrates. Both substrates were conducting fluorine-doped tin oxide (FTO) glass (TEC-15, Pilkington). The substrates were washed by hand in mild detergent and then sonicated firstly in Hellmanex® III (Hellma analytics), secondly in ethanol, and finally in acetone (each for 10 minutes). The substrates were subjected to UV treatment (UV/Ozone ProCleaner™, Bioforce Nanosciences) for 20 minutes right before use.

The photoelectrode substrates were covered with a compact TiO_2 layer deposited by immersing the substrates in deionized water with 1 wt% of titanium(IV) chloride tetrahydrofuran complex for 30 minutes in 70°C. The nanoporous TiO_2 photoelectrode was then screen-printed (AT-60PD, ATMA) on the substrate in three layers: first two layers of smaller, absorbing particles (DSL 18NR-T, Dyesol) and then one layer of larger, light scattering particles (DSL 18NR-AO, Dyesol). The purpose of these larger particles was to reflect unabsorbed light back to the absorbing layer, thus increasing the efficiency of the cell.[19] This process resulted in a 12 μm thick layer with an area of 0.4 cm^2. The printed TiO_2 layer was sintered in 450°C for 30 minutes. After the layer was sintered, the treatment in deionized water with titanium(IV) chloride tetrahydrofuran complex was repeated. The photoelectrode was finalized by sensitizing it by immersing it in a dye solution overnight. The dye solution was 0.3 mmol/L of Z907 (Dyesol) in a 1:1 solvent of acetonitrile (ACN) and tert-butyl alcohol (tBA). Dye Z907 was selected as the sensitizer since it has demonstrated excellent stability in earlier studies.[20]

The counter electrode was prepared by pipetting 4 μL of 10 mmol/L H_2PtCl_6 in 2-propanol on an FTO glass substrate. After the solution had dried, the counter electrode was thermally treated in 390°C for 20 minutes. This resulted in a counter electrode with a thin attached layer of Pt catalyst particles.

The DSCs were assembled by melting a stack of two Surlyn 1702 ionomer resin films (total thickness 40 μm, DuPont) between the edges of the photo- and counter electrodes. Then, the space between the electrodes was filled with a liquid electrolyte by injecting it through a hole in the counter electrode substrate. The electrolyte had 0.05 mol/L I_2, 0.5 mol/L 1-methylbenzimidazole (NMBI), 0.5 mol/L 1-propyl-3-methylimidazolium iodide (PMII), and 0.1 mol/L guanidium thiocyanate (GuSCN) in 3-methoxypropionitrile (MPN). The electrolyte-filling holes in the counter electrode were sealed by melting another Surlyn film with a microscope glass over the holes. Copper tapes were attached to the electrodes, and the electrical contact between the FTO and copper was improved with a layer of silver paint (SCP, Electrolube). The sealing was finished with a layer of 2-component epoxy glue over the interface of the two electrodes and the contact point of the copper tapes.

A fairly standard iodine liquid electrolyte was chosen for this study since it has previously demonstrated high stability and long lifetime.[12] Furthermore, the strong yellow color of the iodine charge carriers allows the tracking of charge carrier concentration through color analysis.

All the fresh DSC samples were placed in light soaking under halogen lamps and a UV filter for 10 hours after they were assembled to ensure they had reached steady-state operation.

The initial and final efficiencies of the cells were measured in simulated AM1.5G conditions with a Peccell PEC-01 solar simulator. The simulator was calibrated with PV measurements Inc Si KG5, and the used potentiostat was a Keithley 2420 3A Sourcemeter.

