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Concentrated sunlight for accelerated stability testing of organic photovoltaic materials: towards decoupling light intensity and temperature

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ABSTRACT

We have demonstrated accelerated degradation studies of organic photovoltaic materials using concentrated sunlight, where the atmosphere, temperature and illumination intensity were *independently* controlled. Testing various schemes for controlling the sample temperature under concentrated sunlight showed that heating of P3HT:PCBM was caused by photons at the absorbed wavelength range and dissipation of excess photon energy, and not necessarily by IR photon absorption. Sunlight chopping was found to be an effective method for independent temperature control under illumination by concentrated sunlight.

The first accelerated degradation tests using sunlight concentration applied to P3HT:PCBM *blends* were reported. P3HT:PCBM blends exposed to concentrated sunlight in the presence of traces of oxygen/humidity showed degradation induced by photo-oxidation of the P3HT backbone within the P3HT:PCBM blend, which is significantly thermally accelerated, in agreement with previous observations. However, this could be demonstrated in a time scale of minutes and hours, that is, significantly accelerated. Exposure of well encapsulated P3HT:PCBM films to concentrated sunlight demonstrated stability up to 3,600 sun∗hours, corresponding to about 1.6 years of operating time. This result was obtained at 300 suns exposure after merely 12 h, demonstrating the advantage of using concentrated sunlight for accelerated stability tests. These tests can therefore combine extremely high acceleration factors with profound understanding of the effect of various, independently controlled factors on the degradation mechanisms.

1. Introduction

The development of organic photovoltaics (OPV) faces the noteworthy challenge of combining high efficiency and operational stability. Recently, the lifetime of polymer solar cells has been considerably improved. For example, well-encapsulated bulk heterojunction solar cells based on poly(3-hexylthiophene) (P3HT) blended with the fullerene derivative phenyl C61 -butyric acid methyl ester (PCBM) [1–4] or poly[[9-(1-octylnonyl)–9H-carbazole–2, 7-diyl]–2,5-thiophenediyl–2,1,3-benzothiadiazole–4,7-diyl–2,5-thiophenediyl] (PCDTBT) blended with PCBM [5] have shown lifetimes well beyond a year. This achievement raises the need for relevant accelerated tests of the operational lifetime, especially as a rapid tool for screening newly developed materials and devices. Accelerated testing can be even more crucial for the study of degradation mechanisms and stability of 'small molecule' OPV devices [6–8], as these bilayer devices exhibited longer lifetimes than polymer-based cells [9].

The introduction of various aggressive conditions can increase the degradation rate relative to conventional degradation at standard test conditions (1 sun=100 mW/cm^2, 25 °C) thus decrease the test time. Stability testing of polymer solar cells and their components is commonly done under natural or simulated

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1 sun illumination, and can be accelerated by elevated temperatures with acceleration factors up to slightly over 20 [10–14]. The use of natural and simulated *concentrated* sunlight has recently shown the potential for further accelerated stability testing of OPV devices [15–19] and materials [16–18]. Concentrated light degradation testing of non-encapsulated layers of pure polymers utilized in OPV active blends demonstrated an acceleration of the polymer photo-bleaching in air, with acceleration factors for degradation in P3HT absorption exceeding 100 for exposure to 150 suns or more [15,16,18].

Degradation mechanisms in OPV are complex and include a variety of processes: photo-bleaching of the conjugated polymers (which in turn can be governed by various mechanisms, for example, the attack by singlet oxygen, formed by energy transfer from the polymer's triplet state [20–22], or photo-generated radical oxidation [23–25]), photo-oxidation of fullerene moieties [26,27], degradation induced by the hole conducting poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) layer [28–31], ion migration from the electrodes and degradation at these interfaces [13,32–36], morphological changes in the device [26,37–39], etcetera. Most of these processes are stimulated by external factors such as light, heat, oxygen or moisture [15], and can be affected by the composition and structure of the OPV materials and the device architecture. As a result, they are almost inseparable under standard device testing and operation. Understanding these degradation mechanisms, which is essential for the development of stable OPV materials and devices, requires detailed characterization of the factors affecting them.

Sample temperature rise due to exposure to concentrated light is a fundamental problem for OPV accelerated degradation testing, which becomes more problematic with increased light intensities and acceleration factors. Such temperature rise can cause difficulties in analyzing the outcome of concentrated light testing, including

- nonlinear dependence of the acceleration factor on light intensity [16], which complicates comparison of the results obtained at various light intensities even for the same exposure dose (1 *sun·hour* has been suggested as a dose unit [16]), and
- difficulties in separating light induced mechanisms from those controlled by the sample temperature.

