

## Introduction

Dye sensitized solar cells (DSCs) are governed by light absorption, charge injection, electron transport and recombination and electrolyte diffusion. One way to improve the efficiency of these devices is by the design of highly ordered nanostructured semiconductor materials.<sup>1</sup> The advantages can be two-fold: Firstly charge transport within the metal-oxide can be enhanced and hence thicker films can be employed and secondly, the complete permeation with a solid-state hole-transport medium of the sensitized metal-oxide can be facilitated.

Nanostructured materials should promote vectorial electron diffusion and have as few recombination sights as possible so as to further enhance electron lifetimes and electron collection efficiencies. These materials should also have a high surface area so as to allow for efficient dye-loading and hence light absorption.

Highly ordered TiO<sub>2</sub> nanostructured films were prepared by reactive sputtering<sup>2, 3, 4</sup> and their charge transport characteristics evaluated in DSCs. These were compared to DSCs employing mesoporous TiO<sub>2</sub> films prepared by doctor blade technique using commercial paste. Charge transport characteristics were evaluated by impedance spectroscopy (IS) and current-voltage (iV) curves under simulated AM1.5G irradiation. Film morphology and structural properties were evaluated by scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively.

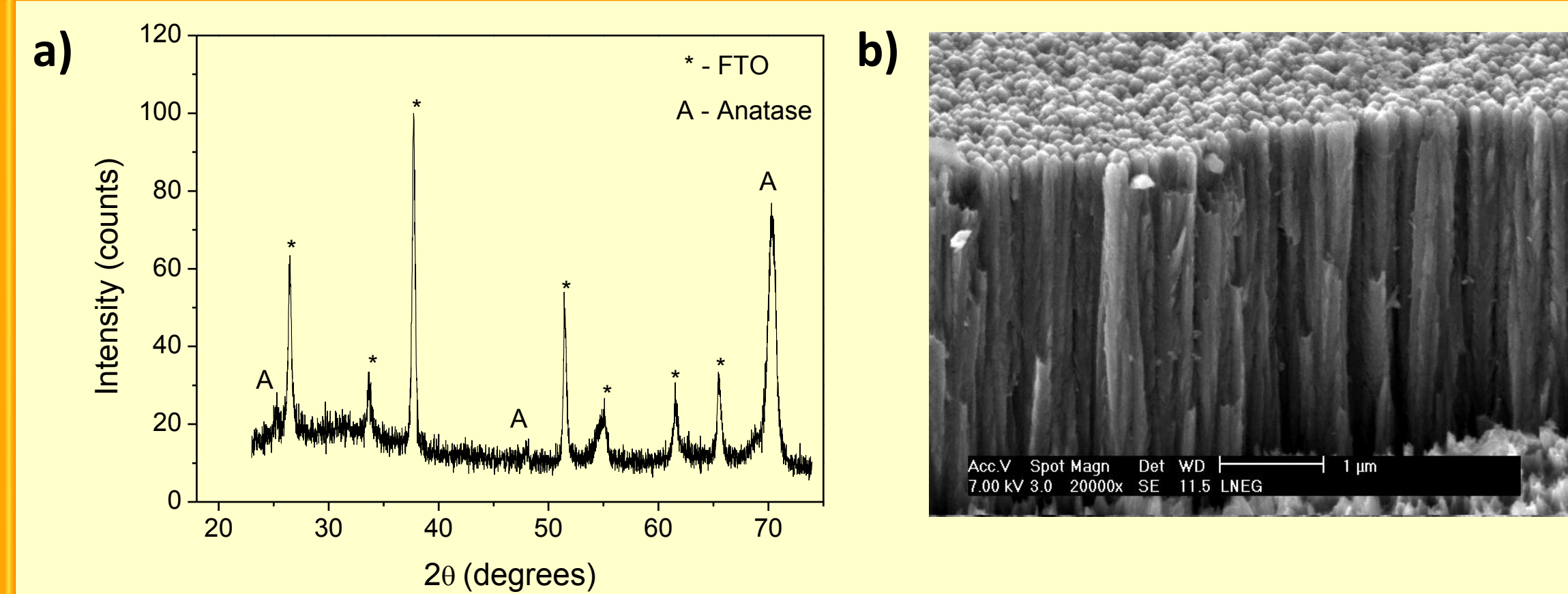


Figure 1 - a) XRD spectra and b) SEM image of a TiO<sub>2</sub> nanostructured film prepared by reactive sputtering.

