

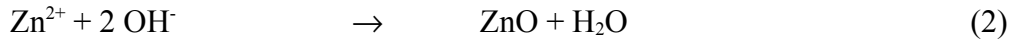
# 1-D ZnO nanostructures and application to ETA-solar cells

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The presentation will focus on the electrochemical/chemical growth of ZnO and ZnO/CdSe nanowires (NWs) and nanotubes (NTs). Investigation and comparison of their optical properties indicate the interest of using ZnO/CdSe NWs and NTs as building blocks for solar cells, especially semiconductor sensitized nanostructured solar cells [1].

An overview of the electrodeposition of ZnO NW arrays from the reduction of dissolved molecular oxygen ( $O_2$ ) in zinc chloride solutions will show the progress made to tailor the dimensions of ZnO-NWs and their optical and electrical properties, by varying the electrodeposition parameters. The electrodeposition of arrays of ZnO NWs occurs from the  $O_2$  reduction in a solution of  $ZnCl_2$  as zinc precursor and KCl as supporting electrolyte, following equations 1 and 2:



The major role played by the  $Cl^-$  ions used in the supporting electrolyte, to controlling the mechanism of formation will be discussed. In spite of the internal structure of ZnO that favors the anisotropic growth along the [0001] direction, it is possible to monitor the ZnO-NW dimensions. The change in the local composition of the electrolyte around the nanowire during the electrodeposition is a major parameter that affects the nanowire growth mechanism. The influence of the ratio between the  $O_2$  reduction rate and the diffusion of  $Zn^{2+}$  at the cathode on the ZnO NWs morphology has been emphasized and the role of  $Cl^-$  concentration ( $[Cl^-]$ ) demonstrated.

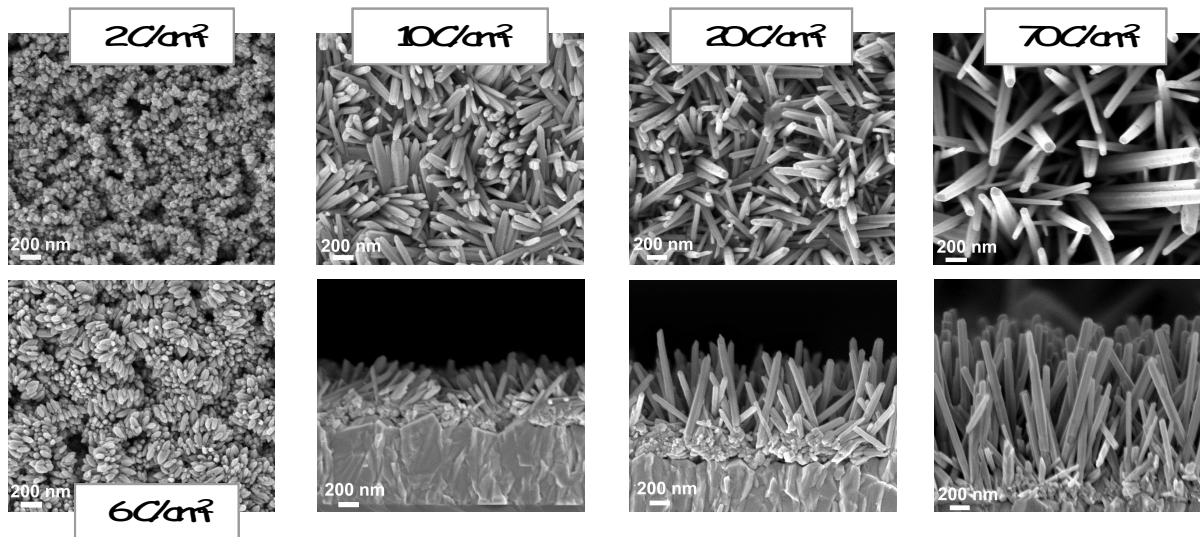


Fig. 1. SEM micrographs of electrodeposited ZnO nanowire arrays in presence of 0.1 M KCl as a function of the charges, Top view and Cross section

For example, no lateral growth of the NWs was observed when the reduction of  $O_2$  was relatively fast, the corresponding deposition efficiency being very low (~5%). This type of

deposition mechanism is favored at low  $[Cl^-] \sim 0.1 \text{ M}$  [2] (Fig. 1). On the contrary, the decrease of the  $O_2$  reduction rate resulted in an enhancement of the deposition efficiency. The highest efficiency (40-55 %) was obtained by using high  $[Cl^-]$  (i.e.  $[KCl] = 3.4 \text{ M}$ ) resulting in an enhancement of the longitudinal growth and a considerable lateral growth [3] (Fig. 2). ZnO-NWs with a diameter between 25 and 500 nm and a length up to 10  $\mu\text{m}$  were successfully obtained, resulting in high aspect ratios up to 50. The influence of the electrodeposition conditions on the donor density of ZnO nanowires was investigated by using electrochemical impedance spectroscopy. Donor densities from  $5 \times 10^{19}$  to  $3 \times 10^{20} \text{ cm}^{-3}$  were obtained for as-deposited samples. They decreased by two orders of magnitude to  $10^{17}$  -  $10^{18} \text{ cm}^{-3}$  after annealing in air (1 hour at 450  $^{\circ}\text{C}$ ) [4, 5].

