High-resolution TEM characterization of ZnO core-shell nanowires for dye-sensitized solar cells

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Abstract. Recently ZnO nanowire films have been used in very promising and inexpensive dye-sensitized solar cells (DSSC). It was found that the performance of the devices can be enhanced by functionalising the nanowires with a thin metal oxide coating. This nm-scale shell is believed to tailor the electronic structure of the nanowire, and help the absorption of the dye. Core-shell ZnO nanowire structures are synthesised at low temperature (below 120°C) by consecutive hydrothermal growth steps. Different materials are investigated for the coating, including Mg, Al, Cs and Zr oxides. High resolution TEM is used to characterise the quality of both the nanowire core and the shell, and to monitor the thickness and the degree of crystallisation of the oxide coating. The interface between the nanowire core and the outer shell is investigated in order to understand the adhesion of the coating, and give valuable feedback for the synthesis process. Nanowire films are packaged into dye-sensitised solar cell prototypes; samples coated with ZrO₂ and MgO show the largest enhancement in the photocurrent and open-circuit voltage and look very promising for further improvement.

1. Introduction
The current methods for converting solar power into electricity have many drawbacks, such as high cost and low versatility. Dye sensitized solar cells (DSSCs) can have low fabrication cost and different fabrication techniques, that can lead to lightweight, flexible and transparent solar cells. ZnO is a good candidate material for such cells [1] because of its stability and the possibility to build nanowire (NW) films with high surface area. Still, work has to be done to optimize the overall behaviour, particularly at the interface between ZnO and the charge generator. It was found that the addition of a suitable coating to the NWs improves the charge injection into the ZnO [2]. Moreover, the synthesis techniques need tuning in order to achieve reproducible, tailored films. In this paper we use high resolution electron microscopy to investigate the growth of ZnO NWs, and study the morphology of various external shells in core-shell structures. This allows a better understanding of the results of the characterization of the devices, including information on the interaction among dye, shell and ZnO.

2. Experimental details
Core-shell nanowires were grown by hydrothermal growth [1][3]. A Zn metal layer (100 nm) was deposited by sputtering on clean ITO (Indium Tin Oxide) glass substrates. The NW hydrothermal growth was carried out from a solution obtained mixing 0.025 M zinc nitrate hydrate and 0.025 M hexamethylenetetramine (HMT) in water. The solution was kept at 95°C for 120 minutes, after which
the substrates were rinsed with deionised water and dried on a hotplate at 100°C. A second hydrothermal growth procedure was then used to fabricate a core-shell structure on the ZnO nanowires. Oxides of different metals have been used as materials for the outer shell, including Mg, Zr, Al and Cs. It should be noted that, being a completely low temperature deposition, this process can be carried out on a variety of substrates, including flexible polymeric ones. This is a significant advantage with respect to other techniques employing a high temperature (>300°C) annealing step.

![Figure 1.](image)

Figure 1. (a) ZnO nanowire with alumina shell, imaged near the [11-20] zone axis. Circles indicate some of the dips on the surface, arrows point out dips on the sidewalls of the NW. (b) Detail of the tip, showing growth along the [0001] direction. (c) FFT of the crystal lattice compared with simulated diffraction pattern. (d) Crystal model. (e) Size distribution of the dips on the surface of NWs.

The morphology of the samples has been verified by imaging with a LEO 1530 VP scanning electron microscope (SEM). The nanowire films were removed from the substrates and dispersed on holey Cu TEM grids. Transmission electron microscopy (TEM) was used to characterize the core-shell nanowire structures using a high resolution dedicated JEOL 4000EX (400kV acceleration voltage) and a FEI Tecnai F20 microscope (200kV).

The ZnO-MgO and ZnO-ZrO nanowires were then used to build DSSCs (using D101 and D149 dyes) in order to test the performances that could be achieved. ZnO NWs, ZnO-MgO and ZnO-ZrO samples were submerged in a solution containing the dye and rinsed with anhydrous acetonitrile. 50 nm thick silver counter electrodes were deposited by thermal evaporation.

3. Characterization
The grown NW films have been imaged by SEM: 2 hours hydrothermal growth resulted in well aligned homogeneous NWs approximately 600 nm long and 60 nm wide.

