

# Modification of surface defects in vertically-aligned ZnO nanostructures to improve power conversion efficiency of excitonic solar cells

Irene Gonzalez-Valls<sup>a</sup>, Juan S. Reparaz<sup>a,b</sup>, Frank Güell<sup>c</sup>, Markus R. Wagner<sup>b</sup>, Gordon Callsen<sup>b</sup>, Belen Ballesteros<sup>a</sup>, Axel Hoffmann<sup>b</sup>, Monica Lira-Cantu<sup>a\*</sup>



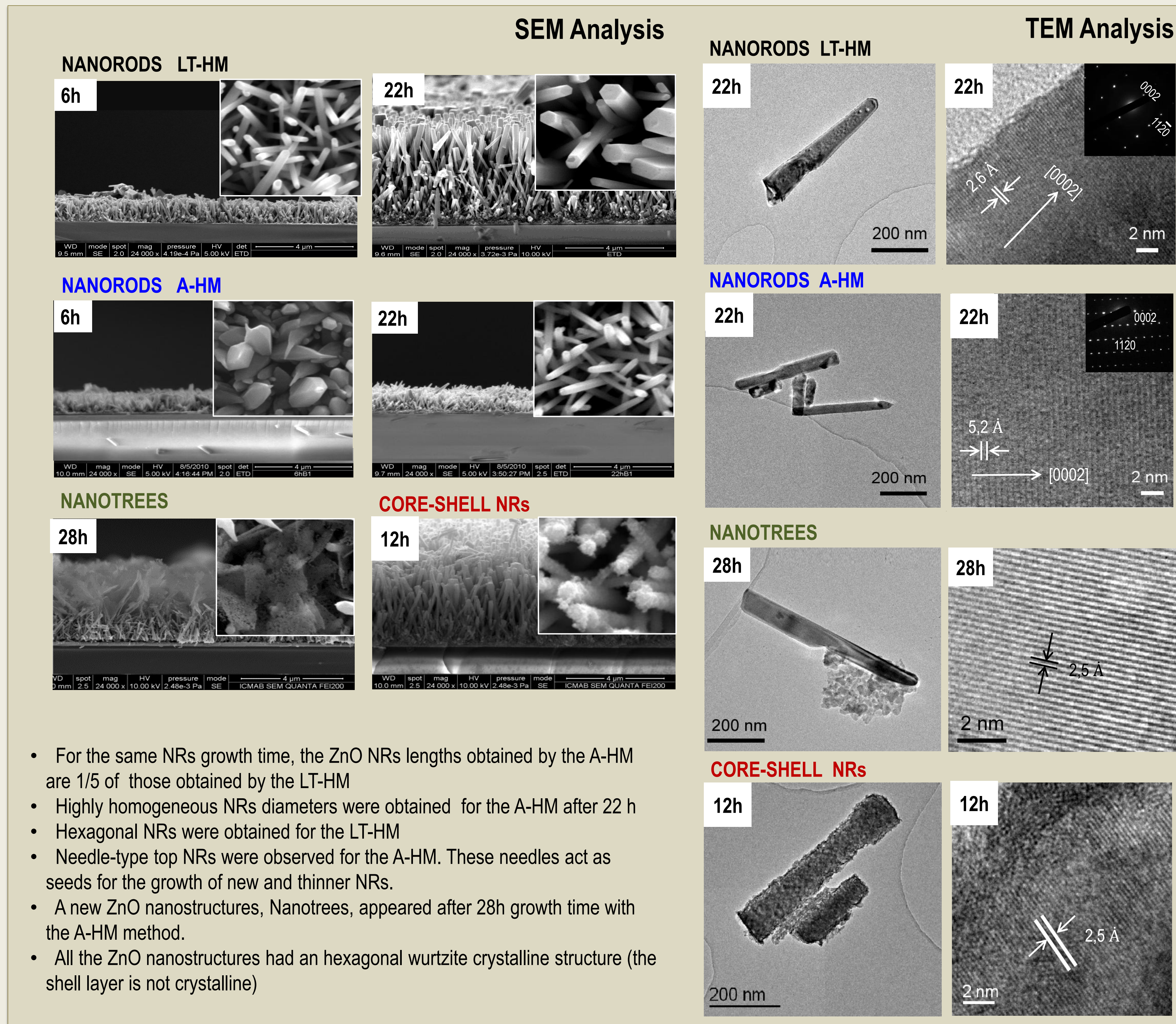
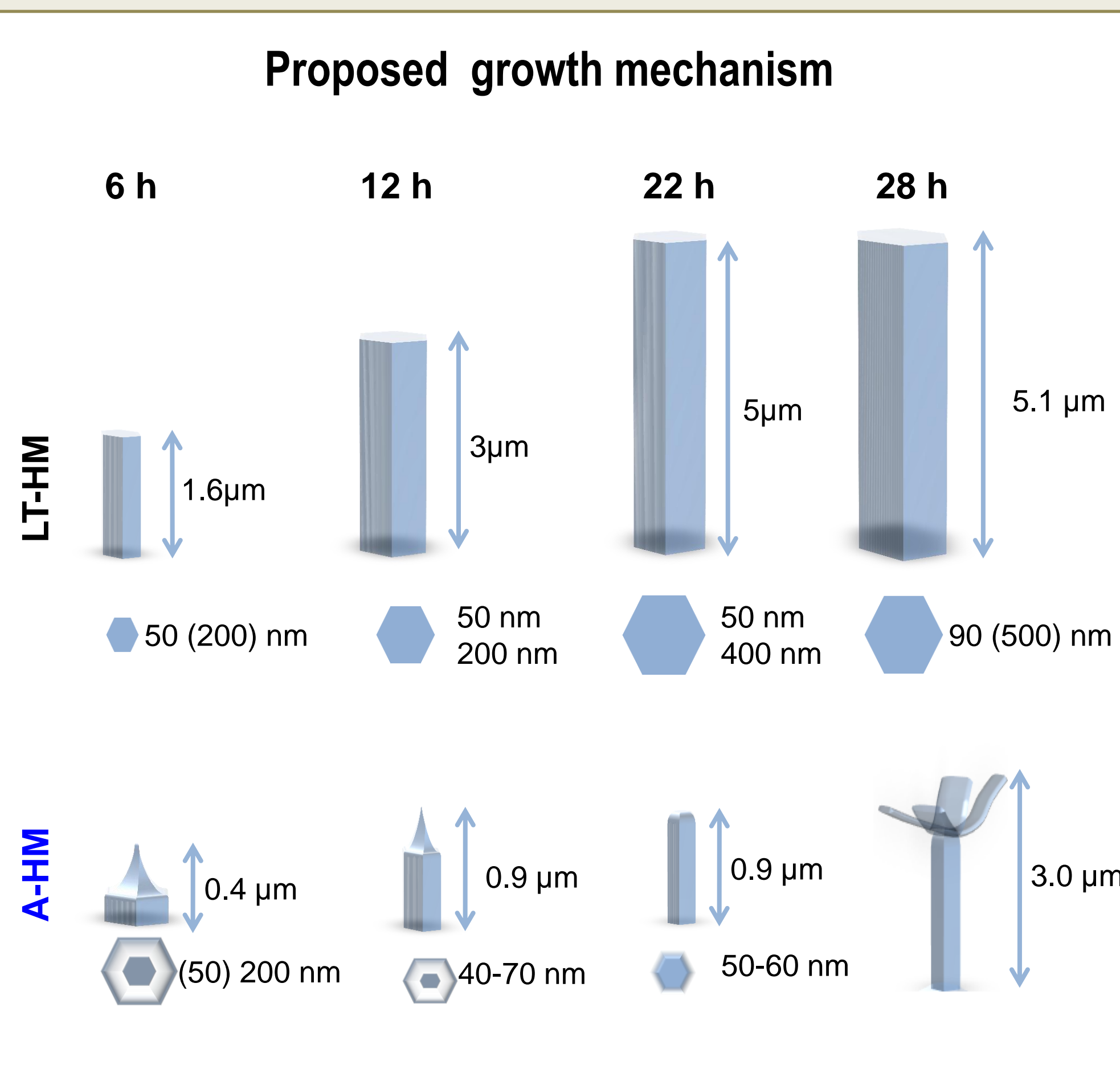
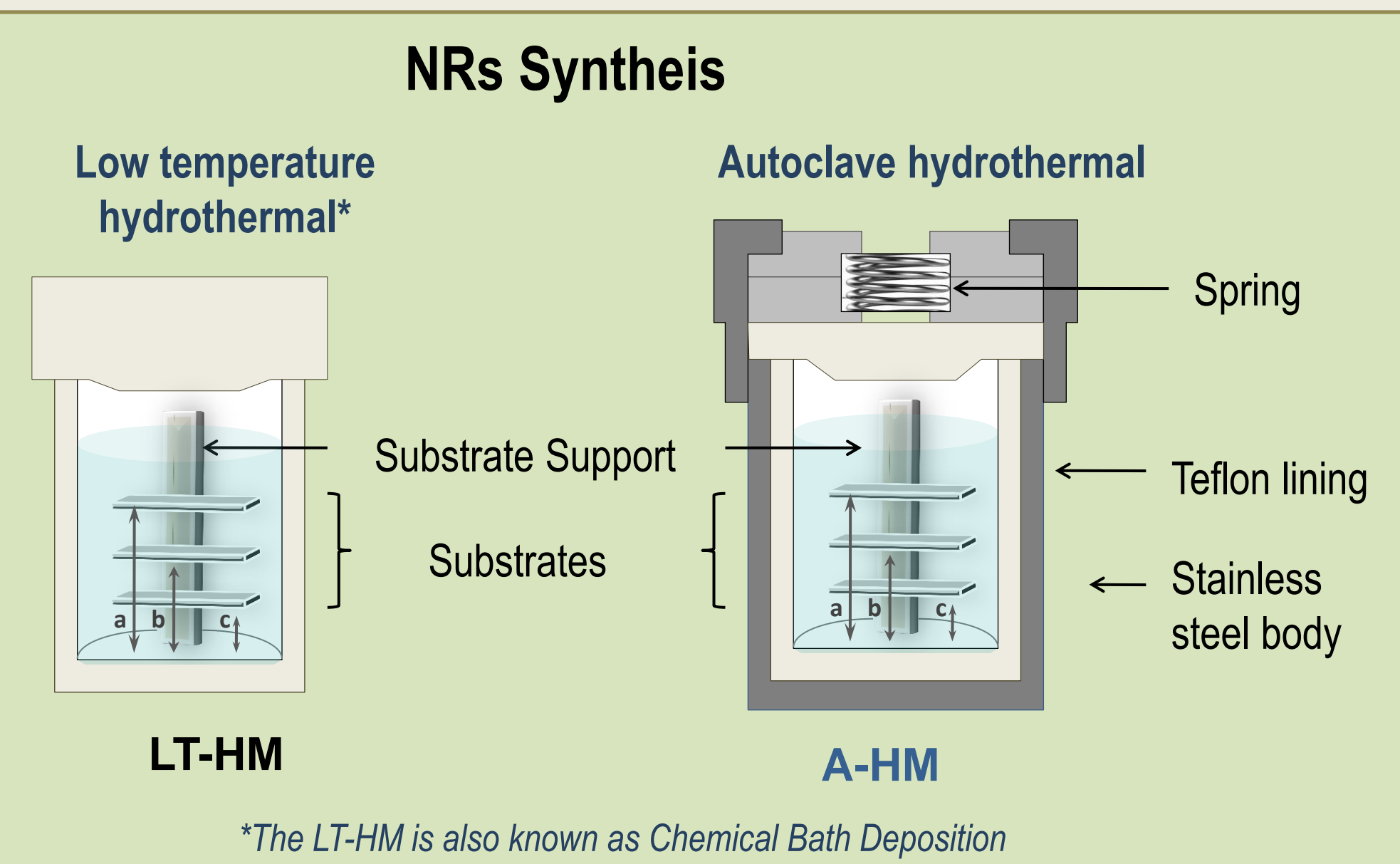
<sup>a</sup>, Centre d'Investigació en Nanociència i Nanotecnologia, Campus UAB, Edifici ETSE, Bellaterra, 09819, Spain..

