Multimodal 3D Characterisation of Carbon-based Perovskite Solar Cells

Jebin Jestine[1*], Richard E Johnston[1*], Cameron Pleydell Pearce[1], Pete Davies[1], Trystan Watson[1], Simone Meroni[1], Carys Worsley[1], Raptis Dimitrios[1], Tom Dunlop[1], Ria Mitchell[2], Tobias Volkenandt[3], Ben Tordoff[3], Stephen Kelly[4], Robin White[4] and Mansoureh Norouzi Rad[4]

[1.] Faculty of Science and Engineering, Swansea University, Swansea, United Kingdom.
[2.] Sheffield Tomography Centre (STC), The University of Sheffield, Sheffield, United Kingdom.
[3.] Carl Zeiss Microscopy GmbH, Oberkochen, Germany.
[4.] Carl Zeiss X-ray Microscopy, Pleasanton, CA, USA.
*Corresponding authors: 872955@swansea.ac.uk & r.johnston@swansea.ac.uk

Carbon-based perovskite solar cells (CPSCs) offer a cost effective and efficient solution to the energy crisis through clean energy harvesting. These cells are made up of multiple layers with a carbon top layer which acts as a counter electrode and solves stability issues that were present with noble metallic materials [1]. During manufacture, the carbon flakes within the top layer can orientate themselves in a way that blocks the infiltration of perovskite [2, 3] – blocking 28% of the active area on average [3]. This has only been observed and measured in 2D on a cross-section of the layers. Multiscale 3D characterisation would reveal the structure across the whole cell. Here we demonstrate a novel multimodal workflow for sample preparation and 3D characterisation of carbon-based perovskite solar cells. Understanding the complex network of pores and the orientation of carbon flakes can identify potential perovskite blocking flakes, and the knock-on effects on the active layers below. With 3D microstructural characterisation becoming a more widely used tool, the manufacturing characteristics could be optimised to control the orientation of carbon flakes to improve efficiency of CPSCs. This workflow demonstrates a new way of characterising these complex layered materials, essential to their development.

The aim is to characterise structures within CPSC devices non-destructively and in 3D using X-ray microscopy. The challenges for characterising this sample relate to the resolution requirements to resolve the carbon flakes, the porosity network, and the subsequent layers beneath the carbon layer. The lack of 3D characterisation could be due to the resolution limitations of the vast majority of lab-based X-ray microCT machines which are unable to spatially resolve the structures within CPSCs, and the challenges with sample preparation for CPSC due to the fragility of the layers. New workflows were required for sample preparation and 3D characterisation of these cells. A two-part multimodal workflow was created where a small (~100 micron diameter) cylindrical sample was FIB milled (Zeiss Crossbeam 550) prior to 3D X-ray microscopy characterisation on a lab-based system (Zeiss Xradia Versa 520) capable of spatial resolution of 700 nm. This was used as an initial characterisation step to validate that low density carbon flakes can be resolved against carbon black powder and porosity. The second part of the workflow involved creating another separate cylindrical sample (~100 micron diameter) using laser femtosecond milling (Zeiss Crossbeam laser 550) prior to phase and absorption-contrast X-ray microscopy on a different lab-based system (Zeiss Xradia 810 Ultra 5.4 keV) capable of an improved spatial resolution of 16 nm. The laser FIB was performed at Carl Zeiss Oberkochen, Germany, and X-ray microscopy Carl Zeiss Dublin, California. The laser FIB enabled faster material removal while minimising the damage imparted to the sample [4]. The milling process to mill out a pillar with diameter 50 microns was 4.75 minutes, including a polishing step. The main differences between these two workflows are preparation time, region of interest, and resolution. The Ultra XRM has an advantage

over the Versa XRM system for samples where small feature resolution is a challenge. The Ultra utilises 3 methods to improve resolution, a high brightness X-ray source, Fresnel zone plates and the option to add a phase ring. The phase ring achieves Zernike phase contrast, key for distinguishing features with similar density or low absorption. The carbon top layer is made of carbon flakes, carbon black and porosity, low density and absorption, phase contrast is key for imaging this layer. The Ultra images at two resolution modes, large field of view (LFOV) of 64 microns, maximum spatial resolution is 64 nm. And a higher resolution mode (HRES), field of view is 16 microns, with maximum spatial resolution 16 nm. The data from the Versa XRM was used to identify the carbon flakes and validate that 3D characterisation of these features distinct from the porosity and other layers is possible. To distinguish individual carbon flakes in CPSCs and be confident in their segmentation, a higher resolution methodology is required. The phase contrast datasets from the Ultra XRM were segmented using Dragonfly ORS (Montreal, Canada). The segmentation was carried out within a region of interest (ROI) in the shape of a cylinder to simplify the segmentation process. This focuses the segmentation on the top layer of the CPSC cell and digitally removed the outer vertical edges of the cylinder in contact with air. The two cylinders are of different dimensions, and they overlap. The same segmentation process was used for both the (LFOV) and (HR) dataset.

