Morphological and Compositional (S)TEM Analysis of Multiple Exciton Generation Solar Cells

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Abstract. Quantum confinement of charge carriers in semiconductor nanocrystals produces optical and electronic properties that have the potential to enhance the power conversion efficiency of solar cells. One of these properties is the efficient formation of more than one electron-hole pair from a single absorbed photon, in a process called multiple exciton generation (MEG). In this work we studied the morphology of nanocrystal multilayers of PbSe treated with CdCl₂ using complementary imaging and spectroscopy techniques to characterise the chemical composition and morphology of full MEG devices made with PbSe nanorods (NRs). In the scanning TEM (STEM), plan view images and chemical maps were obtained of the nanocrystal layers, which allowed for the analysis of crystal structure and orientation, as well as size distribution and aspect ratio. These results were complemented by cross-sectional images of full devices, which allowed accessing the structure of each layer that composes the device, including the nanorod packing in the active nanocrystal layer.

1. Introduction
Formation of multiple electron-hole pairs following absorption of a single energetic photon presents a possible route to improved photovoltaic conversion efficiency, since an additional photocurrent can be generated while bypassing heat generation resulting from electron-phonon scattering. The mechanism of converting excess photon energy in additional charge carriers can increase the efficiency limit of single junction photovoltaic devices to over 40% [1]. The extent to which a hot charge carrier undergoes the MEG process is determined by several factors, such as the strength of the Coulomb coupling between the hot charge and the trion (which consists of a charge carrier at lower energy, formed when a hole or electron is trapped on the QD surface, and an additional electron-hole pair), and by the density of final trion states coupled to the initial hot charge carrier state. The influence of these factors on the MEG process depends on the semiconductor nanocrystal shape and size [2]. In nanocrystals where the physical radius is of the order of, or smaller than, the exciton Bohr radius, quantum confinement leads to discrete excitonic energy levels, and the dimensions of the nanocrystals determine the spatial extent of excitons [3]. Therefore, morphological characterisation of the nanocrystals, as well as the full device architecture is essential to understand how the fundamental processes of these devices are being affected and identify ways to improve device efficiency. In this work we analysed the morphology individual PbSe nanorods treated with CdCl₂ and full...
MEG devices using analytical electron microscopy to characterise their chemical composition and morphology. Lead chalcogenite nanocrystals are interesting for these type of devices due to their small band gap, which is small enough to allow MEG from low energy photons [3]. In addition, the relatively large dielectric constant of Pb chalcogenite materials results in a reduction of carrier-carrier interactions, leading to an increase in the exciton Bohr radius, which could potentially be of the order of the length of the nanorod [4]. The samples studied were probed by combining high-resolution transmission electron microscopy (HRTEM), scanning TEM (STEM) and energy dispersive X-ray spectroscopy (EDX) with focused ion beam (FIB) milling for preparation of cross-sectional specimens. This approach revealed the structure of the different solar cell components at length scales of 1-100 nm.

2. Experimental methods
PbSe nanorods (NRs) of three different bandgaps (1.05 eV, 0.95 eV and 0.80 eV) were synthesized following a method adapted from Koh et al [5], with an additional CdCl$_2$ treatment at the end of the NR synthesis to provide additional surface passivation. The relevant energy levels for the different NCs solutions (conduction band edge and valence band edge) were determined by using a combination of ultraviolet photoelectron spectroscopy (UPS) and absorbance spectroscopy, as described by Ehrler et al. [6].

Samples for electron microscopy analysis were prepared by drop-casting diluted NR solutions on TEM copper grids. High-resolution TEM (HRTEM) and high angle annular dark field (HAADF) STEM images were obtained using a FEI Tecnai F20 microscope operated at 200 kV. For the preparation of the TEM specimens for cross-sectional view, a full solar cell device was thinned by focused ion beam milling (FEI Helios dual beam FEG SEM/FIB microscope), with a final thickness of around 100nm. Energy dispersive X-ray spectroscopy (EDX) mapping of the cross-sectional specimen was performed using a FEI Tecnai Orisis TEM/STEM operating at 200 kV.