<sup>b</sup>, Institut für Festkörperphysik, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin, Germany.

<sup>c</sup>, M-2E, IN2UB, Departament d'Electrònica, Universitat de Barcelona, C/Martí Franques 1, 08028 Barcelona, Catalunya, Spain.

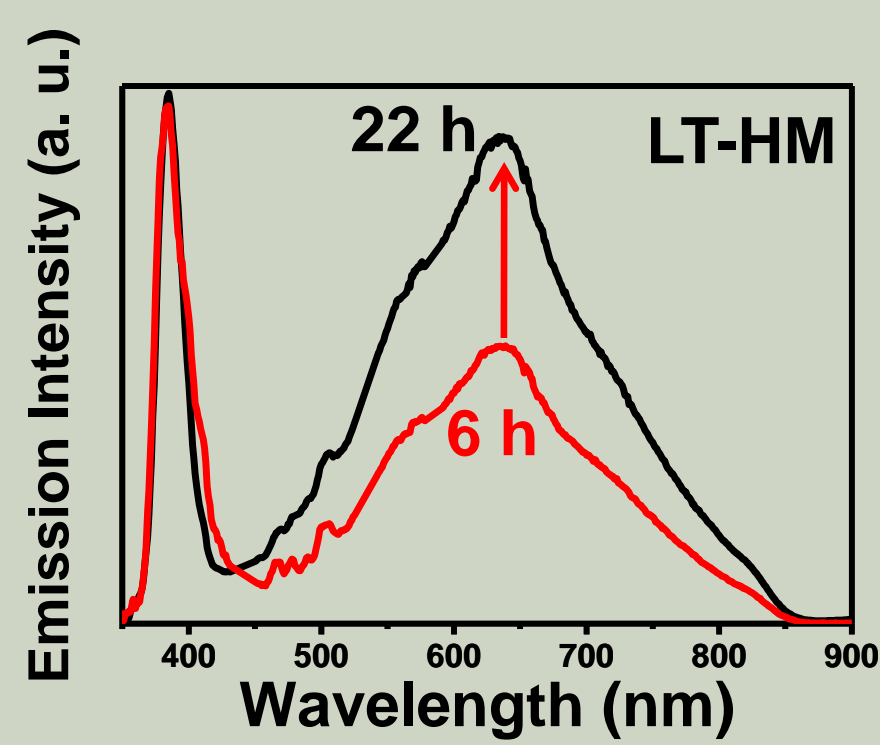
## Abstract

In this work we present the synthesis and photovoltaic application of four different vertically-aligned ZnO nanostructured electrodes: ZnO nanorods prepared by the a) low-temperature hydrothermal method (LT-HM) and the b) autoclave method (A-HM), c) ZnO nanotrees (NTs) and d) ZnO core-shell NRs with an indium sulfide layer as the shell (CS). The electrodes have been applied in Dye sensitized solar cells (DSCs) and Polymer solar cells (PSCs). The photovoltaic properties of each type of nanostructured electrode were optimized separately. Our results show that the optimal power conversion efficiency depends in great extent on NR dimensions (length and diameter) and the final ZnO nanostructure. In this respect, we have observed an increase in power conversion efficiency when the NR nanostructure is modified as follows: ZnO NRs LT-HM < A-HM < NT < CS for any of the two types of solar cells.