Deviation from linear dependence of the degradation rate of P3HT absorption on the light intensity was previously attributed to thermal acceleration of the photo-oxidation caused by sample heating under concentrated light in air. The photo-oxidation mechanism was conserved at various light intensities [18]. Photolysis at nitrogen atmosphere was not thermally activated and was therefore not affected by the temperature [16].

Herein we demonstrate stability testing of OPV materials with highly concentrated natural sunlight up to ~5,000 suns, where the various parameters affecting degradation - atmosphere, temperature and illumination intensity - were *independently* controlled. We report the first accelerated tests using concentrated sunlight applied to P3HT:PCBM *blends* with bulk heterojunction morphology, the 'work-horse' of polymer OPV. Highly concentrated sunlight was used (compared to the concentration levels used for such tests of non-encapsulated layers of pure P3HT [16]) since PCBM is known to increase the P3HT:PCBM blend stability due to excited state quenching [15,40,41]. The degradation in light absorption in the OPV photoactive layer (photo-bleaching) was used to quantify the degradation. Various spectroscopic methods were utilized to determine the degradation mechanism(s). The results demonstrate our ability to separate light from heating effects on degradation up to very high sunlight concentration, and

show the effect of these factors on P3HT degradation mechanisms in the P3HT:PCBM blend - photo-oxidation and photolysis.

2. Experimental details

2.1. Sunlight concentration

Outdoor sunlight was concentrated and transferred indoors using two systems, both developed in-house: (1) in the 'Mini-dish' system sunlight is concentrated using a paraboloidal mirror and focused into a transmissive (quartz-core) optical fiber of 1 mm in diameter and delivered indoors (Fig. S1, Supplemental Information) [42,43]. The intensity was modulated using a pizza-slice iris; (2) In the 'Solar furnace' system a dual-axis tracking flat heliostat reflects sunlight into the laboratory, where a flat mirror (with a hole at its center) tilted at 45° redirects the light upward to a 526 mm-diameter paraboloidal dish of numerical aperture of 0.4, whose focal plane is just below the tilted mirror (Fig. S2) [44,45]. The light intensity was moderated by a louvered shutter between the heliostat and the flat indoor mirror. It should be noted that the spectrum measured at 'noon time $\pm$ 2–3 h' at Sede Boqer (Lat. 30.8°N, Lon. 34.8°E, Alt. 475 m), where the lab is located, is very close to the AM 1.5 G spectrum (Fig. S3).

Flux uniformity in both systems was achieved using kaleidoscopes placed between the distal fiber tip ('Mini-dish') or the paraboloid focal point ('Solar furnace') and the cell (Fig. S4). An increase in the kaleidoscope exit area resulted in deconcentration of the sunlight delivered to the cell. The degree of concentration can be varied gradually from 0 to 100 and 10,000 suns for 1 cm^2 and 1 mm^2 illuminated areas, respectively. The incident power of concentrated sunlight was measured with a spectrally blind pyranometer (thermopile) of 5% accuracy, and the sunlight concentration was calculated taking into account the cell illuminated area. Exposure to 1 sun was performed outdoors with 8 h/day of direct sunlight irradiation. Sunlight exposure dose was quantified in units of sun*hours (1 sun*hour=360 J/cm^2). The reported doses are the actual dose that the samples were exposed to; in the case of chopped illumination only the illuminated period in each cycle was taken into account.

2.2. Sample temperature control

The sample was thermally bonded to the top of a thermoelectric or water cooled plate. The temperature was set to 5 °C unless otherwise noted. To further reduce heating, a 16.5×16.5 cm^2, 2.5 mm thick absorbing short-pass filter (K-5, Schott) was introduced to the 'Solar furnace' to filter IR radiation (wavelengths longer than 900 nm, Fig. S5). A sidelong fan was set to prevent overheating of the filter during irradiation. Although the absorption of P3HT:PCBM is limited to wavelengths shorter than 675 nm, longer wavelength radiation might be expected to increase the cell's temperature if absorbed elsewhere (glass, back contact, etc.).

The 'Solar furnace' can operate in continuous-irradiation or flash-like mode. The latter is achieved by inserting a reflective rotating disk (chopper) of diameter 264 mm with a 30×50 mm aperture close to its circumference for sample illumination, positioned just above the focal plane (Fig. S6a). The disk's rotation frequency can be varied up to 25 ± 1 Hz, and the shortest temporal window for constant sample irradiance is ~1.1 ms. According to the geometry of the chopper disk, the sample is irradiated 5.4% of the cycle time (Fig. S6b). The light power P_{in} during 'light on' periods is equal to that during continuous-illumination. Chopping the light enables effective dissipation of the heat, accumulated during the 'light on' period, during the non-irradiated period, hence better control of the sample's temperature.