Counter Electrodes Based on metal decorated ZnO nanowire array for Dye or Quantum Dot Sensitized Solar Cells

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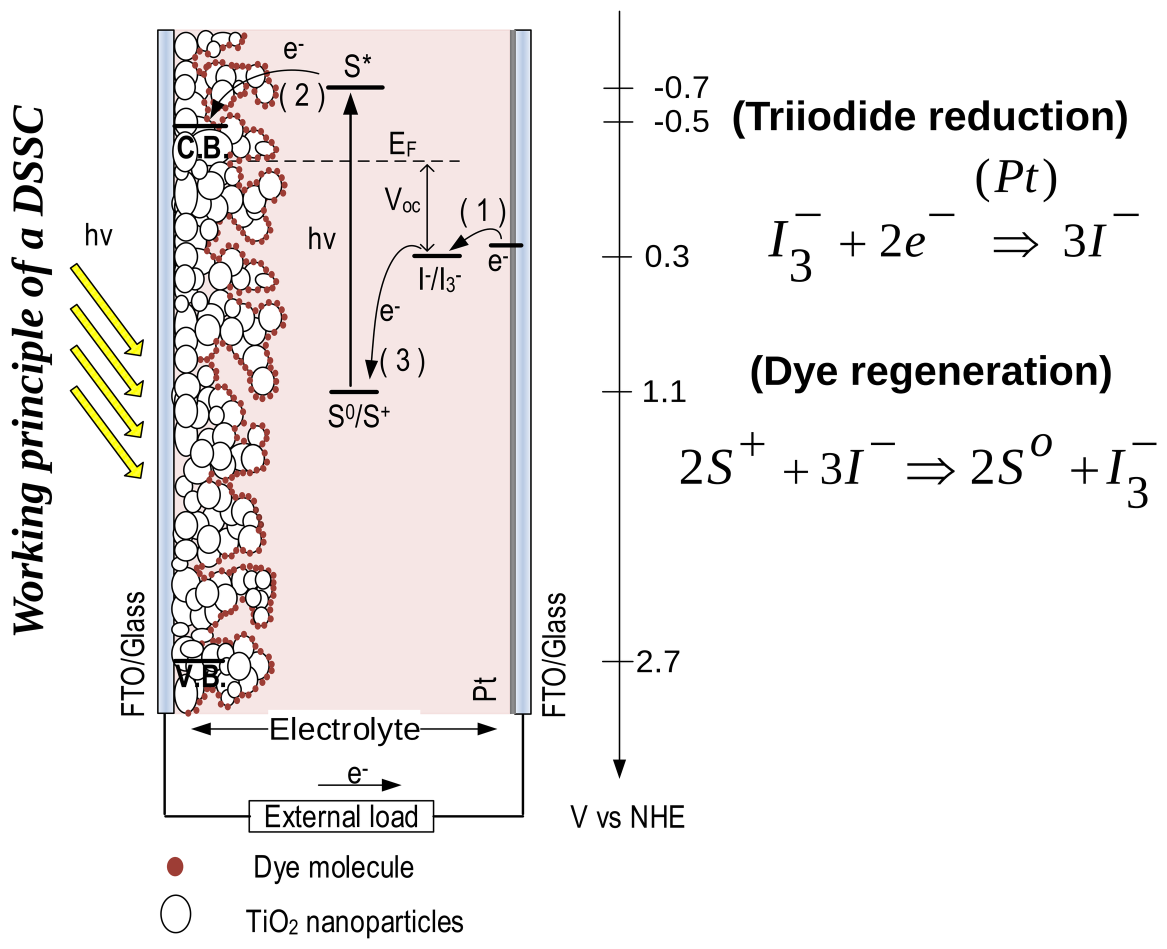
Introduction

Dye or quantum dot sensitized solar cells (DSSC or QDSSC) represent a category of the third generation of solar cells. One of the main components of these cells is the **metallized (Pt or Au) counter electrode (CE),** where the metal is usually deposited on a planar conductive substrate. The main role of the CE is to catalyze the reduction of an appropriate redox shuttle, therefore properties such as high surface area, fast reaction rate and low charge transfer resistance are necessary for high efficiency solar cells.