## Optical quality of ZnO NRs

Photoluminescence (PL)



→ Emission band  $\lambda \approx 380$  nm: near band-edge emission (NBE): recombination of the free exciton (FX).

→ Emission band between 450 nm – 750 nm: deep level emission band, green band.

The green band mainly originates from the surface of the NWs, i.e. the defects are expelled from the core of the NWs.

**Increasing NRs growth time:**

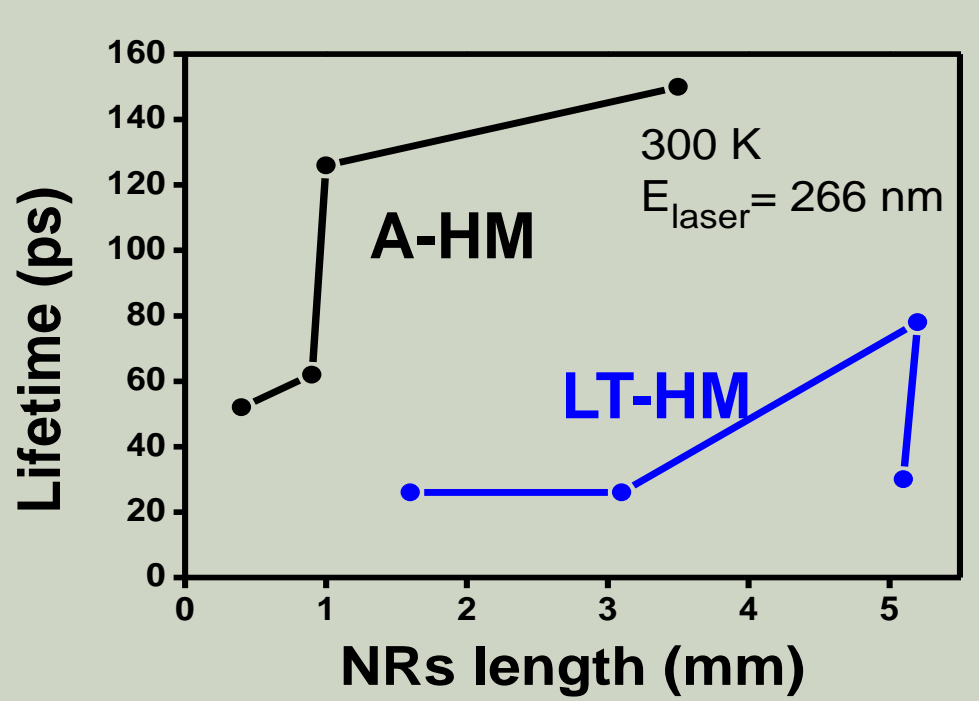
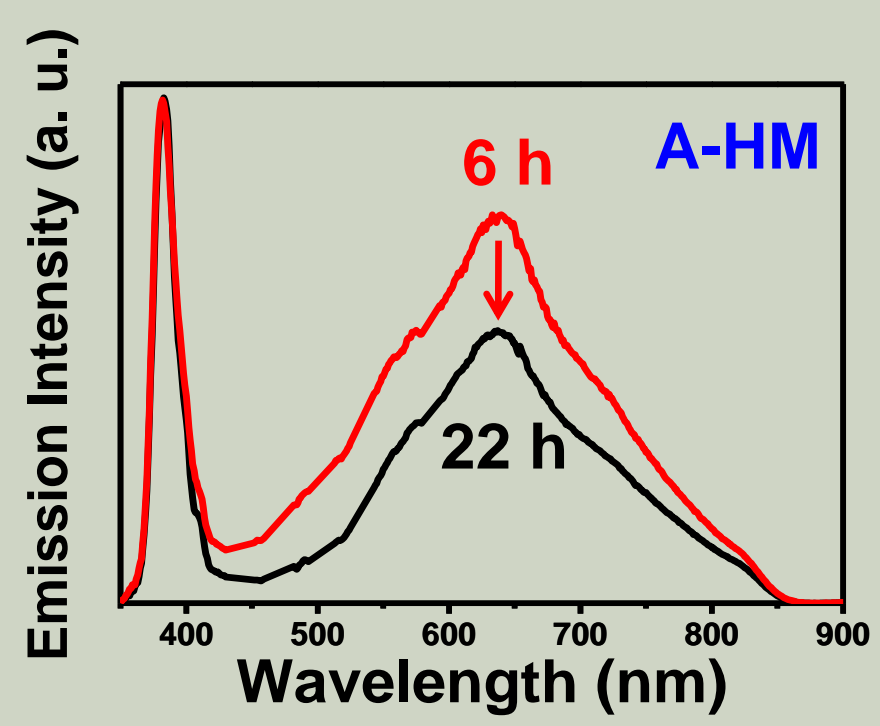
- LT-HM: larger amount of surface defects
- A-HM: lower amount of surface defects

Time Resolved Photoluminescence (TRPL)

The effective time constant for the FX ( $\tau_{EFF}$ ) were observed in two regimens: between 40-140 ps for the A-HM, and between 20-40 ps for the LT-HM.

$$\frac{1}{\tau_{EFF}} = \frac{1}{\tau_{EX}} + \frac{1}{\tau_{NRC}}$$

The faster PL decay observed for the LT-HM is attributed to a larger contribution of the non-radiative recombination channels, i.e. due to charge transfer processes from the FX to the defect states in the surface of the NWs (green band).