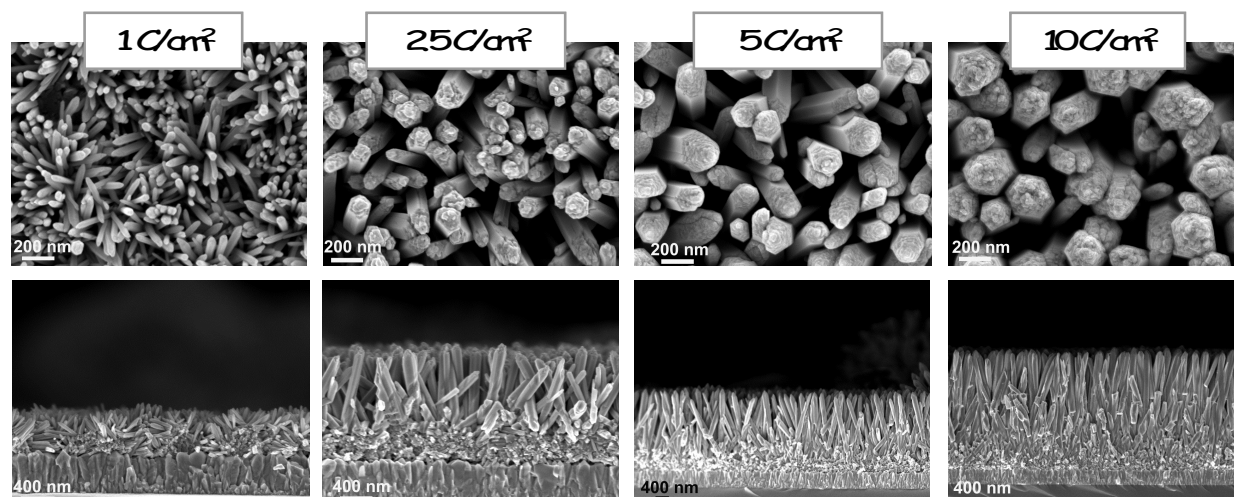


Fig. 2. SEM micrographs of electrodeposited ZnO nanowire arrays in presence of 3.4 M KCl as a function of the charges, Top view and Cross section

The metastability of the ZnO polar surfaces in aqueous solutions has been exploited to dissolve the core of ZnO NWs leading to ZnO nanotubular structures. These surfaces are terminated exclusively by  $Zn^{2+}$  or by  $O^{2-}$  on the  $(0001)$  and  $(000\bar{1})$  ZnO surfaces, respectively, and induce a net electrostatic dipole moment parallel to the  $c$  axis. The adsorption properties of  $Cl^-$  being different on the various ZnO crystalline faces, a strategy to transform in a short time the NWs into ZnO NTs has been developed ( $\sim 2-3$  hours etching in 3.4 M KCl) [6].

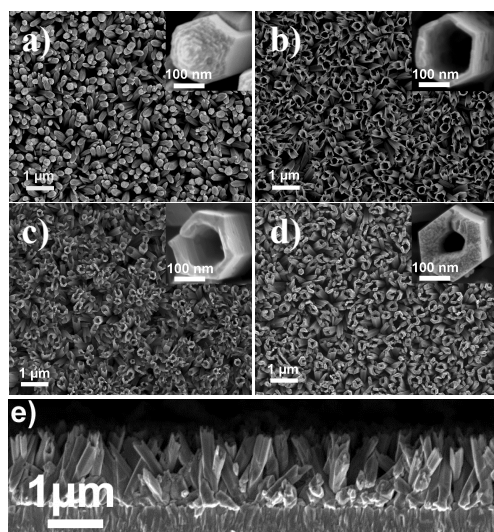


Fig. 3 SEM micrographs of arrays of ZnO NWs and NTs.

- a) ZnO NTs,
- b) after dissolution of the core of ZnO NWs (second step), c and d ) Arrays of ZnO NTs after further ZnO electrochemical deposition (third step, c: 2.5  $\text{C}/\text{cm}^2$  and d: 10  $\text{C}/\text{cm}^2$ ),
- e) cross section of an array of ZnO NTs.

The wall thickness limited to  $\sim 25$  nm in the etching process can be controlled by regrowing a ZnO layer along the inner wall of the NTs (Fig. 3). Optimization of various steps of the process allows to obtain ZnO-NTs with a diameter between 200 and 600 nm, wall thickness and length in the range of 25-100 nm and 0.5-10  $\mu\text{m}$ , respectively.

The structural and optical properties of ZnO NWs and NTs were analyzed by transmission electron microscopy and optical spectroscopy. The influence of the NWs dimensions on the light scattering was studied on arrays of ZnO NWs with different lengths (0.5-2  $\mu\text{m}$ ) and diameters (100- 330 nm). The NW length and diameter were found to be major parameters that can modify the intensity and the wavelength of the scattered radiation, respectively [7]. A significant scattering in the visible range was attained for  $\sim 1.5$   $\mu\text{m}$  long and  $\sim 330$  nm large ZnO NWs. Finally, the influence of the morphology of the 1-D ZnO nanostructures on the light scattering has been emphasized by comparing arrays of ZnO NWs and NTs (Fig. 4).

