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Nanoscale chemical analysis of beam-sensitive polymeric materials by cryogenic electron microscopy

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Abstract
Nanoscale chemical analysis of functional polymer systems by electron microscopy, to gain access into degradation processes during the materials life cycle, is still a formidable challenge due to their beam sensitivity. Here a systematic study on the different stages of degradation in a P3HT-PCBM organic photovoltaic (OPV) model system is presented. To this end pristine samples, samples with (reversibly) physisorbed oxygen and water and samples with (irreversibly) chemisorbed oxygen and water are imaged utilizing the full capabilities of cryogenic STEM-EELS. It is found that oxygen and water are largely physisorbed in this system leading to significant effects on the band structure, especially for PCBM. Quantification proves that degradation concomitantly decreases the amount of C=C bonds and increases the amount of C—O—C bonds in the sample. Finally, it is shown that with a pulsed electron beam utilizing a microwave cavity, beam damage can be significantly reduced which likely extends the possibilities for such studies in future.

KEYWORDS
band structure, cryogenic (scanning) transmission electron microscopy, degradation pathways, electron energy loss spectroscopy, organic photovoltaics, pulsed electron beams

1 | INTRODUCTION
To make the transition from fossil fuels to renewable energy, new materials for energy generation, conversion, and storage are necessary. To date, the use of solar energy is one of the major contenders to replace fossil fuels, via the conversion of solar energy to electricity. Polymeric materials such as organic photovoltaics (OPVs) may play a significant role in this transition on account of their tunable electronic properties. Furthermore, polymers
enable controlled bottom-up design of complex functional morphologies. In this context, OPVs have shown great potential due to their low cost and ease of processing. However, the rapid photo-degradation of OPVs, mainly caused by the uptake of oxygen and water, is one of the main reasons that OPVs have not been able to conquer the market. The uptake of oxygen and water in OPVs can occur either by physisorption or chemisorption. Physiosorption is, in principle, reversible, while chemisorption is irreversible. Physisorption can cause, for example, p-doping in P3HT, whereas PCBM can undergo dimerization or oxidation of the fullerene group. In both cases, this leads to a decrease in aromaticity and conjugation length and, therefore, a decrease in light absorbance and, ultimately, performance efficiency. The chemical degradation of OPVs will thus affect the chemical bonds in the structure, resulting in changes to the band structure of the donor and acceptor materials. This can be noticed in the UV–vis spectrum, where the light absorbance of P3HT decreases upon UV–vis illumination.

To solve above challenges nanoscale chemical analysis of degradation pathways by high resolution techniques, such as transmission electron microscopy, are needed. However, such analysis of polymeric materials is difficult on account of their beam sensitivity. As we have previously shown, cryogenic STEM-EELS is preferred over energy filtered TEM and STEM-EDX to quantitatively analyze oxygen and water uptake across P3HT-PCBM interfaces of columnar model systems. The first results from STEM-EELS analysis show that the physisorption of oxygen and water mainly occurs in the PCBM-rich regions, and no specific interphase uptake is found. It is, however, not the physisorption of oxygen and water, but mainly the chemisorption that is expected to have a large effect on the decrease of the power efficiency. Therefore, a systematic study of the different stages of OPV degradation needs to be carried out, comparing pristine samples with samples exposed to water and with samples exposed to UV illumination in a humid environment, with physisorbed components removed. To do so, the full capabilities of STEM-EELS can be utilized, which go far beyond the quantification of elemental concentrations. By analyzing the shape of the energy loss near edge structures (ELNES) of the carbon K-edge, one can access information about the nature of the chemical bonding in the materials.

In terms of OPV degradation pathways, one can think of a decrease in the number of C=C bonds upon degradation, and hence a decrease in aromaticity, or an increase in number of C—O or C=O bonds due to oxidation. Recently, mono-chromated (STEM-)EELS has been used to analyze the band structure of P3HT and PCBM, calculating the complex dielectric function. Furthermore, energy filtered TEM has been utilized to characterize the microstructure of OPV materials, at energies corresponding to the electronic transition of P3HT and PCBM. This opens up the possibility to locally analyze changes in the band structure upon the exposure of OPV materials to oxygen and water, and upon photodegradation in the presence of oxygen and water.

