Three dimensional electrodes base on core/shell nanowires for photoelectrochemical cells.

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Three dimensional array's offer an increased active surface area for all type of electrodes, in general, and, in particularly, for higher efficiency in photo electrochemistry devices. In this scenario, core-shell nano hetero or homo structures are the essential brick for built-in these electrodes and they become essential to define advanced photo electrochemistry elements or, even, for a more complex and promising artificial photosynthesis systems that require frontal or back illumination according to the photo reactor design related to the production of sun fuels.

However, all their outstanding properties depend on the adequate capability for photon capture and the consequent control of the charge separation. Under these conditions, doping of the inner part of the structure becomes basic for the charge extraction associated with a high transport facility, low internal resistance, as well as the surface conditions are determining for the charge transfer of the other type of carriers. As a consequence, doping management becomes an essential point for energy band engineering and, so, a fundamental key for controlling the overall nanostructure performances.

In this contribution, we report on the growth on electrodes of nanowires with controlled doping and how they can be coated for selected shell material with controlled thickness for having homo and hetero structures with modified surface properties and varied electrical field values at the surface. It contributes to enhance the charge carrier transfer as well as it presents also excellent transport properties. As demonstration, examples of vertically aligned homostructures ZnO:ZnO and heterostructures ZnO/ZnS or ZnO/TiO2, …among others core /shell nanowires will be presented like for discussing the functional matching in these coaxial heterojunction including electrical, optical crystallographic and thermo chemical performances related to their degradation and stability.

In general, these core/shell nanowires have been grown by a facile and low cost electrodeposition two-step process. In this way, due to the controlled surface electrical field, photoelectrochemical properties of these nanowires have been found to be highly enhanced with the presence of these shell layers and an experimental study as function of their thicknesses will be presented and modelized to explain the promotion the surface-related radiative recombination processes. The enhancement factor is proved to depend on the shell thickness. These performances are associated with the improvement of the photogenerated charge carrier separation and surface to neutral inner part transfer capability achieved when increasing the space charge area within the nanowires with a built-in electric field introduced by the doping profile. These features allow the deduction of practical rules for the design and optimization of these three dimensional photoelectrodes for the production of sun fuels.