The DSCs were subjected to constant illumination for the duration of the aging test. The samples under only visible light were illuminated with white LED lamps (CREE Edge HO240), and the cells under UV-filtered (Asmetronic SFC-10 UV filter) full spectrum were aged in a temperature-regulated chamber (Suntest XLS+, Atlas) with a xenon lamp (NXE 1700, Atlas). The spectra of the lamps were measured with OceanOptics USB2+U06662 spectrometer. Relative air humidity during the aging test ranged from 10% to 26%. The temperature was $40 \pm 1°C$ for cells under LED illumination and $55 \pm 2°C$ under the xenon lamp. The IV and EIS characteristics of the cells were measured automatically for the whole duration of the test using a BioLogic SP-150 potentiostat and an Agilent 34980A Multifunction Switch/Measure Unit. The measurement setup was constantly measuring IV and EIS characteristics of the cells: One cell was measured, while the others were in an open circuit. Scan rate of the IV measurements was 5 mV/s. The cells were illuminated, and in open-circuit condition during the EIS measurements, the amplitude of the alternating voltage was 10 mV and frequency ranged from 0.1 Hz to 100 kHz. The EIS results were analyzed by equivalent circuit (see Supporting Information) fits with Zview2 (Scribner Associates, Inc). The temperature of the cells was estimated with a dummy cell. The dummy cell was constructed by placing a thermocouple and a piece of colored paper matching the photoelectrode color between two TEC-15 glass substrates. Then, the edges of the dummy cell were sealed with tapes. The dummy cell was kept in the aging conditions for several hours before the measurement to allow the temperature to stabilize.

In addition to the automated measurements, the cells were photographed weekly in a specifically designed photographing setup to track color changes in the electrolyte of the cells. The electrolyte color has been directly linked with concentration of charge carriers in a previous study.[21] The camera used for photographing was an Olympus E-620. The photographing chamber illuminated the cells with white LEDs, while shielding them from ambient light. The color profiles of the digital images were standardized by creating a profile from an image of a color checker passport (X-Rite) and applying it to all of the images with Adobe Lightroom. RGB values of the electrolyte were obtained from the images with a MATLAB script.

3 | RESULTS AND DISCUSSION

3.1 | Photovoltaic performance

The cells were divided into two equally large groups and aged either under LED or UV-filtered full-spectrum illumination. The two groups had similar initial performance (see Supporting Information). Since both groups of cells were measured under different light spectra during the aging, their IV measurements gave different values already at the beginning of the aging even though the cells were identical. Since we are focused on the progress of cell degradation, the IV parameters are reported relative to the initial value.

The DSCs exposed to UV-filtered full spectrum had degraded to 80% of the initial efficiency by 800 hours and completely (to 20% of the initial efficiency) by 1300 hours (see Figure 1). In contrast, DSCs that were exposed to only visible light were stable with respect to their initial efficiency throughout the approximately 3000 hours test (Figure 1). In the latter case, there was only minor increase in short-circuit density (I_{SC}) and small decrease of open-circuit voltage (V_{OC}), but those differences canceled each other out in terms of changes in efficiency. Initially, the performance of all cells improved during a stabilization period that lasted roughly 300 hours. During the entire aging test, I_{SC} of the cells under only visible light decreased 7% points from the peak value, V_{OC} decreased 13% points, and fill factor (FF) remained constant for the duration of the aging. The cells that were illuminated with UV-filtered full spectrum degraded significantly faster than the cells with only visible light: The I_{SC} of those cells dropped to only 14% of the peak value after 1500 hours of light soaking. Their efficiency was decreased to 10%, V_{OC} to 91% and FF to 64% of the peak value by 1500 hours.

3.2 | Investigating degradation

To study what part of the DSCs suffered most during the light soaking, electrochemical impedance spectra (EIS) of the cells were measured along with the automated IV measurements (Figure 2). EIS measures impedance of the cells when alternating voltage is applied to the cells at varying frequencies. The different components of DSCs respond at different frequencies, therefore allowing in situ identification of their corresponding internal resistances during the aging.