In this manuscript, cryogenic STEM-EELS and mono-chromated cryogenic STEM-EELS in ulitmono mode achieving an energy resolution down to 35 meV is used to study the degradation of a P3HT-PCBM model system across the P3HT-PCBM interphase. First, the uptake of oxygen and water is quantified, making the distinction between physisorbed and chemisorbed uptake. Hereafter a detailed analysis of the oxygen and carbon K-edge is shown, to investigate the chemical bonding in the materials. Thereafter, changes in the band structure as an effect of degradation is studied using state-of-the-art, high-resolution, low-loss STEM-EELS. Finally, a proof-of-principle experiment is carried out to show that beam damage in beam sensitive polymeric materials may be reduced by pulsed electron beams.

2 | EXPERIMENTAL

2.1 | Materials

Poly(3-hexylthiophene) (P3HT, Plexcore OS 2100), poly(styrene (PS, average Mn 35,000 g/mol) and chlorobenzene were purchased from Sigma Aldrich. The solvents acetone, dichloromethane (DCM, stabilized with amylene) and 2-propanol were acquired from Biosolve. Solenne B.V. provided phenyl-C61-butyric acid methyl ester (PCBM, 99.5% purity). TEM grids (carbon film on 200 mesh copper grids, CF200-Cu) were obtained from EMS Diasum. All materials were used as purchased.

2.2 | Sample preparation

To start with, 22.5 mg of P3HT and 7.5 mg of PS were dissolved in 1 ml chlorobenzene. The resulting solution was stirred at 70°C for 24 h to completely dissolve the materials. A custom-made specimen holder, as described in Reference 19, was cleaned by ultrasonication
in acetone for 30 min, followed by rubbing with soap and rinsing with demineralized water. Afterwards, the specimen holder was ultrasonicated in isopropanol for 30 min, followed by a final UV-ozone treatment for 30 min. For all samples the P3HT-PS solution was spin-coated on a TEM grid loaded specimen holder at 2000 rpm for 1 min. The spin coated TEM grid was removed from the specimen holder and submerged in acetone for 1 h, while stirring, to remove all PS. Hereafter, the TEM grid was washed with acetone to achieve complete polystyrene removal. The washed TEM grid was loaded on a freshly cleaned specimen holder, and PCBM was spin-coated on top at 3000 rpm for 1 min.

Three types of samples were prepared:

1. Oxygen- and water-free samples,
2. Samples exposed to oxygen and water containing only physisorbed oxygen and water,
3. Degraded samples with physisorbed oxygen and water removed, thus only containing chemisorbed oxygen and water.

Oxygen- and water-free samples were prepared in a glovebox (M-Braun Labmaster Glove Box System) using an SPS POLOS Spin 150i spin coater. Glovebox samples were submerged in liquid nitrogen, directly after leaving the glovebox for preservation to minimize exposure to air.

Samples exposed to oxygen and water were prepared in air using a Laurel WS-650-23NPP-LITE Spin Coater. These samples were exposed to 100% humidity in a Vitrobot (Mark 3, Thermo Fisher Scientific) for 10 min prior to preservation by plunge-vitrification in liquid ethane.

Degraded samples were also prepared in air using a Laurel WS-650-23NPP-LITE Spin Coater. In addition, they were exposed to UV-illumination for 1 h, where the power of the UV lamp (high-pressure mercury lamp, Dr. Hönle AG) was 142 mW/cm² (50 mW/cm² UVV, 69 mW/cm² UVA, 23 mW/cm² UVB, and 0 mW/cm² UVC), as measured by a UV Power Puck. After degradation in standard lab condition the samples were stored overnight in vacuum (10⁻² mbar) to remove physisorbed components, before submerging in liquid nitrogen for preservation.

2.3 Electron microscopy

The STEM-EELS core-loss signals were acquired on a Talos F200X (Thermo Fisher Scientific at Nanoport Eindhoven), operated at 200 kV, equipped with a field emission gun with X-FEG emitter and a Fischione HAADF detector. The EELS signal was acquired with a Gatan Enfinium Spectrometer and a Ceta 16 M CMOS camera. For cryo transfer a Gatan cryo-holder (model 914) was used. Core-loss spectrum images were acquired with 128 × 128 × 2048 pixels and a 9000 μs per pixel dwell time, a probe current of 328 pA and pixel sizes of 17.12 nm and 0.25 eV. A camera length of 60 mm was used at a magnification of 57 kx, at a convergence semi-angle of 10 mrad and a collection semi-angle of 30 mrad. Zero-loss spectrum images were acquired at the same settings, but with a dwell time of 100 μs/pixel². STEM-EELS sulfur maps and oxygen maps were extracted in Digital Micrograph, selecting the sulfur and oxygen edges, and calculating a background from a 100 eV (sulfur) and 125 eV (oxygen) wide section of the spectrum. Mono-chromated low-loss spectrum images were acquired on a Themis microscope (Thermo Fisher Scientific) at Thermo Fisher Scientific R&D (Eindhoven), operated monochromated in ultimono mode at 60 kV using a Quantum GIF. A Gatan cryo-holder (model 626) was used. The energy resolution (FWHM of the zero-loss peak) in vacuum was 35 meV. A magnification of 63 kx was used with an exposure time of 0.005 s.