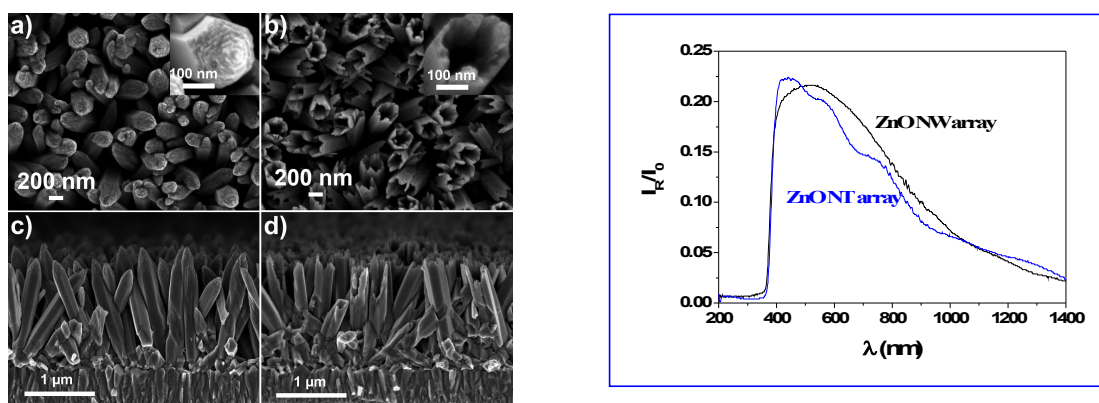


Fig. 4 On the left) SEM micrographs of: a) and d) an electrodeposited ZnO nanowire array; b, and c) the resulting ZnO nanotube array after the dissolution of the core. On the right) Total reflectivity of ZnO NWs and NTs with same external dimensions.

The sensitization of both 1D-nanostructures to solar light was also studied by conformally coating them with a CdSe thin layer (20-40 nm) (Fig. 5), made by electrochemical deposition [1]. A clear correlation between the light scattering before coating and the absorption in the resulting ZnO/CdSe core-shell nanostructures was found [8].

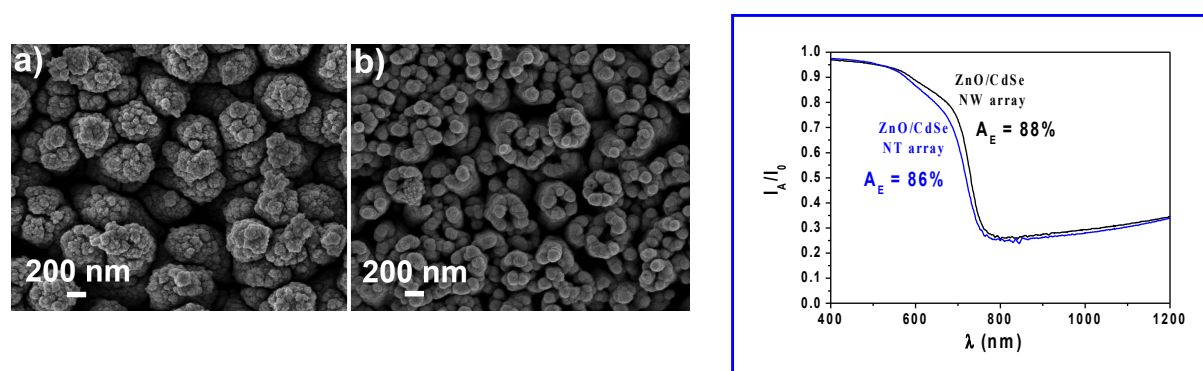


Fig. 5. On the left): SEM micrographs of arrays of core-shell ZnO/CdSe NWs (a) and NTs (b). Thickness of CdSe layer is 40 nm on ZnO NWs and 20 nm on ZnO NTs. On the right): Absorption of ZnO/CdSe NWs and NTs

The enhancement of the scattering for wavelengths at which CdSe exhibits a relatively low absorption coefficient resulted in an effective absorption as high as 88%, in the 400-725 nm range of the AM1.5 solar spectrum range, with a CdSe shell thickness of  $\sim 20$  nm for ZnO/CdSe NTs (Fig. 5). The results will be discussed in the frame of semiconductor sensitized nanostructured solar cells.

ZnO/CdSe/CuSCN ETA solar cells were assembled based on ZnO NWs and NTs with identical external dimensions. On one hand, the characteristics of the solar cells based on arrays of 1-D nanostructures gave insights into the influence of the morphology and dimensions of ZnO NWs and NTs on the solar cell performances. On the other hand, the results confirmed the great potential of ZnO NT arrays, which exhibit a higher porosity and larger surface area than NWs, as building blocks for nanostructured solar cells. Although nanocrystalline CdSe has been used as a light absorber, the present results may be extended to other absorbers such as dye and quantum dots

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