The results of EIS measurements support the findings of the IV measurements: There is barely any change in
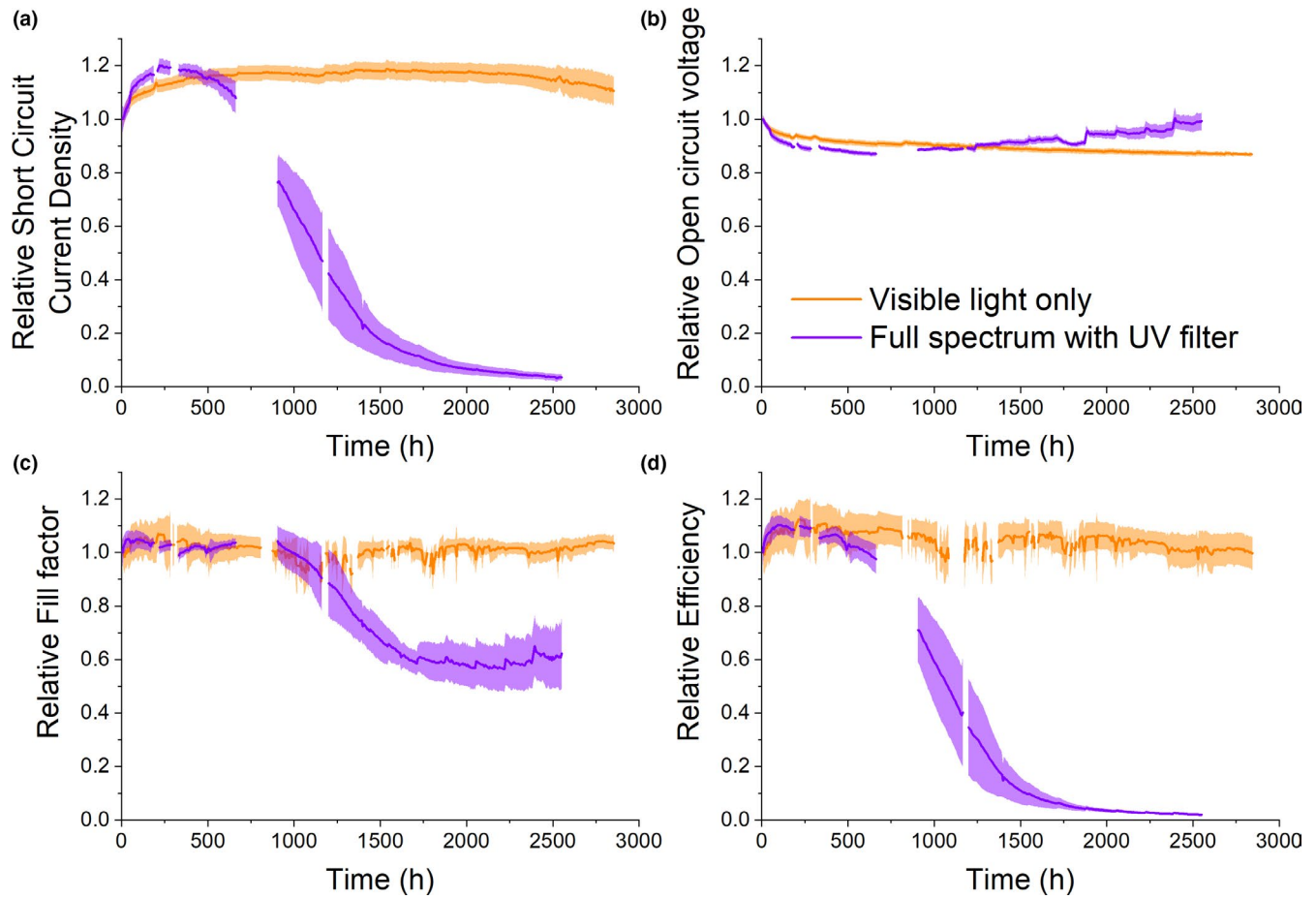
FIGURE 1 The evolution of standardized IV parameters (A) short-circuit current density, (B) open-circuit voltage, (C) fill factor, and (D) efficiency) during the degradation study. Orange curves refer to the cells aged under LED light, and violet curves to the cells that were illuminated by a xenon lamp with a UV filter. The solid line is the average of the samples in each group, and the shaded region signifies the standard deviation between different samples of the group. Gap in the UV-filtered light-spectrum data is due to a data collection error
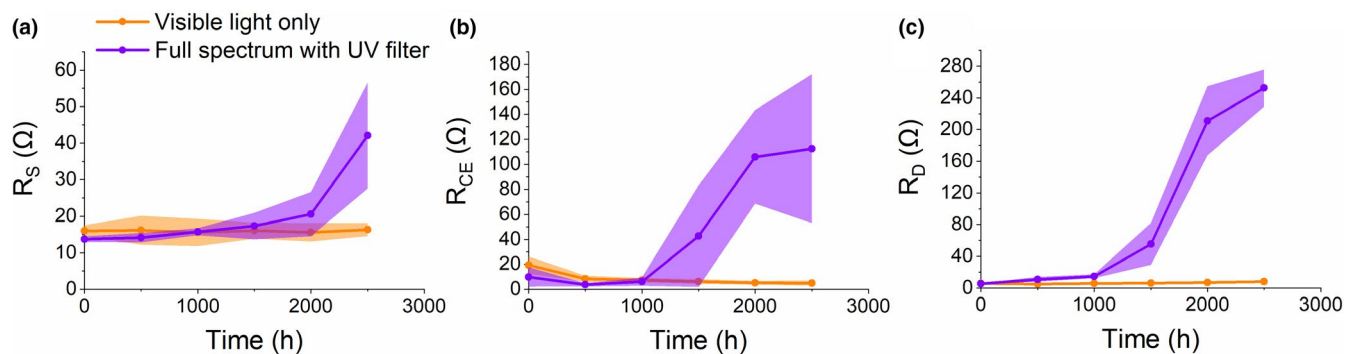
FIGURE 2 The evolution of the internal resistance components (A) series resistance, (B) counter electrode charge transfer resistance, and (C) electrolyte diffusion resistance of the DSCs during light soaking at open-circuit conditions. Dots connected by lines illustrate the averages from different measurements, while shaded area is their standard deviation. The values were obtained from fits to Nyquist plots measured with EIS