Pulsed beam experiments were carried out to investigate whether ultrafast electron microscopy (UEM) offers benefits for studying beam sensitive materials, such as P3HT and PCBM polymers, by extending their damage threshold. For these experiments, a Tecnai F20 with a conventional Schottky FEG electron source was used, operated at room temperature. The microscope was fitted with an experimental resonant RF cavity, designed for an RF frequency of 3 GHz and 75 MHz, resulting in a 6 GHz or 75 MHz train of electron pulses, respectively. This results in a pulsed beam with a pulse length of 1 ps with delay times of 166 ps and 13 ns, respectively. The concept of using RF cavities as dynamic optical elements is analyzed in Reference 29. Dose series of a PCBM-P3HT bulk heterojunction were acquired in diffraction mode with a continuous beam or a pulsed beam at a similar dose rate. The dose rate was set at 5.4 e⁻¹ Å⁻² s⁻¹, and the total electron dose per image was kept constant. The resulting images were analyzed following an earlier developed protocol.³⁰ The critical dose was calculated to be the accumulated electron dose at which the initial intensity of the P3HT diffraction ring at 0.256 Å⁻¹ was lowered by a factor of 1/e.

STEM-EELS data analysis was performed in a similar fashion as described in Reference 19. In brief, a sulfur map was used to create a binary mask, containing circular regions. The outer ring of the circular regions was selected to create an interface mask, which was multiplied with either the oxygen map, the sulfur map or the thickness map. The average intensity within the rings
was calculated. The last two steps were repeated after eroding and dilating the rings of the interface mask, creating an average intensity profile over the PCBM-P3HT interface. For the HR STEM-EELS spectrum images the ADF images were used to create a mask. Due to the lack of sulfur signal in the degraded sample, the ADF image was used for this sample as well. Data analysis was extended to 3D graphs for spectrum images to analyze the shape of the oxygen and carbon K-edge and the HR-EELS spectra, calculating the average spectra per ring instead of average intensity. Afterwards, average spectra were created of the PCBM-rich region, the interphase region, and the P3HT-rich region. A total of five spectra was selected for each region (i.e., the PCBM-rich region, the interphase region and the P3HT-rich region), which were averaged to obtain the graphs that are shown throughout the manuscript. Quantification of the oxygen content was performed in Digital Micrograph, where the loss in oxygen edge intensity due to beam damage was compensated for by multiplying with a factor of 1.65. Plural scattering of the oxygen and carbon K-edge was removed using Digital Micrograph, employing the Fourier ratio protocol.

\[ I(E) = I_m \exp \left\{ -r \left[ \ln \frac{E}{E_m} - \frac{E_m - E_0}{E_m} + \frac{(E_m - E_0)^2}{E_m(E - E_0)} \right] \right\} \]

The ionization continuum of the carbon K-edge was removed by fitting the equation to the spectrum between 300 and 330 eV, where \( E_0 \) is the onset energy (eV), \( E_m \) is the energy loss at the maximum intensity (eV), \( I_m \) is the maximum intensity and \( r \) is a fitting parameter. \( E_0 \) was set at 279 eV, \( r \) was set 15 and \( E_m \) was set at 320 eV. \( I_m \) was fitted to the maximum intensity of the selected part of the spectrum. This ionization continuum was subtracted from the carbon K-edge. To the resulting data, six Gaussians were fitted to access bonding information using the nonlinear least-squares fitting protocol in Microsoft Excel. For all parameters we used unconstrained fitting. The oxygen and carbon K-edges were normalized by subtracting the minimum from each spectrum and dividing each spectrum with its resulting maximum. The HR-EELS data was split up in two parts, where the part of the spectrum between 0 and 1 eV and the part of the spectrum between 1 and 8 eV were normalized separately. This was done because the part of the spectrum between 0 and 1 eV contained remainders of the zero-loss signal, as an effect of imperfect zero-loss subtraction, making it difficult to compare different regions if the spectrum was not split up. The zero-loss signal in the HR-EELS spectra was removed by fitting a power law to the zero-loss signal ranging from 0.1 to 0.3 eV. This was performed in Digital Micrograph. Zero-loss subtracted data were smoothed using a 10-pixel median filter.