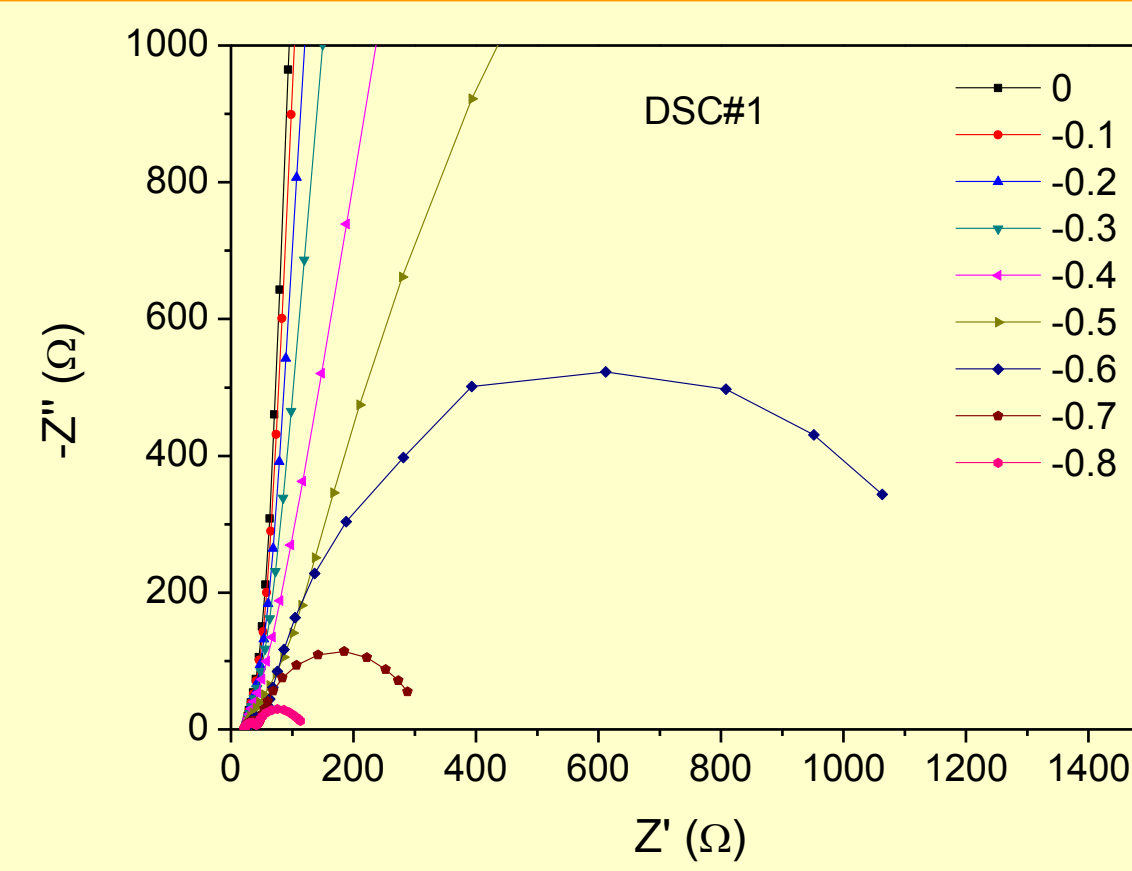


Figure 3 - EIS Nyquist plot of DSC#1 (mesoporous TiO<sub>2</sub> d=2.2µm). Frequency range 1Hz-100 kHz.