In this study correlated/connected multi-scale and multi-modal 3D characterisation of carbon-based perovskite solar cells was carried out for the first time, revealing the complex internal structure of these cells. The workflow allows for comparison of the optimum way to prepare CPSC samples for 'non-destructive' 3D characterisation and highlights the benefits of both workflows in series where workflow 1 identifies the rationale, benefit, and need for workflow 2. Using femtosecond laser preparation alongside high resolution XRM enabled us to segment the constituents from the top carbon layer. Sample preparation time is vastly reduced along with improvements in both spatial and contrast resolution, which is necessary for CPSC materials with features at the micro/nano scale. The reduction in sample preparation time also could enable an increase in the use of 3D characterisation for these cells. The segmentation was successful for identifying the different constituents that makeup the top layer; carbon flakes, carbon black and porosity. Understanding the orientation of carbon flakes could lead to optimisation of the manufacturing of these cells to increase perovskite infiltration and efficiency [5].
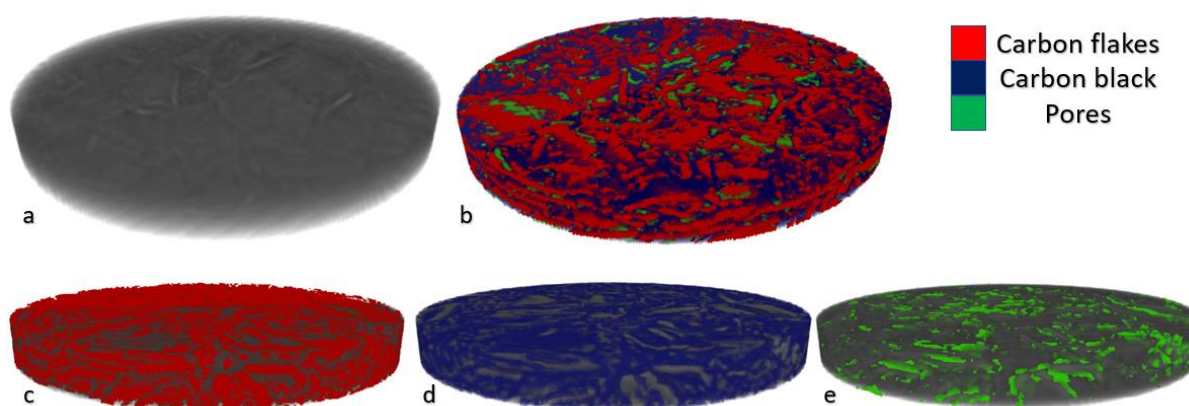
Figure 1a. Cylinder region of interest, radius 20 µm, from LFOV phase contrast dataset. 1b, All segmented phases combined. 1c, red – carbon flakes. 1d, blue - Carbon black. 1e, porosity
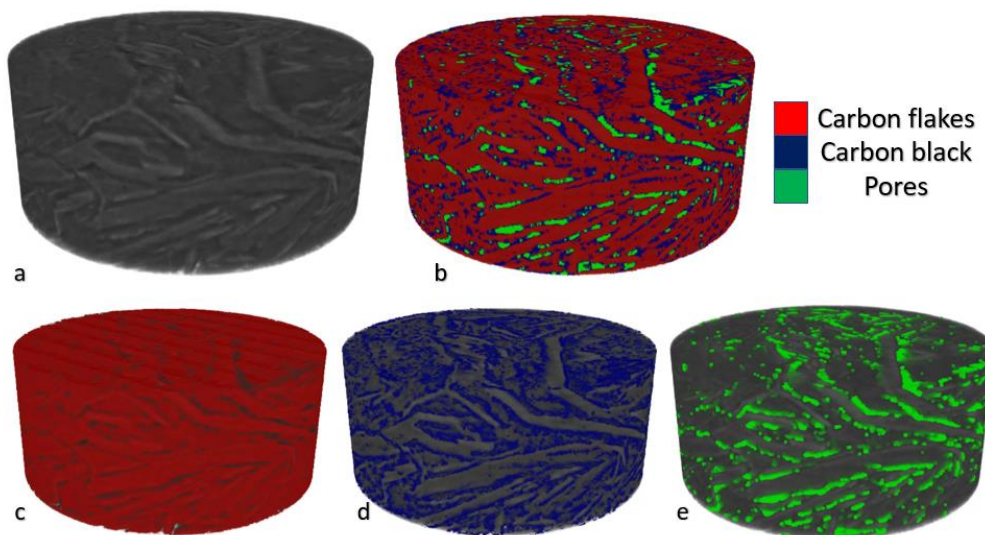
Figure 2a. Cylinder region of interest, radius 10 μm, from high resolution mode phase contrast scan. 2b, All segmented phases combined. 2c Segmented carbon flakes - red. 2d, Segmented carbon black - blue. 2e, Segmented porosity - green.

References:

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