3 | RESULTS AND DISCUSSION

The three samples, that is, the glovebox sample, the exposed sample and the degraded sample are investigated first in terms of oxygen and water concentration to quantify in which phase oxygen and water are mainly absorbed. Next, to assess changes in chemical bonding, the shape of the oxygen K-edge and carbon K-edge are analyzed, before HR-EELS results are shown assessing the effects of oxygen and water physisorption and chemisorption on the band structure of P3HT and PCBM.

3.1 | Quantification of oxygen uptake

Figure 1 shows the oxygen maps of a sample that is not exposed to oxygen and water (a, the “glovebox” sample), a sample that is exposed to humid air (b, the “exposed” sample), containing only physisorbed oxygen and water, and a sample that is degraded in UV light, in the presence of air, and subsequently been held under vacuum for 24 h (c, the “degraded” sample), therefore only containing chemisorbed oxygen and water. Since the images use the same color scale, one can clearly see that the sample exposed to humid air has the highest oxygen intensity (62.9 atoms/nm²), while the glovebox sample has the lowest oxygen intensity (13.4 atoms/nm²), indicating that the amount of oxygen that is physisorbed is larger than the amount of oxygen that is chemisorbed. Furthermore, the images show that the oxygen content in the degraded sample (42.1 atoms/nm²) is higher than in the glovebox sample, indicating the presence of chemisorbed oxygen and water. Furthermore, it is clear that the PCBM-rich regions (the bright regions) show a larger oxygen content.

The image analysis protocol, explained in the experimental section, is applied to the oxygen maps in Figure 1(a–c), leading to the transition profile of the oxygen concentration across the PCBM-P3HT interphase shown in Figure 1(d,e) where the concentration is calculated from the Planar concentration and the thickness. One can clearly see that the exposed sample indeed has the highest oxygen concentration. However, the oxygen concentration in the degraded and glovebox sample seem similar, especially in the PCBM-rich region (at negative
It is, however, expected that the actual oxygen concentration in the degraded sample is higher than in the glovebox sample, since oxygen will react with P3HT and PCBM. The fact that the concentrations are similar can possibly be explained by the fact that the oxygen map of the glovebox sample has a very low signal-to-noise ratio (for details see SI section 1), which causes unreliable quantification. Furthermore, degradation might cause changes in the inelastic mean free path, causing deviations in the calculated thickness that are not accounted for and could also lead to incorrect concentrations. Due to the presence of oxygen, which is slightly heavier than carbon, it is expected that the amount of scattering increases, and that the inelastic mean free path consequently decreases.

This means that the thickness of the degraded sample is likely to be overestimated and, hence, that the oxygen concentration is somewhat underestimated. Finally, the rate of beam damage of the oxygen signal might be lower in the glovebox sample, due to a different nature of the oxygen bonding that is present. Treating the effect of beam damage in the same fashion, using a correction factor of 1.65, for both the degraded and the glovebox sample might therefore artificially increase the oxygen content in the glovebox sample, since the correction factor is likely to be lower for the glovebox sample since less oxygen and water is present.

In Table 1 the parameters of the hyperbolic tangent functions, fitted to the data in Figure 1(d,e) are shown, where we find the oxygen content in the PCBM- and P3HT-rich regions. The average oxygen content in the PCBM-rich region of the exposed sample is 7.4 atoms/nm³, while the average oxygen content in the P3HT-rich region is 1.8 atoms/nm³. Upon degradation and vacuum exposure (which removes the physisorbed oxygen and water), these values decrease to 1.0 and 0.6 atoms/nm³ for the PCBM-rich and the P3HT-rich region of the degraded sample, respectively.