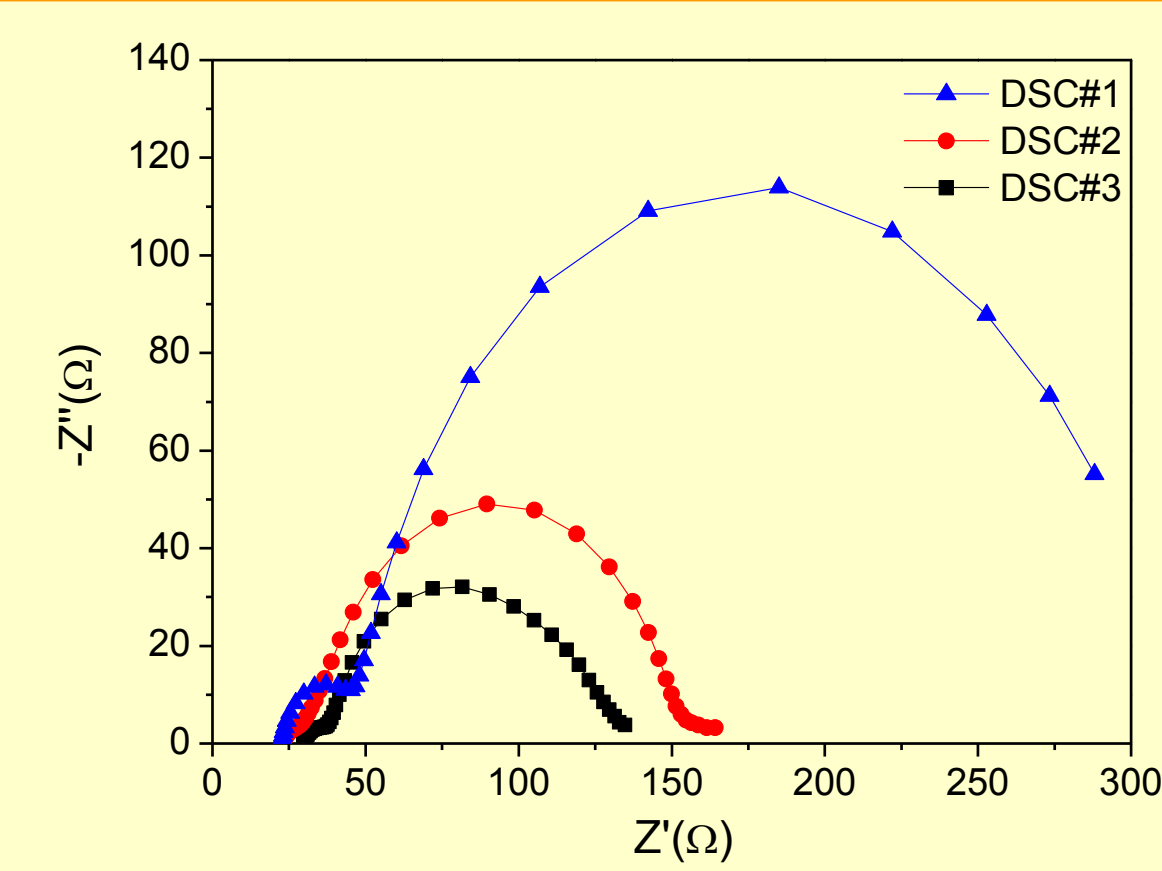


Figure 6 - EIS Nyquist plot at 0.7 V.

➤ The impedance spectra were taken under 530 nm LED illumination resulting in short-current densities and open-circuit voltages similar to those for the cells under simulated AM1.5G irradiation (1Sun).

