Quantitative electron tomography investigation of a TiO$_2$ based solar cell photoanode

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Abstract. The development of efficient thin film solar cells requires a deep knowledge of the nanoscale morphology of the active layers. While conventional investigation is usually limited to 2D information, here we use electron tomography to unravel a complex particle network in a non-ambiguous, 3D reconstruction. We present our study of a dye sensitised solar cell, based on a nanostructured TiO$_2$ photoanode produced by pulsed laser deposition (PLD) and displaying a hierarchical, quasi-1D arrangement. We prepare the sample for electron tomography using focused ion beam (FIB) milling to obtain a micro-pillar, instead of a conventional TEM lamella. This approach has the advantage of allowing higher quality tomographic reconstructions of complex morphologies due to the increased tilt range available and the constant thickness of the section. We analyse the resulting reconstruction to quantitatively investigate the geometry of the TiO$_2$ network. We compare the findings with a photoanode based on a conventional TiO$_2$ paste, determining the anisotropy of the PLD-grown film. To complement our nanoscale TEM characterization, we also employ FIB tomography, to obtain a complete structural characterisation of the photoanode at different length scales.

1. Introduction
The use of solar power is being widely investigated to address the ever-increasing need for energy of modern society in a sustainable way. Research groups all over the world are looking into developing photovoltaic devices which could compete with the established silicon-based technology while offering some benefits, particularly in the energy footprint of the manufacturing, a lower cost or more versatility of use. Dye sensitised and polymer heterojunction cells, in particular, are experiencing a new surge of interest, triggered by the development of novel cobalt-based redox couples which led to an increase in power conversion efficiency above 12% [1, 2]. In order to push the conversion efficiency even further, the structure of the electrode needs to be finely tailored at the nanoscale: the interplay between surface area, crystal structure, defects and electron transport properties is of paramount importance for the behaviour of the macroscopic device [3]. The optical absorption of the device can also be enhanced by exploiting light scattering induced by mesostructures in an appropriate size range (normally hundreds of nm). A deep understanding of the material morphology can be obtained with investigation through electron microscopy, with electron tomography being the technique of choice for obtaining three-dimensionally resolved information on assemblies of nanoparticles.
We investigate the potential of electron tomography on a prototype of a dye sensitised solar cell with a polymer hole transporter (P3HT). The electron acceptor, TiO$_2$, is produced by Pulsed Laser Deposition (PLD) [4], where a TiO$_2$ target is ablated by nano-second Nd:Yag laser pulses ($4\text{ J/cm}^2$ energy density) in a low-pressure oxygen atmosphere (7 Pa). The material experiences a supersonic expansion, followed by deposition on a substrate. The resulting films retain a high porosity and self-assemble in quasi-1D hierarchical structures of branched columns. Similar structures have been demonstrated to be promising when employed as photoanode for a dye sensitised solar cell [5]. For comparison, we also analysed a prototype with a TiO$_2$ paste prototype from commercial nanoparticles (Dyesol 18NR-T). We will refer to the PLD-deposited sample as "H" (Hierarchical) and to the TiO$_2$ paste sample as "P" (Paste).

The morphology of the photoanode was studied using two tomographic approaches - electron tomography in a transmission electron microscope and slice & view tomography in a Focused Ion Beam (FIB), providing information on different size ranges.

2. Methods

Electron tomography was carried out in a FEI Tecnai F20 TEM using HAADF STEM imaging on a sample prepared via Focused Ion Beam (FIB) milling. The specimen was cut into a micropillar geometry in order to provide a high quality reconstruction [6-8], since in this case the projected thickness is constant at all tilt angles. We used a FEI Helios NanoLab for the specimen preparation, shown in Figure 1. For each sample, a tilt series was acquired from -76° to +76°, using a Fischione 2010 on-axis holder (sample H) and a Fischione 2020 tomography holder (sample P).