**Table 1** Parameters of the hyperbolic tangent fit to the oxygen concentration profiles of the glovebox, exposed and degraded samples, along with the $R^2$ values

|          | Glovebox | Exposed | Degraded |
|----------|----------|---------|----------|
| $x_0$    | $-31 \pm 6$ | $-40 \pm 3$ | $-2 \pm 2$ |
| $2\nu$   | $88 \pm 5$ | $76 \pm 3$ | $62 \pm 2$ |
| Max      | $1.20 \pm 0.03$ | $7.35 \pm 0.75$ | $0.98 \pm 0.03$ |
| Min      | $0.28 \pm 0.02$ | $1.81 \pm 0.40$ | $0.62 \pm 0.02$ |
| $R^2$    | 0.999    | 0.999   | 0.999    |
Due to the low SNR of the glovebox sample, the oxygen concentrations of this sample cannot be reliably quantified. Therefore, comparing the trends of the glovebox and the degraded samples in Figure 1(d) should not be interpreted as oxygen and water being mainly chemisorbed in the P3HT-rich region.

Oxidation in the P3HT-rich region might also show up in another part of the core-loss spectrum, that is, the sulfur L-edge. The sulfur edge is completely invisible in the degraded sample, as compared to the glovebox sample. This could be caused by, for example, changes in the sulfur L-edge shape upon degradation, that is, changes in the chemical bonding, or by the fact that the sulfur L-edge becomes more beam sensitive upon UV degradation. The sulfur L-edge spectra can be found in SI section 2. Since the sulfur L-edge is not present in the degraded sample, we unfortunately cannot compare the oxygen content in the degraded sample with the expected oxygen content from the oxygen atoms present in the PCBM molecules, since we cannot quantify the P3HT thickness. The above analysis proves that the amount of oxygen and water that is reversibly physisorbed is much larger than the amount of oxygen that reacts with the photoactive layer upon UV exposure of 1 h, that is, the chemisorbed oxygen content during our degradation protocol.

3.2 Chemical bonding analysis based on the oxygen and carbon K-edge

To analyze the chemical bonds of the oxygen atoms that are present in the different regions, the shape of the oxygen K-edge of each region is analyzed. Figure 2(a–c) shows the average oxygen K-edge shape of the PCBM-rich, the interphase and the P3HT-rich region for the three samples. It is clear that the shape edge is similar in all three samples and regions, apart from the small signal that is visible at 528 eV, which we identified as molecular oxygen (O₂). This indicates that the glovebox sample and the degraded sample are indeed free of molecular oxygen, and proves that the uptake of physisorbed oxygen is measured. Since the maximum intensity of the oxygen signal is the largest in the PCBM-rich region (see SI section 3 for the EEL spectra before normalization) the PCBM-rich region, quantitatively, has a larger O₂ uptake than the other regions. Furthermore, it is clearly visible that the glovebox sample has much larger noise levels, as indicated before, limiting the reliability of the quantification process.

The carbon K-edge contains information about the nature of the chemical bonding of the carbon atoms present in the sample. The EEL spectra of the

![Figure 2](image-url) Detailed analysis of the EELS edges of the glovebox, exposed and degraded samples, with the average oxygen K-edge shown for (a) the PCBM-rich region, (b) the interphase region, and (c) the P3HT-rich region; and Gaussians representing chemical bonding fitted to the carbon K-edge for (d) the PCBM-rich region, (e) the interphase region, and (f) the P3HT-rich region.
carbon edge were processed by removing plural scattering, and removing the ionization continuum (see SI section 4). To gain insight into the different transitions the processed data were decomposed in six Gaussians, finding six bonding specific energies as shown in Figure 2(d-f). These energies are 285 eV (black curve), 287 eV (red curve), 290 eV (green curve), 292 eV (blue curve), 298 eV (pink curve), and 305 eV (orange curve). As each Gaussian can be assigned to a specific chemical bond, the area of the different Gaussians was determined to infer relative occurrence and changes upon oxygen and water exposure, and degradation (Table 2).