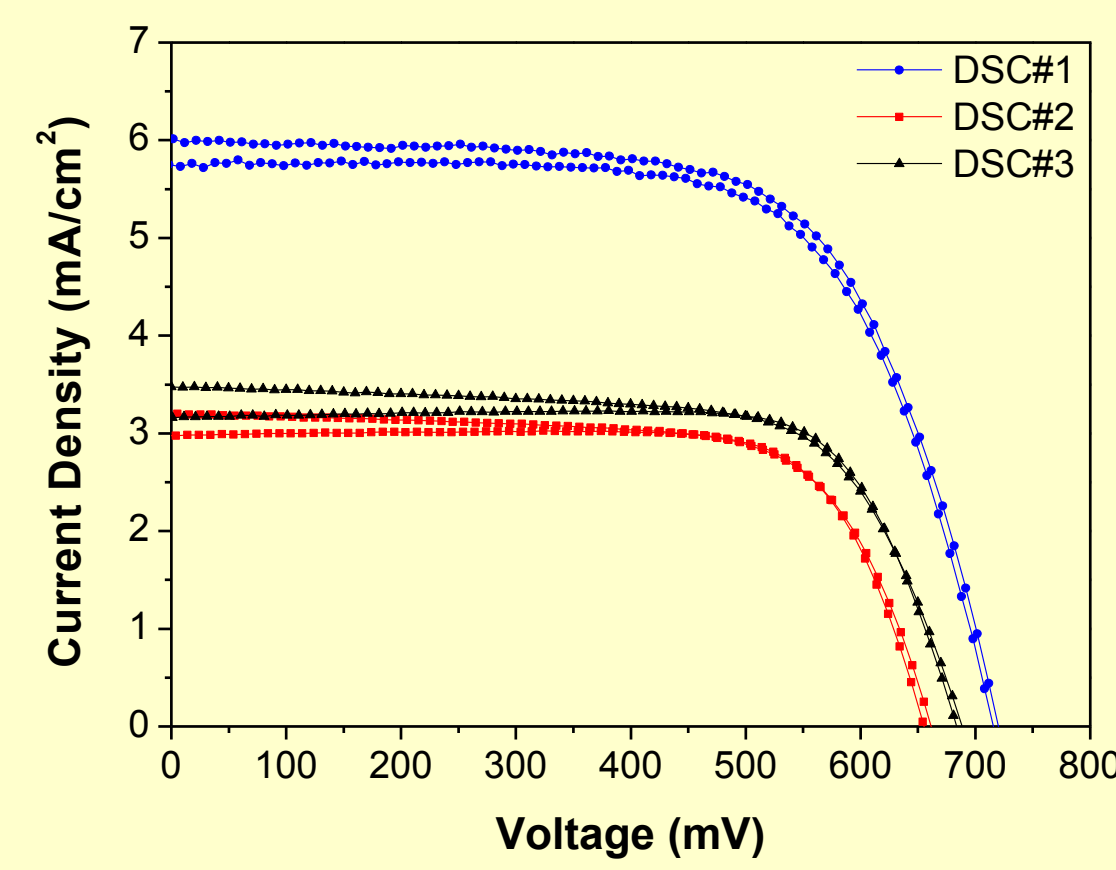


Figure 2 - iV curves under simulated light (100 mW/cm<sup>2</sup>; AM1.5G; T=25°C; Scan rate: 10 mV/s).