One way to increase the surface area is the use of a 3D scaffold for the deposition of the metal. **In the present study, undoped and doped with aluminum ZnO NW arrays have been used as a 3D scaffold for the deposition of Pt or Au**

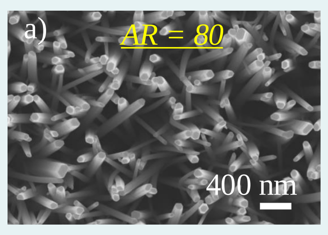
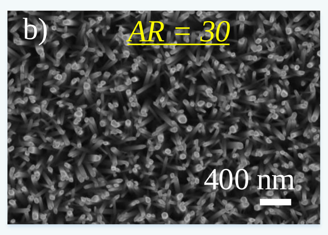
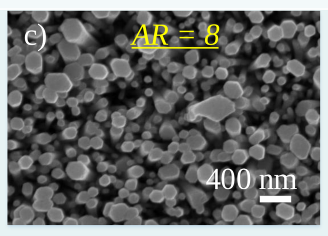
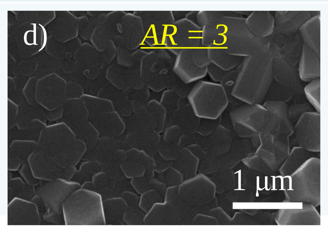


Results

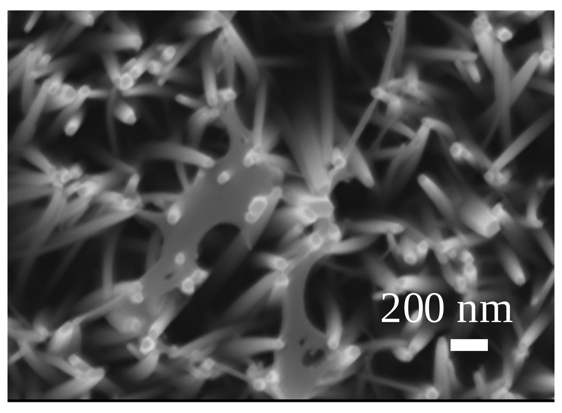
Platinum based electrodes

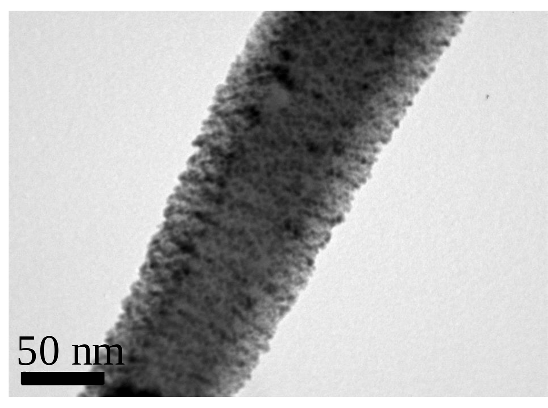
1) Effect of the aspect ratio (AR) of the NWs

Step 1: ZnO NW arrays with aspect ratio ranging **from 80 to 3** were prepared using different aqueous growth solutions

	Aspect ratio	Reagents	Morphology
1	80	0.05M $Zn(NO_3)_2$•$6H_2O$ 0.025M HMT 0.7M NH4OH 0.08g PEI/15 ml (MW 800)	
2	30	0.05M $Zn(NO_3)_2$•$6H_2O$ 0.025M HMT 0.45M NH4OH 0.08g PEI/15 ml (MW 800)	
3	8	0.02M $Zn(CH_3COO)_2$•$2H_2O$ 0.02M HMT	
4	3	0.08M $Zn(CH_3COO)_2$•$2H_2O$ 0.08M HMT	