The signal at 285 eV in Figure 2(d-f) and Table 2 is assigned to the s-\(\pi^*\) transition, that is, the carbon–carbon double bond. As one can see, the area of this signal decreases upon exposure to oxygen and water. Since it is not expected that the mere presence of oxygen and water already starts breaking the carbon double bonds, this decrease can only be explained by electron beam damage. As the exposure to oxygen and water increases the rate of electron beam damage during data acquisition, the carbon–carbon double bond will be broken at a faster rate in the exposed sample, leading to a smaller peak area. (This could be proven by using dose fractionation, that is, acquiring four spectrum images at 100 e\(^{-}\) Å\(^2\) each and comparing the area of the signal in each spectrum image, where in this case a decrease of area is expected as a function of accumulated dose.) In the PCBM-rich region and in the interphase region, the peak area decreases further upon degradation, indicating the C=C bonds in the fullerene part of PCBM are broken. In the P3HT-rich region, the peak area stays approximately constant upon degradation, indicating that oxygen and water do not tend to react with the double bonds present in the thiophene ring. The peak present at 287 eV has previously been assigned to the s-\(\sigma^*\) transition in the C=O bond. However, a more likely explanation is that the peak represents a s-\(\sigma^*\) transition to an orbital delocalized on the carbonyl function (C=O) appearing upon breaking of carbon–carbon double bonds in the PCBM-rich region that is usually located at 288 eV. Since there does not seem to be a decrease in C=C bond- ing in the P3HT-rich region, no clear increase in the number of C=O bonds is expected here.

The third signal, at 290 eV, can be assigned to the s-\(\sigma^*\) transition of the C=O=C bonds. There is a clear increase in peak area upon degradation, indicating that oxidation takes place, mainly in the P3HT-rich and interphase region. Upon exposure, there are no clear changes present in this signal. Since no clear decrease is seen in C=C bonds in the P3HT-rich region, it is expected that oxygen will mainly react with the alkyl tail, or at the sulfur site of the thiophene ring. The latter is also indicated

| Region | Sample | Position | Area | Position | Area | Position | Area |
|--------|--------|----------|------|----------|------|----------|------|
| PCBM   | Glovebox | 285 | 0.61 | 287 | 0.33 | 291 | 0.24 | 290 | 0.39 | 289 | 0.24 | 291 | 0.30 | 291 | 0.25 | 291 | 0.25 |
|        | Exposed | 285 | 0.66 | 287 | 0.33 | 291 | 0.24 | 290 | 0.39 | 289 | 0.24 | 291 | 0.30 | 291 | 0.25 | 291 | 0.25 |
|        | Degraded | 285 | 0.40 | 287 | 0.45 | 291 | 0.24 | 290 | 0.39 | 289 | 0.24 | 291 | 0.30 | 291 | 0.25 | 291 | 0.25 |

| Interphase | Glovebox | 285 | 0.56 | 287 | 0.33 | 291 | 0.24 | 290 | 0.39 | 289 | 0.24 | 291 | 0.30 | 291 | 0.25 | 291 | 0.25 |
|            | Exposed | 285 | 0.46 | 287 | 0.45 | 291 | 0.24 | 290 | 0.39 | 289 | 0.24 | 291 | 0.30 | 291 | 0.25 | 291 | 0.25 |
|            | Degraded | 285 | 0.59 | 287 | 0.56 | 291 | 0.24 | 290 | 0.39 | 289 | 0.24 | 291 | 0.30 | 291 | 0.25 | 291 | 0.25 |

| P3HT     | Glovebox | 285 | 0.46 | 287 | 0.45 | 291 | 0.24 | 290 | 0.39 | 289 | 0.24 | 291 | 0.30 | 291 | 0.25 | 291 | 0.25 |
|          | Exposed | 285 | 0.46 | 287 | 0.45 | 291 | 0.24 | 290 | 0.39 | 289 | 0.24 | 291 | 0.30 | 291 | 0.25 | 291 | 0.25 |
|          | Degraded | 285 | 0.59 | 287 | 0.56 | 291 | 0.24 | 290 | 0.39 | 289 | 0.24 | 291 | 0.30 | 291 | 0.25 | 291 | 0.25 |
by the decrease of the sulfur L-edge, which could be caused by a change in peak shape (for analysis of the sulfur chemical bond, STEM-EDX might be a more suited technique, since STEM-EDX can probe the sulfur K-edge, which is located at a too high energy loss for EELS analysis).

The remaining signals are harder to assess and are usually assigned to s-σ* transitions of C−C bonds.21–22,39 Upon degradation, there is a clear increase in peak area of the signal at ~300 eV, while the peak area of the final signal decreases significantly upon degradation.