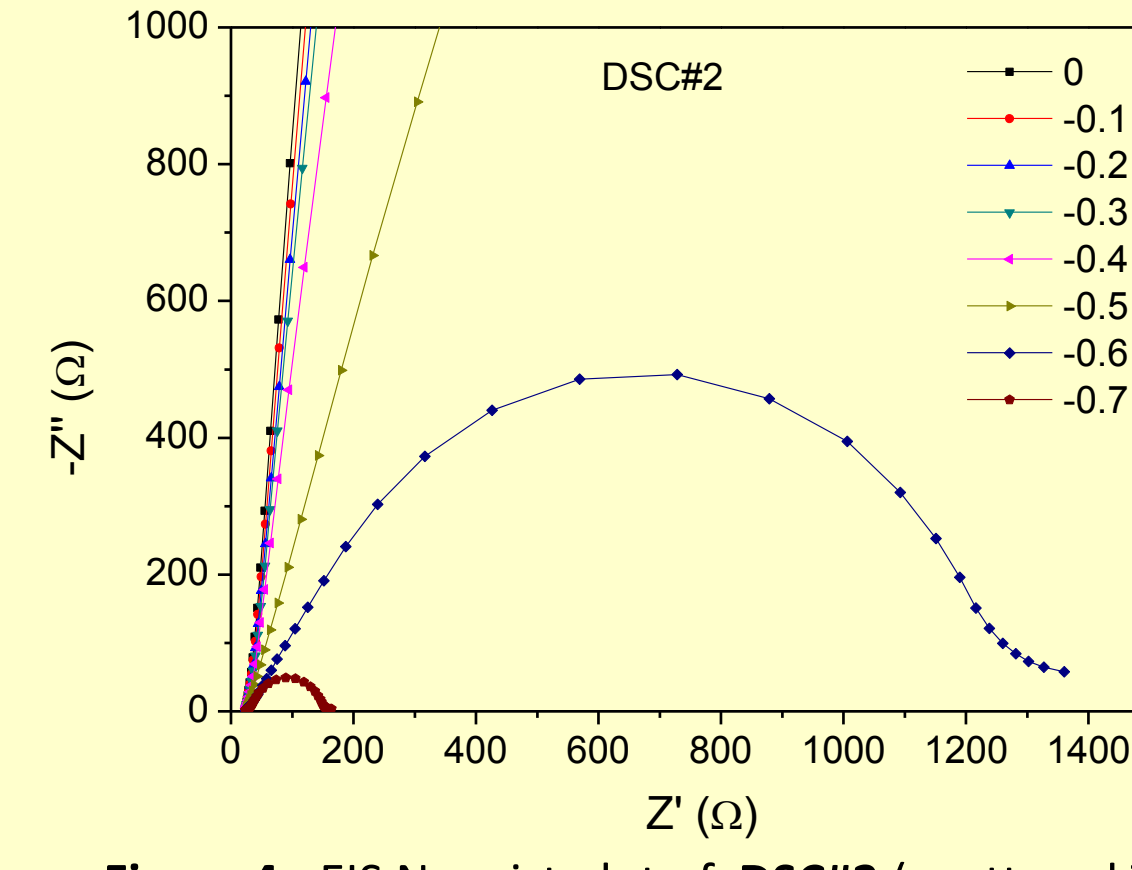


Figure 4 - EIS Nyquist plot of DSC#2 (sputtered TiO<sub>2</sub> d=1.2µm). Frequency range 0.1Hz-100 kHz.