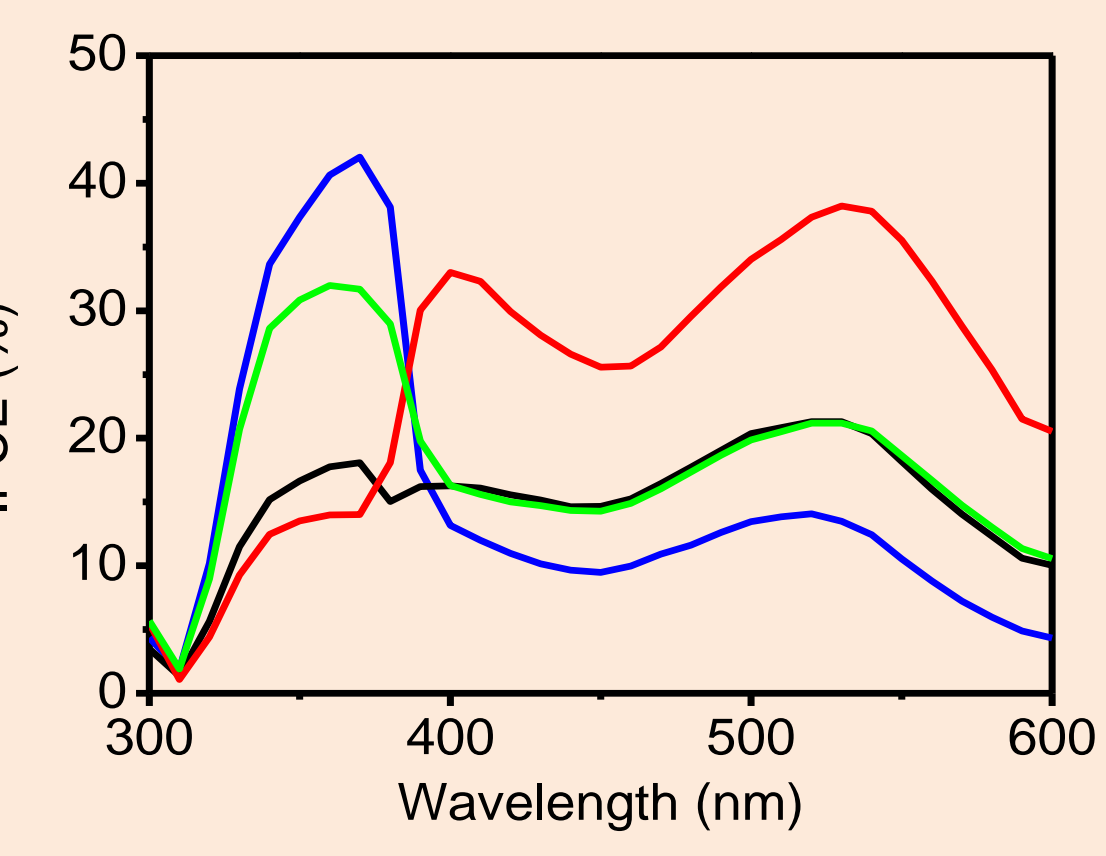
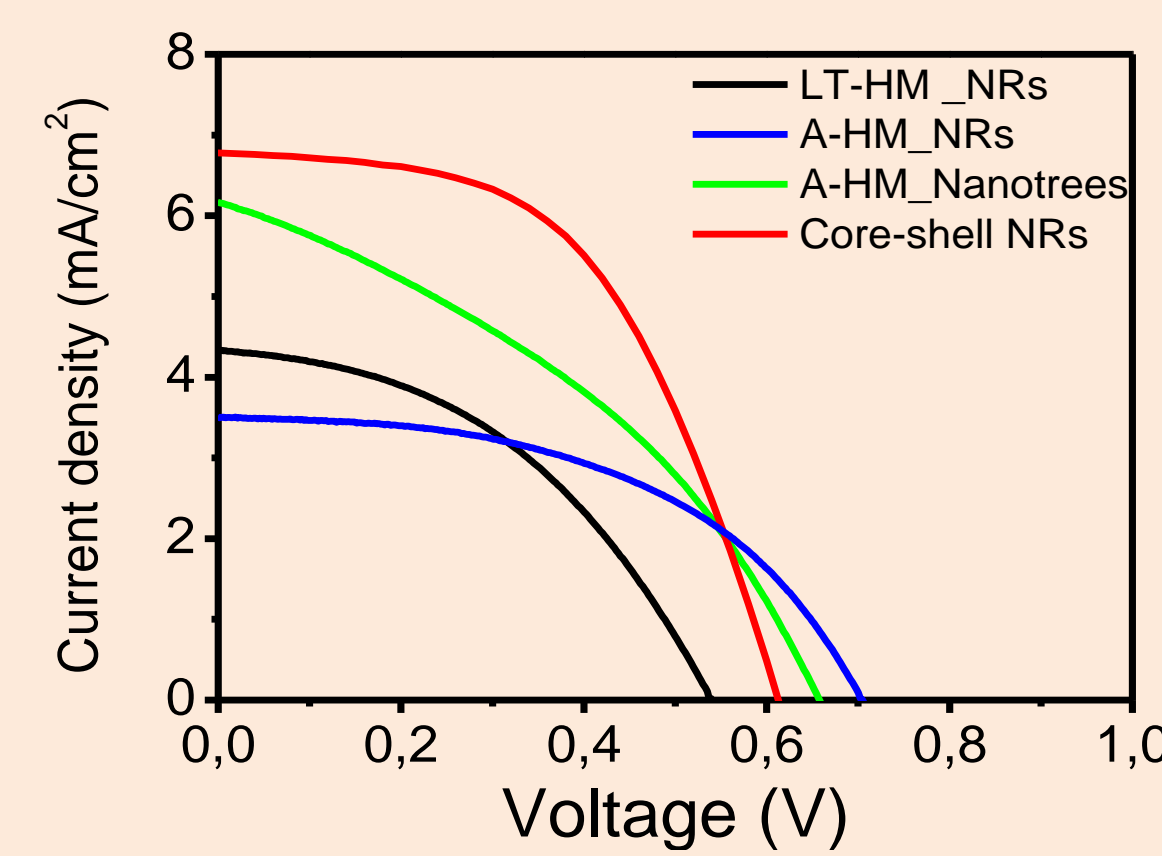