It is, however, hard to assign what actually occurs in this region of the spectrum, since the quality of fit of the ionization continuum will have a large influence on this part of the spectrum. Theoretical calculations would have to be performed to assign each peak to a bonding state with higher certainty, since literature is not conclusive on the location for each of the electronic transitions.21–22,39

3.3 | High-resolution low-loss EELS analysis of the P3HT and PCBM band structure

In addition to changes in the chemical bonding, changes in the optical part of the spectrum will also have a large effect on functional properties such as device efficiency, since this part of the spectrum describes the energy levels of the P3HT and PCBM molecules. The optical part of the spectrum is located below 10 eV in the EELS spectrum. High energy-resolution STEM-EELS has to be used to analyze this low-loss part of the spectrum. Figure 3 shows average high-resolution EELS spectra of the low-loss region of the PCBM-rich, the interphase and the P3HT-rich region of the glovebox, the exposed and the degraded sample. All spectra are the average of five spectra in each region. First, one can see a signal located at 0.4 eV in all spectra, although the signal is most pronounced in the PCBM-rich region, in the exposed and degraded samples. In the P3HT-rich region of the glovebox sample, this signal only appears as a shoulder on the remainders of the zero-loss signal, which are present due to an imperfect zero-loss signal subtraction. The signal at 0.4 eV (around 3200 cm$^{-1}$) is assigned to an O−H bond stretch.24 This shows that the (physi- or chemisorbed) water content is the highest in the PCBM-rich region, and that water is present in both the exposed and the degraded sample. The small signal observed in the glovebox sample indicates that the water concentration is indeed lower in the glovebox sample. With this we conclude that the water and/or oxygen concentration is indeed higher in the degraded sample than in the glovebox sample, strengthening the earlier conclusion that the signal-to-noise ratio of the oxygen signal is too small to provide a reliable quantification, since this quantification shows an equal oxygen concentration for the glovebox and degraded sample in the PCBM-rich region.

Furthermore, in the PCBM-rich region of the degraded sample, an extra signal is present at ~0.2 eV. Due to the uncertainty in the background subtraction it is, however, highly unlikely that the exact location and chemical information of the signal can be resolved. Finally, the interphase signal seems to be a linear combination of the P3HT-rich and the PCBM-rich region, especially for the glovebox and the exposed sample, showing no specific interphase effect. This part of the spectrum can most likely be resolved by using aloof beam EELS, where the zero-loss peak is not recorded.40–41

At an energy loss between 1 and 8 eV, the energy levels of P3HT and PCBM are present as broad peaks. The π-π* transition in P3HT occurs at about 2.6 eV, while for PCBM multiple broad peaks at 3.7, 4.8, and 6.5 eV are found.26 In the PCBM-rich region of the glovebox sample

![Figure 3](https://wileyonlinelibrary.com)
(Figure 3(a)), there are indications of the broad PCBM transitions at 3.7 and 4.8 eV, while the transition at 6.5 eV is clearly visible, along with a broad P3HT signal at around 2.6 eV, indicating that there still is P3HT present in the PCBM-rich region. When this sample is exposed to oxygen and water, the electronic transitions seem to fade in the PCBM-rich region. This infers that the physisorption of oxygen and water can already influence the band structure of OPV devices, proving the importance of, for example, encapsulation of organic solar cells to keep the device oxygen- and water-free. Upon degradation, the transition at 6.5 eV appears again. This indicates that the electronic transitions in PCBM are mainly hindered by the physical uptake of oxygen and water, or oxygen doping, as is the case for C$_{60}$ molecules, and not by oxidation. Furthermore, the P3HT transition starts to appear clearly in the degraded sample, indicating that intermixing takes place upon UV-illumination or upon heating. Moreover, the increase of the P3HT signal can be caused by thermal annealing, which is a well-known method to increase the power conversion efficiency. Since heating is a side-effect of UV-illumination, it might be the case that thermal annealing occurs in this system upon degradation. The increase in the PCBM signal at 6.5 eV might be caused by the removal of oxygen and water in vacuum after degradation, minimizing oxygen doping.

In the interphase region (Figure 3(b)), the P3HT signal at 2.6 eV and the PCBM signal at 6.5 eV are present, and there is a slight indication of the PCBM signal at 4.8 eV being present as well. This indicates a mixed phase of P3HT and PCBM, which is expected in the interphase region. After exposure to oxygen and water, the PCBM signal at 6.5 eV disappears, as in the PCBM-rich region. However, the P3HT signal remains visible, which is not the case in the PCBM-rich region, indicating that either more P3HT is present, causing the signal to remain above the noise level, or that the effect of oxygen and water on P3HT is possibly reduced in the interphase. After degradation, the P3HT signal and the PCBM signal at 6.5 eV are prominently visible again, once more indicating thermal annealing of P3HT and the removal of oxygen doping in PCBM.