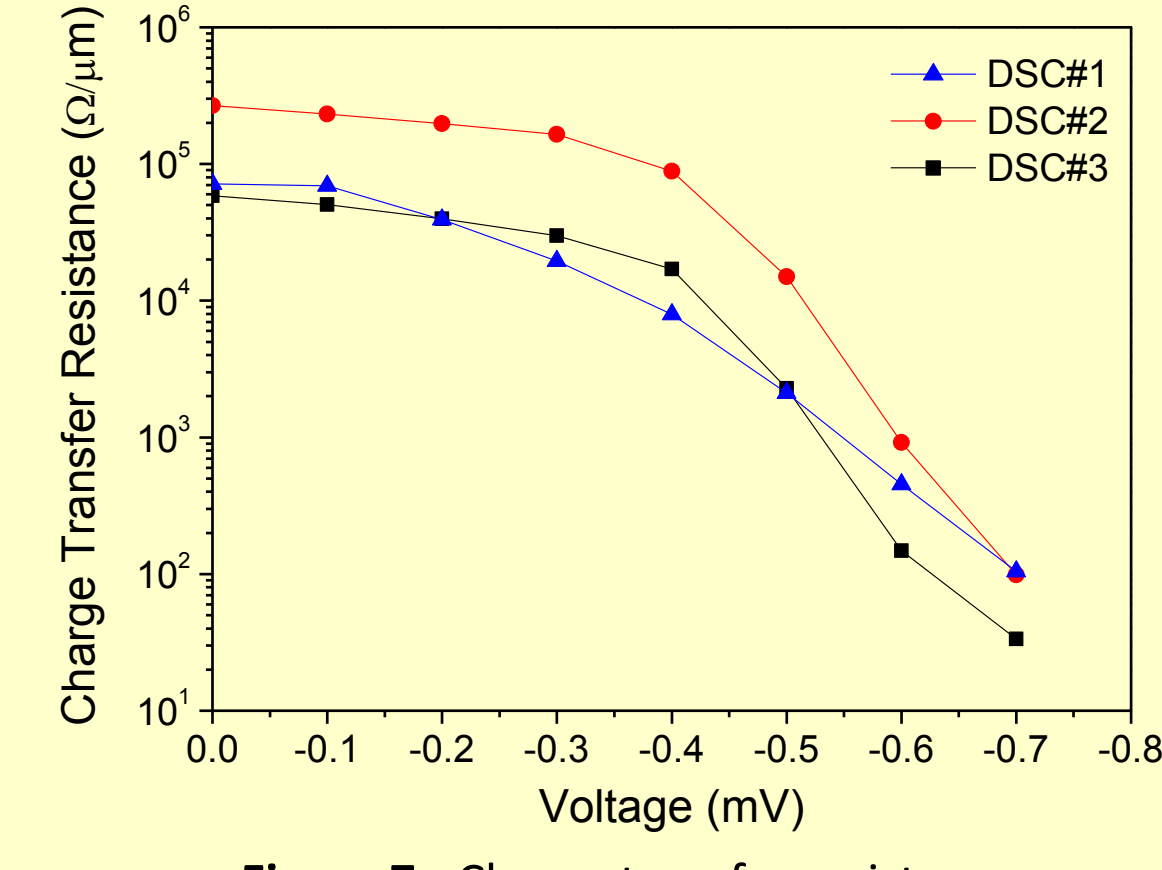


Figure 7 - Charge transfer resistance.

➤ Capacitance (C) and charge transfer resistance (R<sub>ct</sub>) were calculated by fitting a simple RC circuit to the central arc of the impedance spectra.