## Photovoltaic properties

Each ZnO electrode was optimized. The best photovoltaic response is presented

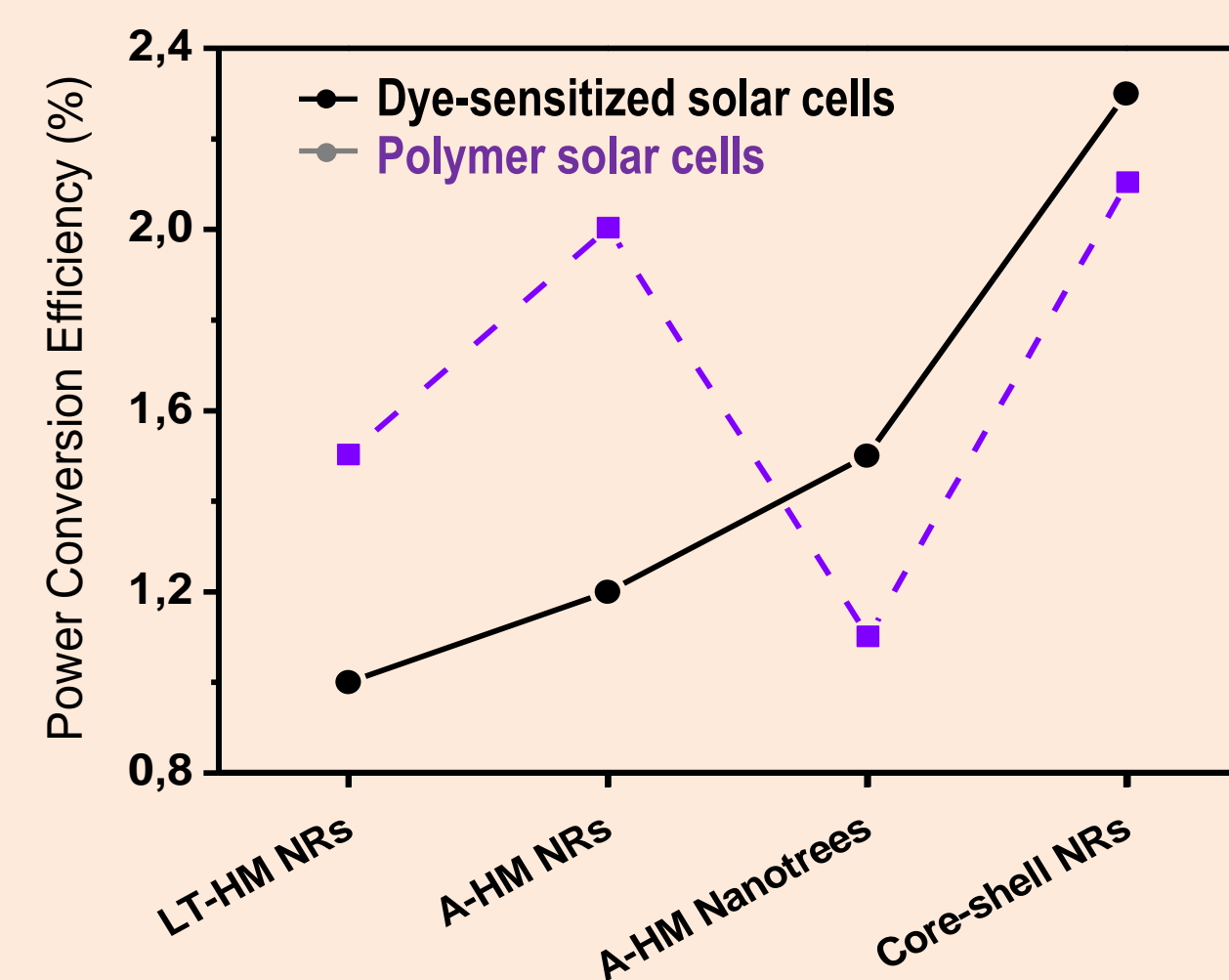