the internal resistances of the cells soaked only in visible light, while the resistances increased for the cells under UV-filtered full spectrum (Figure 2). Ohmic series resistance R_S, typically related to the sheet resistance of the TCO coating and the current collector contacts, remained stable in both groups for the first 1000 hours, after which

it started to increase in the cells exposed to UV-filtered full-spectrum light. This increase, however, became substantial only after the other internal resistances had degraded the DSCs to below 10% of their initial efficiency. Thus, the changes in the R_S were irrelevant to the operation of the DSCs here.

The largest contribution to increase in internal resistance was in the electrolyte diffusion resistance (R_D) of the cells under UV-filtered full spectrum. Initially, their R_D was 5.2 ± 0.5 Ω, but at the end of the study it had reached 250 ± 20 Ω (Figure 2C), corresponding to a massive 50-fold increase. For the cells in visible light, the change was insignificant, from 6 ± 2 Ω to 8 ± 1 Ω. The increase of R_D for cells under filtered UV began as a slow, steady increase for the first 1000 hours in the samples under full-spectrum illumination but accelerated from that point onward. The increase of diffusion resistance is often connected with the loss of charge carriers in the electrolyte, since it is inversely proportional to the concentration of charge carriers in the electrolyte.[5,21] In the case of iodine electrolyte that was used in this study, I_3^- is the current limiting charge carrier and its loss is generally the reason behind increased diffusion resistance.[22]

The charge transfer resistance at the counter electrode/electrolyte interface (R_{CE}) also increased notably in the cells aged under UV-filtered full spectrum, from the initial value of 10 ± 7 Ω to 110 ± 60 Ω at the end of the aging (Figure 2B), which is an average increase of 1100%. Also, in this case the resistance had remained constant up until 1000 hours of degradation, when the increase began. R_{CE} is dependent on charge transfer in both the electrolyte and the counter electrode catalyst layer. Since the development of R_D indicates that charge diffusion in electrolyte has deteriorated and Pt counter electrodes can be considered stable,[23] it is likely that the increase in R_{CE} has the same cause as increase of R_D. Thus, the massive increase in both R_{CE} and R_D is likely caused by loss of charge carriers in the electrolyte. The increased R_{CE} and R_D in the solar cells under full light spectrum are also substantial enough to explain the major decrease of FF seen in Figure 1C. The R_{CE} of DSCs in only visible light had in contrast decreased during the aging from 19 ± 7 Ω to 5 ± 2 Ω (Figure 2B).

The loss of charge carriers can be studied in more detail by tracking the color changes in the electrolyte of the cells.[3,5,21] Since tri-iodide gives the electrolyte its distinct yellow color, the loss of tri-iodide is observable as bleaching of the electrolyte. This was studied by photographing the cells weekly in carefully controlled illumination conditions and calculating the average yellow value from a small area in the electrolyte of the cells (Figure 3). The electrolyte in both of the cell groups bleached during the aging, but the rate of bleaching was much faster in the cells exposed to the UV-filtered full spectrum (slope of linear fit was −0.025 Y-units/h compared to −0.012 Y-units/h). The bleaching was relatively linear which suggests that the loss rate of charge carriers was consistent during the light soaking.