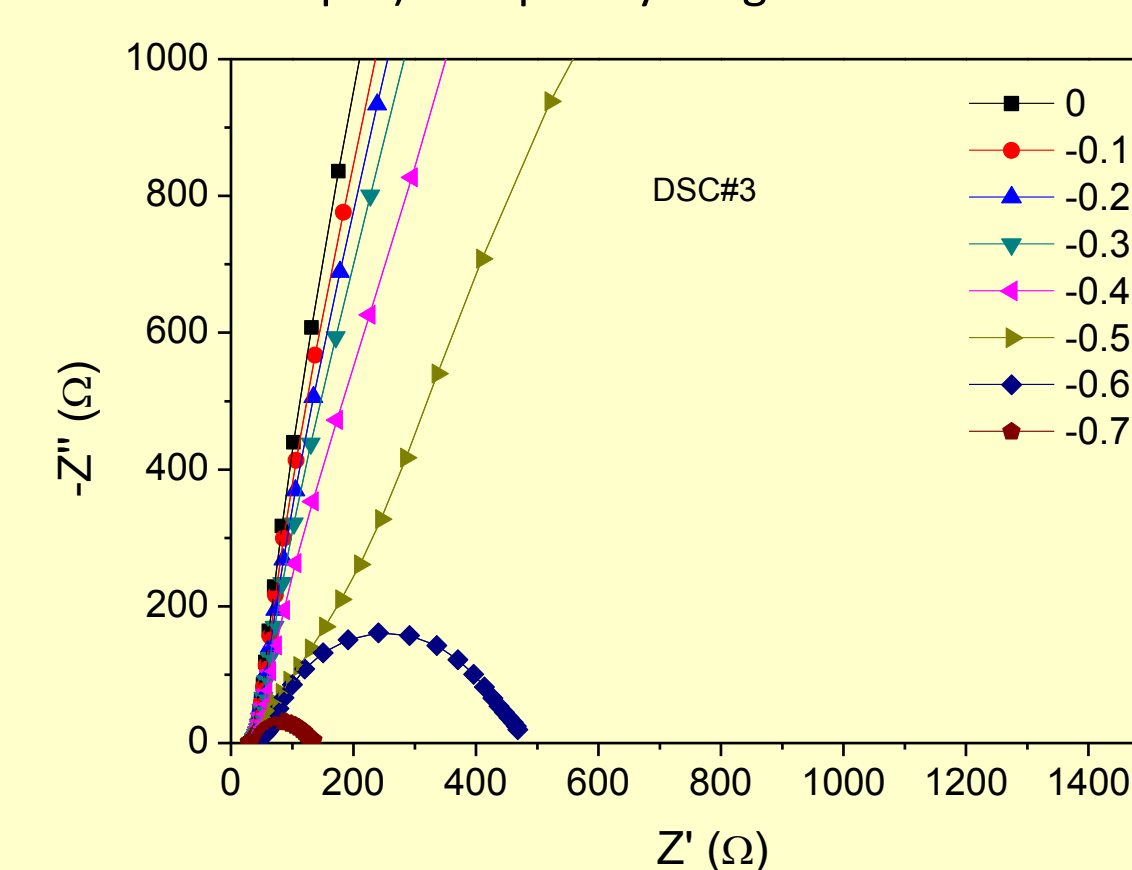


Figure 5 - EIS Nyquist plot of DSC#3 (sputtered TiO<sub>2</sub> d=2.5µm). Frequency range 0.1Hz-100 kHz.