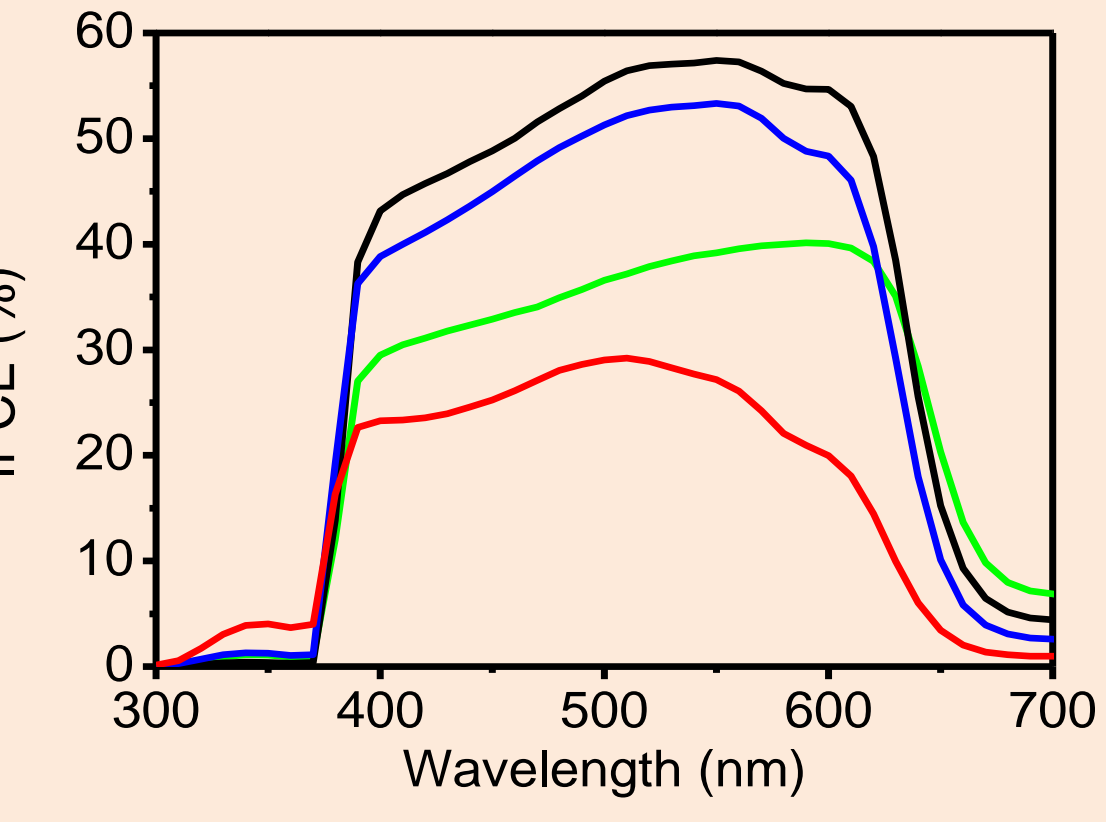
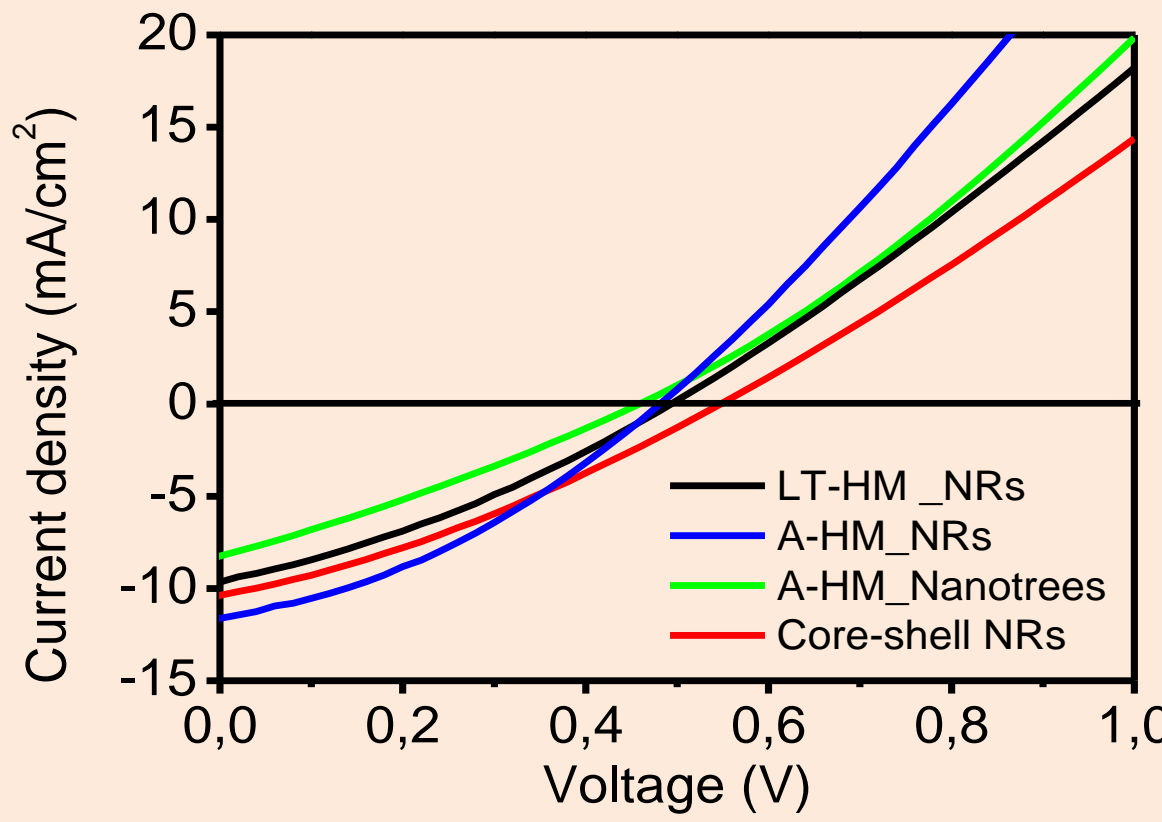
Dye-sensitized Solar Cells (DSC)