The two groups of cells had almost identical aging conditions. The illumination intensity had been set to represent 1 Sun conditions, and the aging setups were located next to
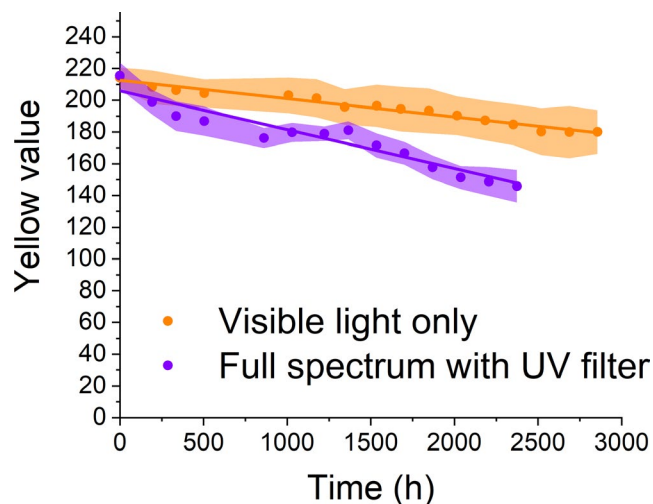
FIGURE 3 Decrease of the yellow value of the electrolyte in both of the studied groups. RGB color of the electrolyte was converted to CMYK color space, from which a value for the yellow color can be obtained. The dots are the averages of each measurement, while the shaded area is the standard deviation. The lines are a linear fit to the data with following fit parameters: for visible light slope was −0.0116 Y-units/h and R-value 0.986, and for UV-filtered full-spectrum slope was −0.0245 Y-units/h and R-value 0.943. See Supporting Information for example photographs

each other in same ambient conditions. Only differences were caused by the light soaking lamps themselves. The lamps had differences in emission spectra shapes and produced heat. The average temperature was 40°C (no cooling) for cells illuminated by LED lamps and 55 ± 2°C (with maximum cooling provided by the unit) for cells illuminated by Xenon lamps. The cells in full light spectrum could not be cooled down any further, and adding heating for UV system was complicated. While high temperatures tend to accelerate DSC degradation, the temperatures in this study are low enough to not to be the main cause for accelerated loss of charge carriers in cells: It has been shown that degradation due to temperature start to be significant at 80°C and above.[12,20]

However, we wanted to further rule out the role of temperature as the driving degradation mechanism. We did an additional test where a DSC was illuminated with no UV light in the spectrum under 9 Sun intensity at 52 ± 2°C (similar to the temperature experienced by "full spectrum with UV filter" cells). The sample showed no I_{sc} degradation after 1000 hours of degradation (see Supporting information for the data) in contrast to the "full spectrum with UV filter" that had already lost more than 20% of their initial I_{sc}. This is even with 9 Sun intensity, and literature suggests that testing under higher light intensities expedites aging tests.[24] Had the temperature been the main driving factor for the differing degradation rates of our "visible only" and "full spectrum with UV filter" cells, this sample cell should have degraded at a similar or higher rate to the "full spectrum with UV filter" cells. The test confirms that the temperature difference in the

original experiment did not cause the observed difference in degradation rates in Figure 1.

This leaves the spectra of the light soaking lamps (Figure 4) as the main difference between the cell groups. While the spectra differ on all wavelengths, the low wavelength (high photon energy) region is of most interest when it comes to DSC degradation. Two mechanisms for UV-induced degradation have been suggested to be at work in DSCs. Firstly, it is theorized that holes generated by direct excitations of electrons in the TiO_2 layer react with oxygen radicals adsorbed on the TiO_2 surface. This creates surface trap states which are then capable of reacting with charge carriers of the electrolyte irreversibly, decreasing the amount of viable charge carriers.[25,26] The effect of exposed TiO_2 surface to accelerate electrolyte degradation has also been shown experimentally.[21] The second electrolyte degradation path is related to the presence of water inside DSCs. It is possible that UV light causes water splitting inside the cell and the reaction products react further with the charge carriers, degrading the electrolyte.[14,27] It is entirely possible that both of these mechanisms are affecting the cells simultaneously.