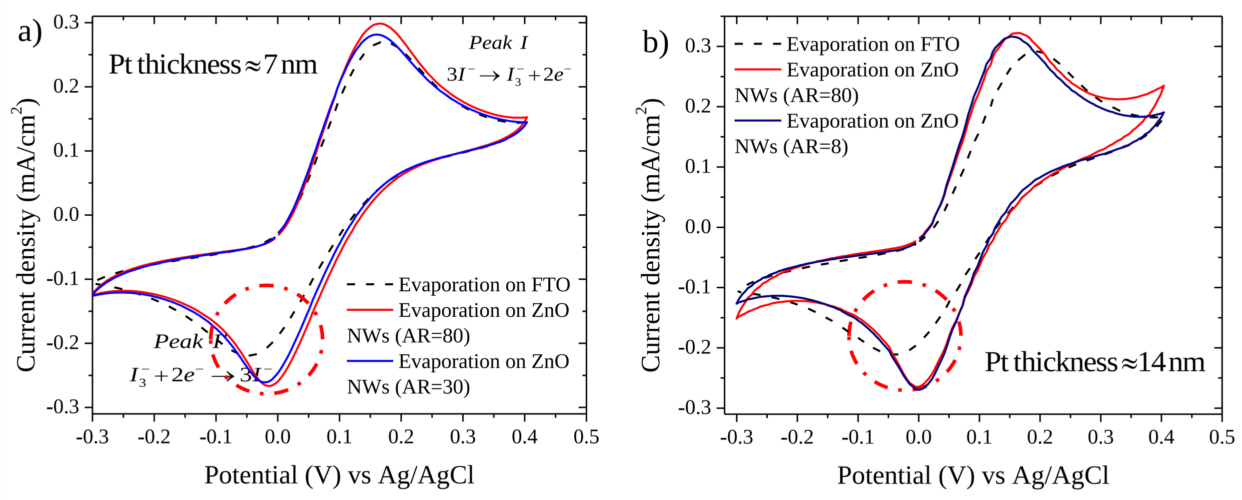
Step 2: The ZnO NW arrays with different aspect ratio were used as **a scaffold for the deposition of platinum** using thermal evaporation

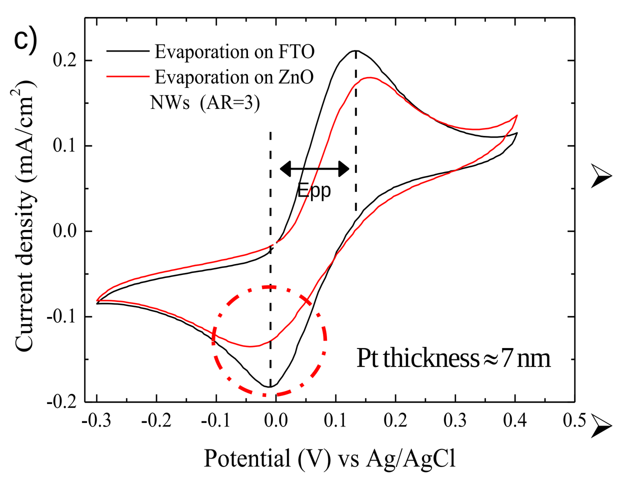




FE-SEM image of a Pt-based electrode, prepared by thermal evaporation of Pt on ZnO NW arrays **(left)** and a TEM image of a corresponding ZnO nanowire **(right)**

Step 3: The electrocatalytic properties of the Pt-based electrodes against the iodide/triiodide redox couple were examined using cyclic voltammetry. *(electrolyte: 10 mM KI, 1 mM I_2, 0.1 M $LiClO_4$ in propylene carbonate, scan rate: 10mV/s)*

