

Direct growth of highly oriented arrays of crystalline rutile SnO₂ nanorods with square cross section onto various substrates from aqueous solutions at 95°C

Lionel Vayssieres^{a,b} and Michael Graetzel^b

^aInternational Center for Young Scientists, National Institute for Materials Science, Tsukuba, Ibaraki, 305-0044 Japan

^bPhotonics and Interface Laboratory, Institute of Chemical Sciences and Engineering, Swiss Federal Institute of Technology (EPFL), CH-1015 Lausanne, Switzerland

The hierarchical design of well-defined and highly oriented three-dimensional (3-D) arrays of conventional 1-D nanomaterials such as nanorods and nanowires in general, and their large scale manufacturing at low cost in particular, remain crucial challenges to unfold the very promising future of nanotechnology. In addition to economical manufacturing of nanomaterials, a better fundamental knowledge of their electronic structure, physical, interfacial and structural properties, as well as their stability is required to fully exploit their fascinating physical and chemical potentials. To fulfill such essential requirements, the creation of stable and structurally well-defined and well-ordered nanomaterials at low cost is essential. A novel concept based on a general thermodynamic model of nucleation and growth monitoring by chemical and electrostatic control of the water-oxide interfacial tension and an aqueous thin film processing technique has been developed to fabricate very large 3-D arrays of crystalline metal oxides onto various substrates at mild temperatures¹. The goal is to design at low-cost a new generation of functional *purpose-built* metal oxide materials at nano-, meso- and micro-scale with controlled particle size, morphology and orientation (fig.1). Such well-designed materials should lead to a better fundamental understanding of their electronic structure² and physical/chemical properties as well as to develop novel and optimized devices³.

SnO₂ is an insulator and an important, colorless, low-cost, large bandgap (n-type) semiconductor material when doped by oxygen vacancies or by Sb or F ions. It is widely utilized as transparent conducting oxide substrate (TCO) and gas sensor as well as electrode material for energy conversion and storage applications. Thus, designing SnO₂ 1-D nanomaterials with novel and well-defined morphology and, in particular, as highly oriented three-dimensional arrays, is of noteworthy importance for basic fundamental research as well as of relevance for various fields of industrial and high-tech applications.

We are reporting here a simple, one-step, aqueous low temperature growth process for the inexpensive fabrication of large (several tens of cm²) three-dimensional arrays of highly oriented and crystalline SnO₂ nanorods of typically 50 nm in width and 500 nm in length with a unique designed architecture and without the need of template, surfactant, applied field, or undercoating onto various substrates. Well-defined and perpendicularly oriented crystalline nanorods of squared cross-section (elongated along the c-axis and exhibiting (110) prismatic faces) are obtained directly onto polycrystalline, single-crystalline or amorphous substrates from the controlled heteronucleation of SnO₂ by aqueous precipitation of Tin(IV) salts at mild temperatures². Based on thermodynamic stability and crystal symmetry arguments, well-defined and highly oriented rutile SnO₂ nanorods have been successfully grown directly onto various substrates of large physical areas without template, surfactant, applied field, or undercoating at mild

temperature from aqueous solutions. Such nanorods are c-axis elongated and exhibit the most stable prismatic (110) faces, which results in nanorods with square cross-section.

Besides the great stability of (110) faces, It has been demonstrated that such surface provides the best efficiency for the chemisorption and dissociation of oxygenated compounds at the SnO₂ interface due to the lowest interatomic distances between tin atoms (compared to (101) and (111) faces) Such particularity is of crucial importance to improve the current efficiency of SnO₂ photocatalytic and sensing devices. Given that the exposed prismatic faces of the SnO₂ nanorods presented here are the most stable (110) faces, such unique architecture, that is c-elongated and squared cross-section with well-defined faces, confers to these arrays a great capability to develop innovative and functional SnO₂ nanosensors. For instance, better sensitivity and selectivity is foreseen due to the optimized exposed faces as well as a fast response (lower latency time) due to the direct growth of the nanorod bundles onto various substrates, their perpendicular orientation and their anisotropy along the c-axis, which offers a direct and very efficient electron pathway.

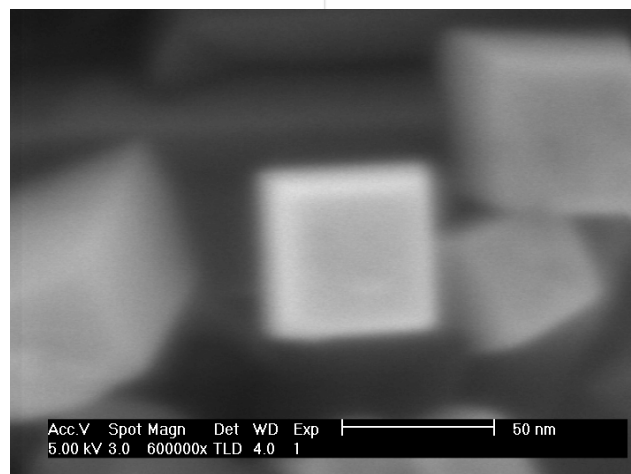
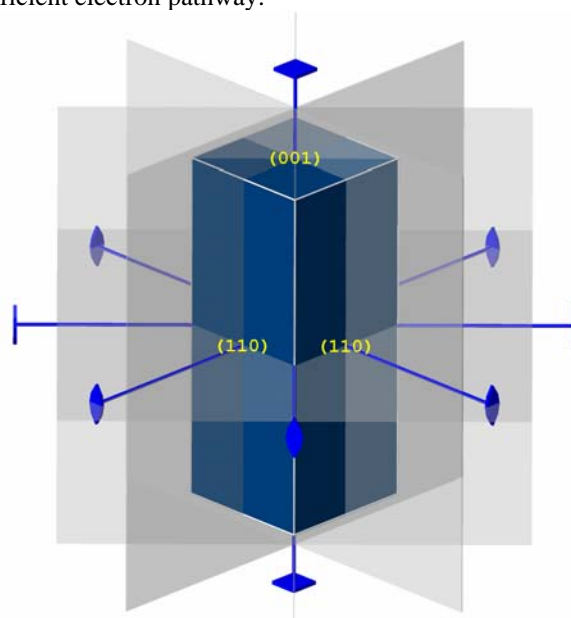


Fig. 1) Crystal habit and symmetry elements of a c-elongated rod of rutile SnO₂ (cassiterite) with square cross section (top); Field emission gun scanning electron microscope (FEG-SEM) image of highly oriented nanorod arrays of rutile SnO₂ (cassiterite) grown onto various substrates without template, surfactant, applied field, or undercoating (bottom).

References

1. L.Vayssieres, *Int. J. Nanotechnology* **2004**, 1(1-2), 1-41
2. L. Vayssieres and M. Graetzel, *Angew. Chem.* **2004** in press