Both of these suggested degradation mechanisms are triggered by UV light revealing that the high-energy end of the solar spectrum has to be monitored carefully when aiming for stable DSCs. Comparing the spectra in Figure 4 reveals that even with a UV filter, the spectra of Xenon lamps reaches lower wavelengths than LED light. It is possible that photons in this wavelength region, between roughly 395 nm and 415 nm, have enough energy to trigger the aforementioned degradation mechanisms even though it is still above the wavelength corresponding to the band gap of pure anatase TiO_2 (386 nm). For perovskite solar cells containing TiO_2, cutoff filters as high as 440 nm have been suggested.[26]
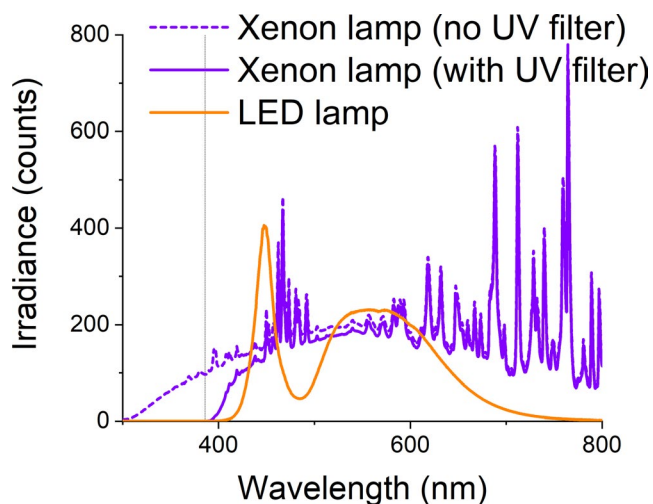
FIGURE 4 Spectra of the lamps used for aging the DSCs. The spectrum of the xenon lamp is displayed both with (solid line) and without (dashed line) the UV filter. The vertical line marks the wavelength corresponding to the band gap of anatase TiO_2 (386 nm)

Another possible source UV light is any UV light transmitted through the cutoff filter. Although the amount of transmitted light below 395 nm was below the detection threshold of our spectrometer, it is possible that small amounts of light passed the filter and triggered UV degradation of the cells. Our previous studies with full UV light without any filter indicated that similar DSCs degraded to 20% of their initial efficiency in 200 hours.[28] Since DSCs are extremely sensitive to UV illumination, here even minor UV light might also be the cause of the observed accelerated degradation.

Previous studies prove that a UV filter is necessary to extend the device lifetime since without any filter the cells last only some days (50-100 hours),[5,28] and here, the devices with the filter lasted ten times longer. But these results raise the question what kind of filter would be sufficient to stabilize the cells. While the filter used here did have a high cutoff wavelength (not only UV light but also high-energy visible light was cutoff) and over 95% protection in wavelengths below the cutoff,[29] it still had either too low cutoff wavelength (400 nm), transmitted too large amount of UV below the cutoff, or both. It slowed the degradation when compared to a case without any UV filter, but it was insufficient in reaching stable results gained with visible light only. It should be remembered that UV cutoff filters also decrease the total amount of radiation that reaches the absorbing layer of the DSC. Therefore, the choice of the cutoff wavelength is a trade-off between extended device lifetime and high performance. For example, calculated from typical Z907 dye quantum efficiency curve, 400-nm cutoff filter decreases the absorption spectrum of a DSC device by 20% and 440-nm cutoff filter by 30%. The IPCE results used to calculate these are from[22] and the filters were assumed to have zero transmittance below cutoff wavelength and 100% transmittance above it. Choosing the optimal cutoff wavelength can thus impact the overall efficiency of the device significantly.