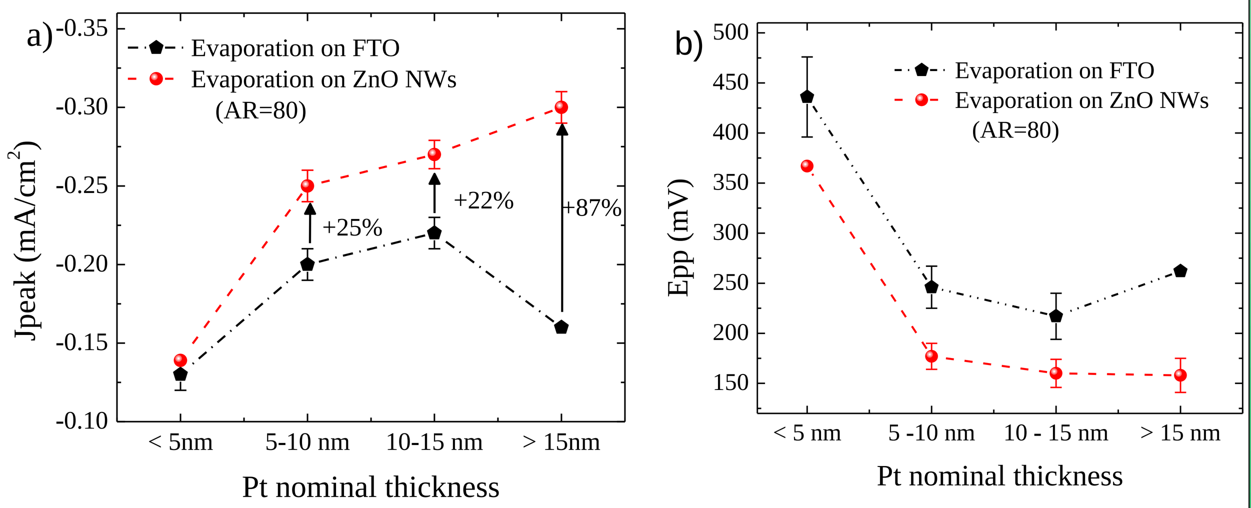




- Electrodes with **planar like geometry (Evaporation on FTO and on ZnO NW arrays with AR=3)** exhibit the lowest current density and largest peak to peak value (Epp)
- The **3D structured electrodes** provide an **enhanced surface area for Pt deposition**, facilitating the diffusion of ions to the catalytic active sites ⇨ improved current density and reduced peak to peak value (Epp)
- The electrocatalytic properties **are unaffected by the AR**, except from one case (AR=3), due to the **low Pt loading**

2) Effect of the amount of deposited Pt

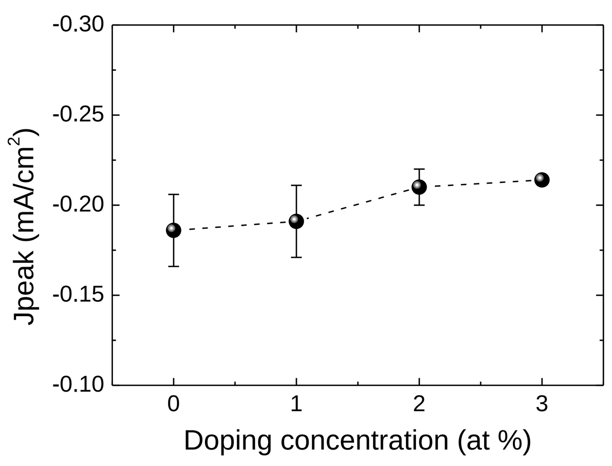
Electrodes with various thicknesses of Pt layer were prepared, both on planar substrates (FTO) and on ZnO NW arrays (AR=80).



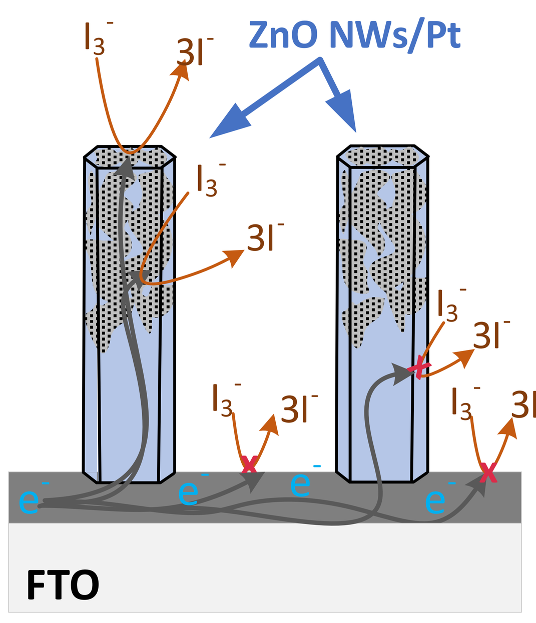
- The increment in peak current density was **20% to nearly 90%,** depending on the **amount of deposited Pt**
- For **thickness below 5nm** the catalytic active sites are **not enough** to support a **high peak current density** and **present an unduly high Epp**, in both cases.

3) Aluminum doping

A **small increment (up to 15%)** in peak current density was observed, when Al-doped ZnO NW arrays were used as a 3D scaffold for the deposition of Pt.