![Figure 1. Preparation of the sample for electron tomography using FIB milling (here shown for sample H). A cylindrical part of the specimen is isolated (a) and moved to a mount compatible with a sample holder (a tomography post or an Omniprobe grid) (b). The needle is thinned by progressive milling of annular regions until electron transparency, corresponding to 2-300 nm for this material (c).](image1)

The tilt series were aligned and the original volume was reconstructed using FEI Inspect3D. ImageJ was used to analyse the result, extracting information on particle size, porosity and network structure [8].

In order to obtain morphological information on a larger length scale, the electron tomography characterisation was integrated with "slice & view" FIB tomography carried out in a FEI Helios NanoLab. The volume under analysis was 3.32 µm (sample P) and 4.85 µm (sample H) wide and 1.52 mm (P) and 2.56 mm (H) deep in the direction parallel to the "slicing". The larger volume in sample H was chosen to better sample the morphology, which is less homogeneous than in sample P. Avizo 7 was used to align the SEM images and segment the resulting volume, which was then processed using ImageJ.
3. Discussion

3.1 Electron tomography

Figure 2. Orthoslices before and after segmentation for samples P (a) and H (b) from the reconstructed volumes, taken along the micropillar axis. The width of the pillar is here 180 nm (P) and 210 nm (H). Channels can be seen in sample H between different columns. (c) Comparison of particle size, obtained through iterated erosion in 3D. The high counts for small particles in sample H are attributed to noise in the reconstructed volume.

Although the two systems present similar particle size (see Figure 2) and crystallinity, their arrangement is different. While sample P presents a homogeneous network of spherical particles, features in sample H resemble conical columns which tend to align at a constant angle to the growth axis of the structure. Some gaps between different structures or between branches of the same structure, as shown in figure 2, run through the film. Porosity and surface area measured from the reconstruction are shown in Table 1, along with the light conversion efficiency measured for the complete device: sample P has higher porosity and surface area. This suggests that the combination of lower porosity and the hierarchical ordering favour electron transport, and enhanced scattering increases light absorption, compensating for the lower surface area and resulting in a better light conversion efficiency.

Table 1. Comparison of performance and morphology for the two solar cell prototypes.

| Specimen     | Porosity | Surface area | Light conversion efficiency (\(\eta\)) |
|--------------|----------|--------------|---------------------------------------|
| Paste        | 0.483    | 88.5 m²/g    | 2.64 %                                |
| Hierarchical | 0.354    | 41.2 m²/g    | 2.83 %                                |

3.2 FIB Slice & View

FIB tomography was carried out on both samples. Differences at the length scale of 100-1000 nm can be seen. As expected, sample P has a homogeneous structure over several microns, while sample H shows a semi-regular arrangement of columnar hierarchical structures with side branches. To quantify the properties of the pore space in the two samples, the area coverage (defined as the ratio between TiO₂ and total area) and the number of pores per slice parallel to the electrode surface have been calculated (Figure 3). Sample H presents a higher area coverage. Sample P seems to become more compact away from the FTO substrate, although the effect is small (a change from 0.90 to 0.93) and might be due to artefacts or to the film becoming more compact upon polymer infiltration. The sharp decrease in coverage far from the substrate corresponds to the top surface of the nanostructured film. The number of pores is constant through the thickness of sample P, confirming its homogeneity. Sample H has a more complex behaviour: close to the electrode (thickness < 200 nm) the number of pores decreases as the bases of the hierarchical columns are progressively more densely packed; then the film presents an intermediate region in which the structures are closely packed and the number of
pores is roughly constant. Finally, in the 500-800 nm close to the surface, side branches open out, with an obvious increase in pore number.

4. Conclusions
The combination of electron and FIB tomography is a very powerful tool for the characterisation of increasingly popular composite structures, where both nano- and meso-scale need to be analysed quantitatively. The approach shown here for solar cell photoanodes can be extended to other fields of nanoscience, such as electrochemical cells and photocatalytic devices.

Acknowledgements
The authors acknowledge funding from the ERC under grant number 259619 PHOTO EM.

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