High resolution transmission electron microscopy (HRTEM) was used in order to understand the morphology of the NWs and characterize the different core-shell structures. All samples have shown highly crystalline ZnO NWs, whose structure is completely preserved through the hydrothermal shell
fabrication step. Fast Fourier Transform (FFT, figure 1-c) analysis of the high resolution images of the
lattice confirmed that the growth occurs in the direction of the c axis of the wurtzite unit cell, the
[0001] direction (figure 1-d), as reported in other papers [3][4].

The imaged NWs did not display uniform contrast, but -in bright field TEM mode- presented
lighter patches of 2-14 nm in diameter randomly distributed on all surfaces, as seen in figure 1. They
could also be seen from the side as dips on the walls of NWs. Such patches are visible on parts of
the sample that have just been shortly exposed to the beam, and appear beneath the coating, therefore they
can’t be ascribed to beam damage. The most reasonable explanation is that these areas are shallow
cavities formed during the hydrothermal growth process, caused either by defects in the crystal lattice
or by impurities in the growth solution.

The MgO coating on the nanowires had been previously characterized by the group [1]. Further
analysis showed that the coating is highly reproducible, is amorphous and around 2-5 nm thick. Coatings
made with other oxides (ZrO₂, Cs₂O, Al₂O₃) resulted in homogeneous coverage of the ZnO
surface, proving the flexibility of this growth process. The ZnO-ZrO₂ core-shell NWs showed a
regular coating with a thickness ranging from sub-nanometre to 8 nm. The shell is homogeneous for
all the length of the NWs. A similar structure has been found for the ZnO-Al₂O₃ samples. The Cs₂O
coatings were slightly less homogeneous (up to 5 nm). On all the samples that have been examined by
HRTEM the outer shell has been found to be amorphous. On a few NWs, though, the shell was very
thin (few atomic layers): in this condition the contrast in the images is also compatible with a
crystalline coating matching the underlying ZnO lattice. This has been observed on zirconia (figure 2-
c) or magnesia (figure 2-a) coated ZnO NWs. On a larger scale, in some cases the external oxide
coating filled the gaps between nanowires. This reduces the surface area that can be put in contact with
the electrolyte and limits the overall efficiency of the device. Optimization of the hydrothermal shell
growth should reduce this phenomenon and increase performances of obtained DSSCs.

Figure 2. HRTEM images showing the different surface coatings of ZnO nanowires. In (c) the
amorphous region to the left is the carbon film supporting the specimen, while the coating is
probably less than 1 nm thick and not clearly distinguishable from the NW. (a) MgO, (b) and (c)
ZrO₂, (d) Al₂O₃, (e) Cs₂O.
4. Performance and discussion
The functionalized ZnO films have been packaged into DSSCs and tested under an AM 1.5 G solar simulator. A significant performance improvement has been found for the MgO and ZrO$_2$ devices over the pristine NW ones [5]. The ZrO$_2$ coating improved the short circuit current from 0.72 to 2.14 mA/cm$^2$. The best achieved device efficiency $\eta$ was 0.71% with ZnO-ZrO$_2$ core-shell NWs [5]. These results are an improvement over the ones obtained by our group [1] with ZnO and ZnO-MgO nanowires prepared with the same technique. The improvement is mainly due to two reasons. On one hand, as shown in figure 3, the oxide layer over the NWs allows to “bandgap engineer” the device, optimizing the charge separation and the injection of electrons into the ZnO core. On the other hand, the ruthenium based dyes that have been employed in the past are less suitable for ZnO devices. Such dyes have the tendency to agglomerate, limiting charge transfer [6]. Small molecule organic based dyes have shown here to be more suitable for ZnO, leading to a boost in overall performance.

5. Conclusions
ZnO NWs have been fabricated with different oxide coating via hydrothermal synthesis. The addition of the outer shell significantly increases device performances. Zirconia coating was the most effective coating, leading to a three-fold improvement in short circuit current and bringing the device efficiency to 0.71%. The whole fabrication process is carried out at temperatures below 100°C and is thus fully compatible with polymeric substrates. Further optimization and improvement in the fabrication and the packaging of the devices can lead to commercially interesting cheap and versatile solar cells.

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