When looking at the P3HT-rich region (Figure 3(c)), one can clearly see the presence of the P3HT transition at 2.6 eV, as is expected. The PCBM signals are, however, not present, or lost in background noise. No clear changes are visible between the glovebox and the exposed spectrum. In the degraded spectrum, the PCBM transition at 6.5 eV does, however, appear again, as well as a clearer signal for P3HT at 2.6 eV. Thus, the uptake of oxygen and water has a large effect on the band structure of PCBM, while less changes are visible in the P3HT band structure. Upon degradation and vacuum treatment, the band structure of PCBM starts to reappear, due to the removal of volatile oxygen and water, removing oxygen doping.

3.4 | Extending the damage threshold for EM analysis using pulsed electron beams

As above analysis is always limited by beam induced sample damage, a proof-of-principle experiment was carried out using pulsed electron beams. As has been shown for different materials, pulsed electron beams (that is, UEM) may provide the solution to significantly extend the damage threshold for beam sensitive materials as compared to exposure to a continuous but temporarily random electron beam. Here a PCBM-P3HT bulk heterojunction was exposed to a conventional/random electron beam and two UEM beams with different pulse spacings and diffraction patterns recorded. To gauge beam effects a standard technique, that is, the fading of diffraction rings was employed with the results shown in Figure 4. It can be clearly seen that a pulsed beam with a frequency of 75 MHz delays the fading of diffraction rings, that is, increases the critical dose from 8 to 41 e$^{-}\text{Å}^{-2}$. At 6 GHz repetition rate, no significant benefit from the pulsed beam as compared to a continuous beam is observed (critical dose of 11 vs. 8 e$^{-}\text{Å}^{-2}$). Further details of the analysis and differences in the spread of measurement points are provided in the supporting information section 5.

Above results seem to indicate that electrons cause an excited state that, upon interaction with a second
electron shortly after, results in damage. However, if enough time is given for relaxation of the excited state between electron exposure, the critical dose threshold can be significantly increased. Thus, it may become possible to determine the lifetime of excited states by measuring the critical dose threshold in dependence of the pulse rate utilizing, for example, a fully frequency tunable RF cavity. If all above holds true for a broad range of materials this may constitute a new method for mitigating damage in beam-sensitive materials and increase the achievable resolution in TEM.47–49

4 | CONCLUSIONS

In this article, we present a nanoscale chemical analysis of the degradation of a P3HT:PCBM model system, due to the uptake of oxygen and water. It is found that the amount of oxygen and water that is physisorbed is much larger than the amount of oxygen and water that is chemisorbed (7.4 vs. 1 atom/nm³ in the PCBM-rich region and 1.8 vs. 0.6 atoms/nm³ in the P3HT-rich region). An examination of the oxygen K-edge shows the presence of molecular oxygen in the exposed sample, proving that via cryogenic preservation the native sample state including volatile species such as oxygen is retained. Detailed analysis of the carbon K-edge allows us to track changes in the chemical bonding structure upon degradation, showing a decrease in C=O bonds and an increase in C–O–C bonds. The electronic band structure of the materials was investigated by cryogenic, monochromated STEM-EELS in the region below 10 eV, showing that the presence of physisorbed oxygen and water decreases the detectability of the PCBM energy levels. Surprisingly, upon degradation, parts of the PCBM transition start to reappear, indicating that oxygen doping is reversible and a main cause of changes in the band structure of PCBM. By analyzing the near-infrared part of the spectrum, it could be shown that the O–H bond is mainly present in the PCBM-rich regions.

Since the information obtainable in above experiments is always limited by beam induced damage to the specimen, a proof of concept experiment was carried out to show that pulsed electron beams have the potential to extend the damage threshold in the investigated PCBM-P3HT system and possibly also in other beam sensitive polymeric materials.

The techniques employed in this article can be used in the future to analyze chemical changes in beam sensitive materials, especially materials of which a thorough understanding of the electronic structure is needed, such as new-generations of OPVs, perovskites, and other materials for energy generation, conversion, or storage.

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AUTHOR CONTRIBUTIONS

Zino J. W. A. Leijten, Maarten J. M. Wirix, Sorin Lazar, and Wouter Verhoeven performed the microscopy; Zino J. W. A. Leijten prepared samples, performed data analysis supervised by Gijsbertus de With and Heiner Friedrich; Zino J. W. A. Leijten, Gijsbertus de With, and Heiner Friedrich wrote the manuscript with contributions from all authors.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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