FTO/ZnONRs/Dye/Electrolyte/Pt



Polymer Solar Cells (PSC)

FTO/ZnONRs/P3HT:PCBM/PEDOT:PSS/Ag



Type	Growth Time	ZnO nanostructure	Length (μm)	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	FF (%)	Eff (%)
DSC	22h	Nanorods	5.0	0.603	3.72	45	1.01
	22h	Nanorods	1.0	0.705	3.50	50	1.24
	28h	Nanotrees	3.0	0.656	6.15	38	1.53
	12h	Core-shell NRs	3.0	0.702	5.46	60	2.32
PSC	6h	Nanorods	1.6	0.493	9.65	32	1.51
	6h	Nanorods	0.4	0.492	11.63	35	1.96
	28h	Nanotrees	3.0	0.459	8.25	28	1.07
	6h	Core-shell NRs	0.4	0.548	10.37	31	2.14

## Conclusions

We have synthesized four different ZnO nanostructured electrodes: two bare ZnO NRs obtained by the low temperature hydrothermal method (LT-HM) and the autoclave method (A-HM), nanotrees (NT) and the In<sub>x</sub>S<sub>y</sub> core-shell ZnO Nanorods (CS). All these electrodes were characterized by SEM, TEM microscopy, x-ray diffraction analyses (XRD) and photoluminescence spectra (PL). The different ZnO nanostructures were applied in dye-sensitized solar cells (DSC) and polymer solar cells (PSC). A comparison of the best results obtained for each ZnO nanostructured electrode in the solar cell devices is presented. Comparison between ZnO NRs obtained by the LT-HM and the A-HM revealed best power conversion efficiencies for the A-HM electrodes due to the reduced amount of surface traps. Longer ZnO NRs presented better performances in DSCs, however lower performances in PSCs. The latter was caused by a poor organic P3HT:PCBM blend infiltration into the long ZnO NRs. The ZnO nanotrees had good performances in DSCs but low in PSC due also to the worse infiltration problems observed on this nanostructure. Higher power conversion efficiencies were observed when the core-shell electrode was used in DSC (2.32%) and PSC (2.14%).

## References

- [1] I. Gonzalez-Valls and Lira-Cantu, M. *Energy Environ. Sci.*, **2** (2009), 19.
- [2] I. Gonzalez-Valls and M. Lira-Cantu, M. *Energy Environ. Sci.*, **3** (2010), 789.
- [3] I. Gonzalez-Valls, Y. Yu, B. Ballesteros, J. Oro and M. Lira-Cantu, *J. Power Sources*, **196** (15) (2011) 6609-6621
- [4] I. Gonzalez-Valls, J. S. Reparaz, F. Güell et al., Submitted (2012)
- [5] I. Gonzalez-Valls, D. Angmo, J. S. Reparaz, S. A. Gevorgyan, F. C. Krebs and M. Lira-Cantu, *J. Pol. Science B: Physics*, Accepted (2012).

## Acknowledgements

To the projects ENE2008-04373 and the Ph.D. scholarship awarded to I.G-V (BES-2009-028996) from the Spanish Ministry of Science and Innovation, MICINN. To the Xarxa de Referència en Materials Avançats per a l'Energia, XaRMAE (Reference Center of Advanced Materials for Energy) of the Catalonia Government and Consolider NANOSELECT project (CSD2007-00041).