

3D Highly Oriented Nanoparticulate and Microparticulate Array of Metal Oxide Materials

Lionel Vayssieres, Jinghua Guo and Joseph Nordgren

Department of Physics, Uppsala University, Box 530, SE-75121 Uppsala, Sweden

ABSTRACT

Advanced nano and micro particulate thin films of 3d transition and post-transition metal oxides consisting of nanorods and microrods with parallel and perpendicular orientation with respect to the substrate normal, have been successfully grown onto various substrates by heteronucleation, without template and/or surfactant, from the aqueous condensation of solution of metal salts or metal complexes (aqueous chemical growth). Three-dimensional arrays of iron oxide nanorods and zinc oxide nanorods with parallel and perpendicular orientation are presented as well as the oxygen K-edge polarization dependent x-ray absorption spectroscopy (XAS) study of anisotropic perpendicularly oriented microrod array of ZnO performed at synchrotron radiation source facility.

INTRODUCTION

Our strategy to generate advanced nano and micro-particulate thin films is a chemical approach and a general concept named “*purpose-built materials*” [1], well-sustained by a thermodynamic model for the monitoring of the nucleation, growth and ageing processes by experimental control of the interfacial tension (surface free energy) of the system [2]. Such control has been well-illustrated on the nanoparticle size control of magnetite (Fe_3O_4) over an order of magnitude [3]. This concept and synthetic method allows to design and create novel metal oxide nanomaterials with the proper morphology, texture and orientation in order to probe, tune, and optimize their physical properties. Particulate thin films materials are obtained by direct growth onto various substrates from the condensation of aqueous precursors at low temperature. Such approach to material synthesis offers the competence to generate anisotropic nanoparticles as well as the capacity to control their orientation on substrates. Indeed, the ability to grow and align anisotropic nanoparticles into large arrays on a substrate requires taking into account the homogeneous and heterogeneous nucleation phenomena. In most cases, homogenous nucleation of solid phases (metal oxide in particular) requires a higher activation energy barrier and therefore, heteronucleation will be promoted and energetically more favorable. Indeed, the interfacial energy between the crystal and the substrate is smaller than the interfacial energy between the crystal and the solution, and therefore nucleation may take place at a lower saturation ratio onto a substrate than in solution. Nuclei will appear onto the entire substrate and if their rate is controlled and maintained limited by the precipitation conditions, epitaxial crystal growth will take place from these nuclei, along the easy direction of crystallization, and if the concentration of precursors is high, a condensed phase of single-crystalline nanorods perpendicular to the substrate will be generated. On the other hand, if the number of nuclei is not limited by the precipitation conditions, a condensed phase of single-crystalline nanorods parallel to the substrate will be generated. Such approach has been successfully applied for the growth of advanced nano and micro particulate metal oxides thin films and nanocomposite thin film materials such as for instance, large three-dimensional arrays of ferric oxides nanorods [4, 5], nanocomposite array of Fe-Cr sesquioxides [6], and nanorods [7], microrods [8] and microtubes [9] particulate thin films of ZnO as well as bio-nanomaterials [10].

In addition, growing large arrays of nano-/micro-crystallites with well-controlled orientation and morphology allows carrying out measurements on well-defined materials. Consequently, a direct feedback between theoretical and experimental data should contribute to the improvement and optimization of the existing devices as well as obtaining a better fundamental knowledge of the investigated physical/chemical properties.

MATERIALS AND METHODS

The materials synthesis is performed according to the purpose-built concept and general template-free thin film processing technique developed by Vayssieres et al. [11]. The nanorods of hematite have been created by thermodynamic stabilization and heteronucleation of the metastable β -FeOOH crystal phase from iron salts at low pH and high ionic strength and subsequent heat treatment in air at 450°C according to reference 4. The ZnO microrod particulate thin films have been obtained by the condensation of an aqueous solution of an amino-complex of Zn(II) and heteronucleation onto the substrates [8]. The crystalline 10 μm in length and 1.5 μm in width hexagonal microrods are elongated along the c axis and are oriented normal to the substrate surface.