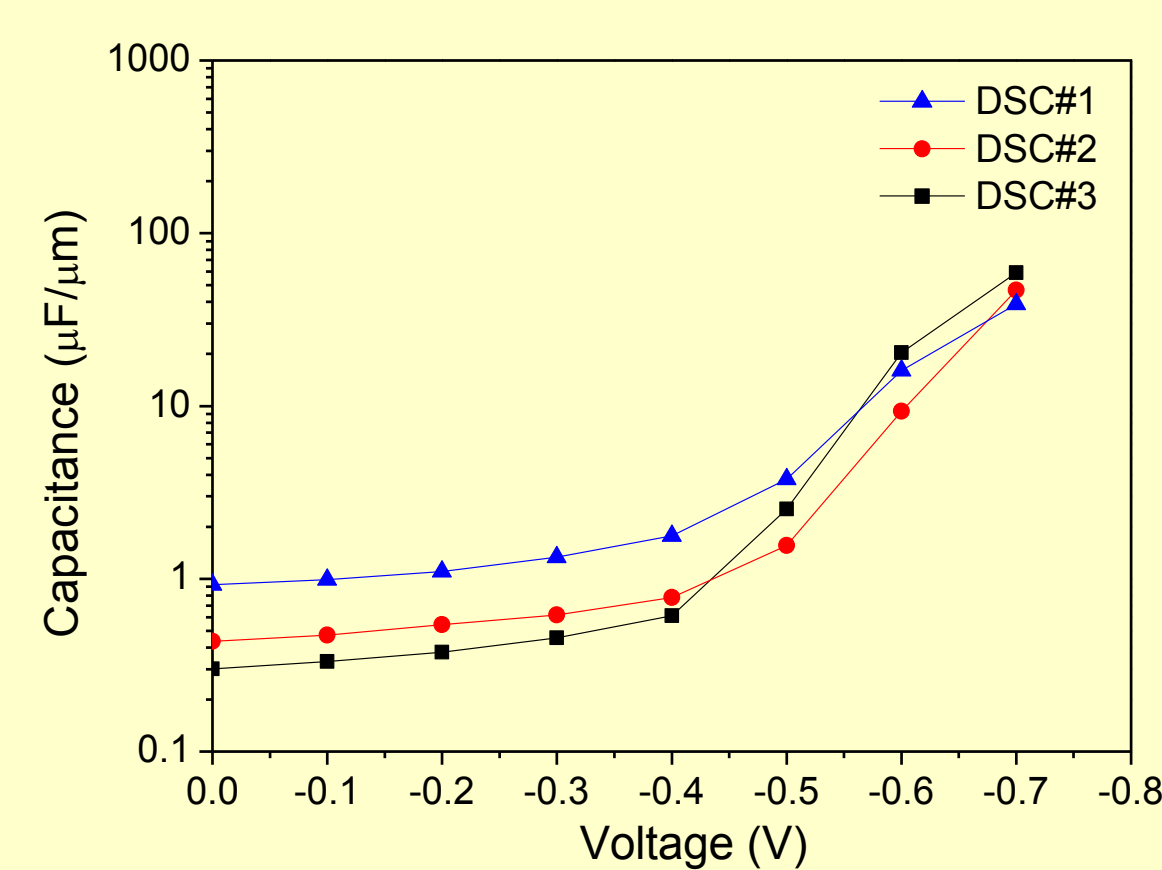


Figure 8 - Capacitance in TiO<sub>2</sub> film.

## Experimental Results

	TiO <sub>2</sub>	J <sub>sc</sub> (mA/cm <sup>2</sup> )	V <sub>oc</sub> (mV)	FF (%)	η (%)	R <sub>s</sub> (Ω)	d (µm)
DSC#1	Commercial	5.75	720	68	2.8	27.3	2.2
DSC#2	Sputtered	2.94	660	76	1.5	33.3	1.2
DSC#3	Sputtered	3.11	691	77	1.7	39.8	2.5

Films were immersed in dye solution (C=0.14 M N719 in ethanol/acetonitrile (1:1)) for 24 hours; Active area: 0.196cm<sup>2</sup>  
Electrolyte: 0.1M LiI, 0.05 M I<sub>2</sub>; 0.5 M tert-butylpyridine (TBP) in acetonitrile; Platinum coated counter electrodes;

Table 1 - Photovoltaic performance of ruthenium sensitized solar cells.

## Final Remarks

- The open-circuit voltages of the devices are comparable (c.a. 700 mV), and thus what defines the difference in the power conversion efficiency is the short-circuit current density, which could be related to different surface-to-volume ratios and dye surface coverage.
- According to impedance data (Figure 3, 4 and 5) the large central arc in the impedance spectra is related to high charge transfer resistances for all these films because the films are thin.
- The charge transfer resistance remains fairly constant for potentials up to c.a. -0.4 V because of the expected quasi-Fermi level distribution in the film due to diffusion driven charge transport. Only at potentials where the applied bias approaches that of the internal quasi-Fermi level, does the internal Fermi-level begin to rise and as such one observes an exponential:
  - ❖ Decrease in the charge transfer resistance
  - ❖ Rise in the measured capacitance.
- The overall behavior of the devices employing sputter deposited TiO<sub>2</sub> is similar to that of the standard device, suggesting that electron transport and recombination behaves similarly.
- Further work is to enhance the efficiency of the devices by:
  - ❖ Increasing film thickness
  - ❖ Further understand the morphology of the films so as to enhance dye loading and hence photocurrents and
  - ❖ Determine to what point or not orientated TiO<sub>2</sub> films actually enhance electron transport.

## References

- Maçaira, J. et al, *Review on nanostructured photoelectrodes for next generation dye-sensitized solar cells*. Journal of Renewable and Sustainable Energy Reviews 2013, 27, 334-349
- Meng, L. et al., *Sputtered Highly Ordered TiO<sub>2</sub> Nanorod Arrays and Their Applications as the Electrode in Dye-Sensitized Solar Cells*. Journal of Nanoscience and Nanotechnology 2011, 11, 929-934.
- Parreira, P. et al., *Dye-sensitized 1D anatase TiO<sub>2</sub> nanorods for tunable efficient photodetection in the visible range*. Sensors Actuators B Chemical 2012, 161, 901-907.
- Parreira, P. et al., *Optoelectronic properties of sputtered nanocrystalline TiO<sub>2</sub>*. HOPV 2010, 23-27 May, Assisi (Italy).