3. Results and discussion
Figure 1 shows HAADF-STEM images of PbSe nanorods presenting three different band gaps, namely: 0.80 eV, 0.95 eV and 1.05 eV. Low-magnification images indicate that PbSe nanocrystals display the expected rod-like morphology, and are monodisperse with uniform diameter and length. The 1.05 eV NRs displayed a less uniform morphology, and a fraction of the nanorods were not straight, exhibiting kinks and bends. The average diameter for the samples was of the order of 4-6nm and average length of around 10-16nm. Histograms presented in figures 1(a) and 1(b) show the size distributions for the nanorods of each band gap. Previous studies [7,8] correlated the aspect ratio of PbSe nanorods with the carrier multiplication and Auger recombination, indicating that carrier multiplication in NRs occurs in a similar way to that in QDs, but with an enhanced Coulomb interaction due to the one dimensional character of electronic states [9]. The enhanced Coulomb interaction increases the carrier multiplication efficiency in NRs with moderate aspect ratios of up to 6 [8]. The results shown in Figure 1(c) and 1(d) indicate that the aspect ratio of the samples analysed is around 2.5-3, being within the values considered favourable for an increase in carrier multiplication, as shown in work by Padilha et al. [8].

Detailed crystal structures of single PbSe nanorods were characterized by HRTEM, as shown in Figure 2. The analysis of different parts of each sample indicated that the nanorods are single-crystalline with a crystal structure is rocksalt and a growth along the [0 0 2] direction. STEM-EDX was used to obtain elemental maps of the PbSe nanorod films, as presented in Figure 1 (b)-(e). The maps obtained provide a qualitative evaluation of the nanorod film composition. The maps presented in Figure 1 confirm the composition of the nanorods and indicate the presence of the CdCl$_2$ passivating layer, which is important to reduce the density of trap states in the surface of the nanorods, as demonstrated by Ip et al. [10].
Figure 1. HAADF-STEM images of PbSe nanorods of the 3 different band gaps: (a) 0.08 eV, (b) 0.95 eV and (c) 1.05 eV. (d) and (e) show the histograms for the diameter and length distributions of the nanorods, respectively.

Figure 2. (a) HRTEM image of a PbSe nanowire. The inset shows the corresponding FFT pattern that shows that the nanorod is viewed on the [1 1 0] zone axis, (b)-(e) STEM-EDX elemental maps of the PbSe nanorods with a CdCl₂ passivation layer.

The nanorod solutions analised were used to produce full solar cell devices by depositing an
array of PbSe NRs on a ZnO film which was produced using a sol-gel method. The NRs were deposited in a layer-by-layer approach using the ligand 1,2-ethanediol (EDT) for the first layers and hydrazine as the exchanging ligand for the final NR layer. The final device presented an efficiency of 2.5%, and an external quantum efficiency of 120%. Figure 3 shows a HAADF-STEM image of a cross-section of the full device. The micrograph shows a clear difference in NR packing between the layers deposited with EDT (right of the dashed line), which presents a thickness of 56 nm, and hydrazine (left of the dashed line) with a thickness of 48 nm. The hydrazine treatment appears to improve NR packing, reducing the distance between the rods and forming a uniform dense layer, with no cracks or pinholes, which should result in an enhanced film conductivity.

Figure 3. Cross-sectional TEM outlining the device architecture (rotated left 90°). The dashed line indicates the interface between the two ligands used for deposition of the NRs: EDT (right) and hydrazine (left).

4. Summary
Detailed morphological and compositional study of PbSe NR films showed that the nanocrystals presented a uniform size distribution with an aspect ratio of the order of 2.5-3, being within the values considered favourable for an increase in carrier multiplication in MEG devices. Additional STEM-EDX analysis gave qualitative information of the NR films composition, indicating the presence of the CdCl₂ passivating layer, responsible for improving surface conductivity in the NRs. Further analysis of cross-sectional specimens prepared from full devices using FIB technique revealed that the hydrazine treatment used during PbSe deposition improves NR packing, forming a uniform film.

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