UV cutoff filters are not the only method for reducing the amount of UV light absorbed by a DSC device. The use of different UV-blocking particles has also been suggested.[30] It is also possible to avoid the losses caused by a UV-blocking layer and still protect the DSC from UV by downconverting or downshifting the incoming UV light. By adding a layer or particles capable of converting UV photons to longer wavelengths, thus avoiding the detrimental effects of UV light, but still allowing the utilization of UV photons in energy conversion.[8,31–33]

4 | CONCLUSIONS

Our results show that the degradation of DSC performance is significantly accelerated even by minor amounts of UV illumination. DSC protected by a 400-nm cutoff filter and continuously illuminated with a Xenon arc lamp reduced

their initial efficiency to 20% of the original value in less than 1500 hours, while cells exposed to LED light maintained 100% of their initial efficiency for 3000 hours. EIS measurements and electrolyte color analysis revealed that the cause for the degradation was the loss of tri-iodide charge carriers in the electrolyte of the cells also known from previous literature.[4]

The UV part of the solar spectrum has often been overlooked in previous aging studies, which even tend to lack adequate description of the aging measurement conditions.[11] The impact of UV on DSCs is often dismissed as an issue that can be easily dealt with by introducing a UV filter.[7] Only 15% of reported accelerated aging tests have UV light and quantify the intensity of UV light.[11] Present study demonstrates that UV degradation is still a topical, urgent matter in DSC stability, and should be considered in research on DSC lifetime in simulated real-world conditions.

While the UV filter used here had a high cutoff wavelength extending to visible light and an excellent protection below the cutoff, it was still insufficient in stabilizing the devices. If a higher cutoff is needed that goes even deeper to visible light range, it has an adverse effect on the photon flux that reaches the photoelectrode of the device to produce current. An optimal cutoff filter is a trade-off between high solar conversion efficiency and long device lifetime. Since even a small amount of transmitted UV light suppresses device lifetime, the efficiency of the selected UV-blocking method should be considered carefully.

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REFERENCES

1. Fraunhofer Institute for Solar Energy Systems. *Photovoltaics Report*; 2019.
2. O'Regan B, Grätzel M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO2 films. *Nature*. 1991;353:737-740.
3. Mastroianni S, Asghar I, Miettunen K,, et al. Effect of electrolyte bleaching on the stability and performance of dye solar cells. *Phys Chem Chem Phys*. 2014;16:6092-6100.
4. Bari D, Wrachien N, Meneghesso G, et al. Study of the effects of UV-exposure on dye-sensitized solar cells. *IEEE Int Reliab Phys Symp Proc*. 2013;4B.3.1-4B.3.7.
5. Miettunen K, Poskela A, Tiihonen A, et al. From identification of electrolyte degradation rates to lifetime estimations in dye solar cells with iodine and cobalt redox couples. *Nano Energy Syst*. 2016;1(2):29-41.
6. Pettersson H, Gruszecki T. Long-term stability of low-power dye-sensitised solar cells prepared by industrial methods. *Sol Energy Mater Sol Cells*. 2001;70:203-212.
7. Carnie M, Watson T, Worsley D. UV filtering of dye-sensitized solar cells: the effects of varying the UV cut-off upon cell performance and incident photon-to-electron conversion efficiency. *Int J Photoenergy*. 2012;2012:1-9.
8. Liu J, Yao Q, Li Y. Effects of downconversion luminescent film in dye-sensitized solar cells. *Appl Phys Lett*. 2006;88:10-13.
9. Lepikko S, Miettunen K, Poskela A, Tiihonen A, Lund PD. Testing dye-sensitized solar cells in harsh northern outdoor conditions. *Energy Sci Eng*. 2018;6(3):187-200.
10. Kato N, Takeda Y, Higuchi K, et al. Degradation analysis of dye-sensitized solar cell module after long-term stability test under outdoor working condition. *Sol Energy Mater Sol Cells*. 2009;93:893-897.
11. Tiihonen A, Miettunen K, Halme J, Lepikko S, Poskela A, Lund PD. Critical analysis on the quality of stability studies of perovskite and dye solar cells. *Energy Environ Sci*. 2018;11(4):730-738.
12. Asghar MI, Miettunen K, Halme J,, et al. Review of stability for advanced dye solar cells. *Energy Environ Sci*. 2010;3:418.
13. Hinsch A, Veurman W, Brandt H, Flarup Jensen K, Mastroianni S. Status of dye solar cell technology as a guideline for further research. *ChemPhysChem*. 2014;15:1076-1087.
14. Tiihonen A, Miettunen K, Rendon S,, et al. The effect of electrolyte purification on the performance and long-term stability of dye-sensitized solar cells. *J Electrochem Soc*. 2015;162:H661-H670.
15. Hahlin M, Johansson EMJ, Schölin R, Siegbahn H, Rensmo H. Influence of water on the electronic and molecular surface structures of Ru-dyes at nanostructured TiO2. *J Phys Chem C*. 2011;115:11996-12004.
16. Sumita M, Sodeyama K, Han L, Tateyama Y. Water contamination effect on liquid acetonitrile/TiO_2 anatase (101) interface for durable dye-sensitized solar cell. *J Phys Chem C*. 2011;115:19849-19855.
17. Law C, Pathirana SC, Li X,, et al. Water-based electrolytes for dye-sensitized solar cells. *Adv Mater*. 2010;22:4505-4509.
18. Zhu K, Jang S-R, Frank AJ. Effects of water intrusion on the charge-carrier dynamics, performance, and stability of dye-sensitized solar cells. *Energy Environ Sci*. 2012;5:9492.
19. Ito S,Zakeeruddin SM, Humphry-Baker R, et al. High-efficiency organic-dye-sensitized solar cells controlled by nanocrystalline-TiO2 electrode thickness. *Adv Mater*. 2006;18:1202-1205.
20. Harikisun R, Desilvestro H. Long-term stability of dye solar cells. *Sol Energy*. 2011;85:1179-1188.
21. Asghar MI, Miettunen K, Mastroianni S, Halme J, Vahlman H, Lund P. In situ image processing method to investigate performance and stability of dye solar cells. *Sol Energy*. 2012;86:331-338.
22. Poskela A, Miettunen K, Tiihonen A, Lund PD. The state of external circuit affects the stability of dye-sensitized solar cells. *Electrochim Acta*. 2018;275:59-66.
23. Yun S, Lund PD, Hinsch A. Stability assessment of alternative platinum free counter electrodes for dye-sensitized solar cells. *Energy Environ Sci*. 2015;8:3495-3514.