4) Proposed mechanism

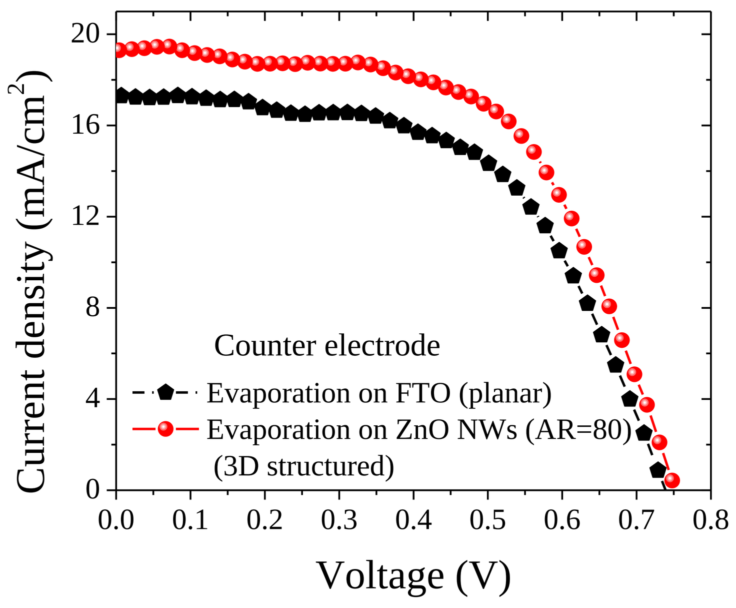


The improved properties are due to a number of reasons:

- High surface area
- The porous nature facilitates diffusion of triiodide ions
- High electron mobility along the NW axis
- Direct pathway for the electrons to the catalytic active sites
- No exchange of electrons when the electrolyte is in direct contact with the FTO substrate or with the uncovered area of the NWs

5) Dye Sensitized Solar Cells

J-V curves for devices using a **planar (Evaporation on FTO)** and a **3D structured (Evaporation on ZnO NW, AR = 80)** counter electrode



Photovoltaic properties of DSSCs using the two kinds of CEs

Counter electrode	Voc (V)	Jsc (mA/cm²)	FF	Efficiency %
Planar	0.72±0.04	19±2	0.53±0.08	7.3±0.6
3D structured	0.73±0.02	20±2	0.56±0.04	8.2±0.5

12% increment for the 3D structured CE compared to the planar

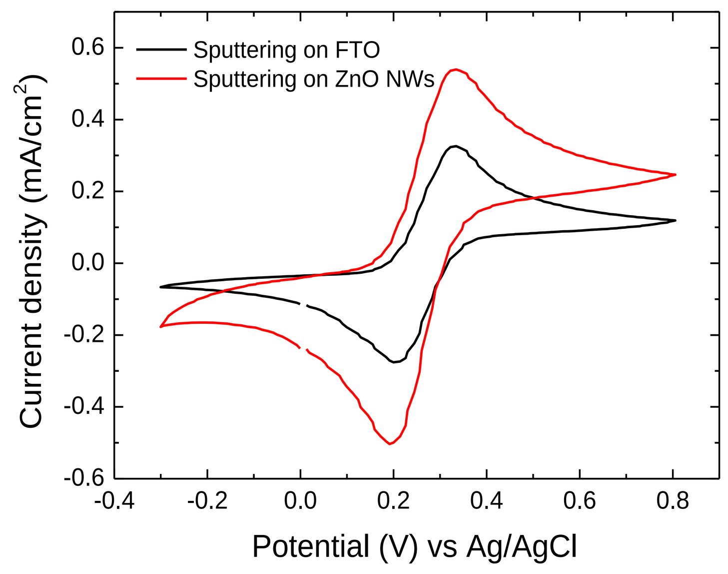
Gold based electrodes

Step 1: ZnO NW arrays with **AR= 80** were prepared

Step 2: The ZnO NW arrays were used as **a scaffold for the deposition of gold** using sputtering

Step 3: Annealing at 450°C/2h followed the deposition of gold

Step 4: A **cobalt based redox electrolyte** was used for the cyclic voltammetry experiments . *(electrolyte: 0,2 mM Co(II), 0.1 M $TBPAF_6$ in acetonitrile, scan rate: 50mV/s)*



- The increment in peak current density was more drastic in this case and further work has to be done to identify all the reasons for this behavior

Conclusions

- ZnO NW arrays can be used as a 3D scaffold for the evaporation of Pt or Au to prepare CEs with high surface area, for dye or quantum dot sensitized solar cells.
- The prepared 3D electrodes exhibited **an increment in peak current density for triiodide reduction up to 87%**, compared to planar (Pt evaporation on FTO) electrodes.
- The AR of the ZnO NW arrays has a minimal effect, due to low Pt loading
- The resulting devices with a 3D structured electrode, showed a **12% increment in efficiency**, compared to devices having planar CEs.
- The improvement in the properties of the 3D CEs is attributed to the enhancement in the surface area for the deposition of the metal, due to the presence of ZnO NW arrays.

Acknowledgments

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