24. Law C, Miseikis L, Dimitrov S, et al. Performance and stability of lead perovskite/TiO2, polymer/PCBM, and dye sensitized solar cells at light intensities up to 70 suns. *Adv Mater*. 2014;26:6268-6273.

25. Weidmann J, Dittrich TH, Konstantinova E, Lauermann I, Uhlendorf I, Koch F. Influence of oxygen and water related surface defects on the dye sensitized TiO2 solar cell. *Sol Energy Mater Sol Cells*. 1999;56:153-165.

26. Leijtens T, Eperon GE, Pathak S, Abate A, Lee MM, Snaith HJ. Overcoming ultraviolet light instability of sensitized TiO2 with meso-superstructured organometal tri-halide perovskite solar cells. *Nat Commun*. 2013;4:1-8.

27. Lu H-L, Shen TF-R, Huang S-T, Tung Y-L, Yang TC-K. The degradation of dye sensitized solar cell in the presence of water isotopes. *Sol Energy Mater Sol Cells*. 2011;95:1624-1629.

28. Poskela A, Miettunen K, Borghei M, et al. Nanocellulose and nanochitin cryogels improve the efficiency of dye solar cells. *ACS Sustain Chem Eng*. 2019;7:10257-10265.

29. METOLIGHT® UV-Filter. https://www.asmetec-shop.de/asm_datenblaetter/METOLIGHTUV-Filter-DB-E.pdf. Accessed 24th February 2020

30. Sun H, Weickert J, Hesse HC, Schmidt-Mende L. UV light protection through TiO2 blocking layers for inverted organic solar cells. *Sol Energy Mater Sol Cells*. 2011;95:3450-3454.

31. Riaz R, Ali M, Maiyalagan T,, et al. Dye-sensitized solar cell (DSSC) coated with energy down shift layer of nitrogen-doped carbon quantum dots (N-CQDs) for enhanced current density and stability. *Appl Surf Sci*. 2019;483:425-431.

32. Kennedy M, Ahmed H, Doran J, et al. Large Stokes shift downshifting Eu(III) films as efficiency enhancing UV blocking layers for dye sensitized solar cells. *Phys Status Solidi Appl Mater Sci*. 2015;212:203-210.

33. Klampaftis E, Ross D, McIntosh KR, Richards BS. Enhancing the performance of solar cells via luminescent down-shifting of the incident spectrum: a review. *Sol Energy Mater Sol Cells*. 2009;93:1182-1194.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section.