In order to probe and demonstrate the orbital character and symmetry as well as its contribution to the conduction band of ZnO materials, UHV experiments have been performed due to the high atomic and site selectivity (core levels transitions) as well as the orbital and symmetry selectivity (dipole selection rules) of absorption spectroscopy and polarized x-rays from synchrotron radiation sources. The electronic structure was investigated by polarization dependent soft x-ray absorption spectroscopy (XAS) at synchrotron facilities (Advanced Light Source, Lawrence Berkeley National Laboratory, BL 7.0.1). The x-ray absorption spectra were measured by recording the total electron yield from the sample while scanning the photon energy over the O K-edge region. The photon energy resolution was set to 0.2 eV. The XAS experiments were carried out on two different (isotropic and anisotropic) homogeneous crystalline ZnO (zincite) particulate thin film samples, i.e. ZnO spheres, which consist of monodisperse spherical particles of 150 nm in diameter, and ZnO rods consisting of monodisperse, anisotropic and highly oriented crystallites grown on a commercial transparent conducting glass (TCO).

RESULTS AND DISCUSSION

Figure 1 shows the high-resolution field-emission gun scanning electron (FEG-SEM) micrographs of nanoparticulate thin film of iron sesquioxide (hematite, α -Fe₂O₃) made of aligned nanorods with two different orientations, i.e. parallel and perpendicular to the substrate obtained by controlled aqueous chemical growth. The thin films consist of 50 nm nanorod bundles, made of nanofibers of 3 nm in diameter and about 0.7 to 1 μm in length regardless of their orientation onto the substrates.

Such advanced particulate thin films have been designed to develop electrodes for wet photovoltaic cells. Indeed, the diameter of the nanorods is an excellent match for the minority carrier diffusion length of hematite [12]. Accordingly, a very efficient photogenerated charge separation was obtained as well as a high incident photon-to-electron conversion efficiency (IPCE), which led to the creation of a sandwich-type (2-electrode) hematite photovoltaic cells [13].

In addition to applied knowledge, general fundamental understanding is reached by probing and demonstrating the influence of the orientation of nanoparticles on the photoelectrochemical properties of metal oxide photo-anodes. Besides the designed grain boundary-free direct electron pathway, and the structural match with the hole diffusion length, a two-dimensional quantum confinement has also been suggested and investigated by resonant inelastic x-ray scattering (RIXS) at synchrotron radiation source facility [14] to account for the unusual high efficiency of the hematite nanorod-array photoanodes.

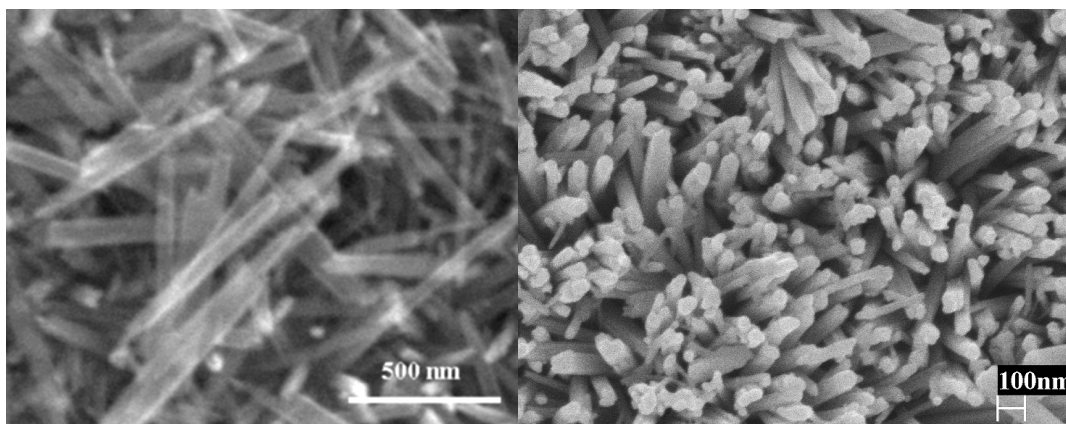


Figure 1. FEG-SEM micrographs of hematite ($\alpha\text{-Fe}_2\text{O}_3$) nanoparticulate thin film consisting of oriented nanorods; parallel (left) and perpendicular (right) to the substrate.

Such theoretical approach and synthetic method is also suitable for other metal oxides particulate thin films and have been demonstrated by the creation of nanoparticulate ZnO thin films consisting of crystalline hexagonal nanorods, oriented parallel or perpendicular with respect to the substrate surface (figure 2). Such materials have been designed to study the electronic structure and luminescent properties of a wide bandgap II-VI semiconductor as well as to probe such low cost and well-designed materials for nanolaser applications due to the large exciton binding energy of ZnO [15, 16].

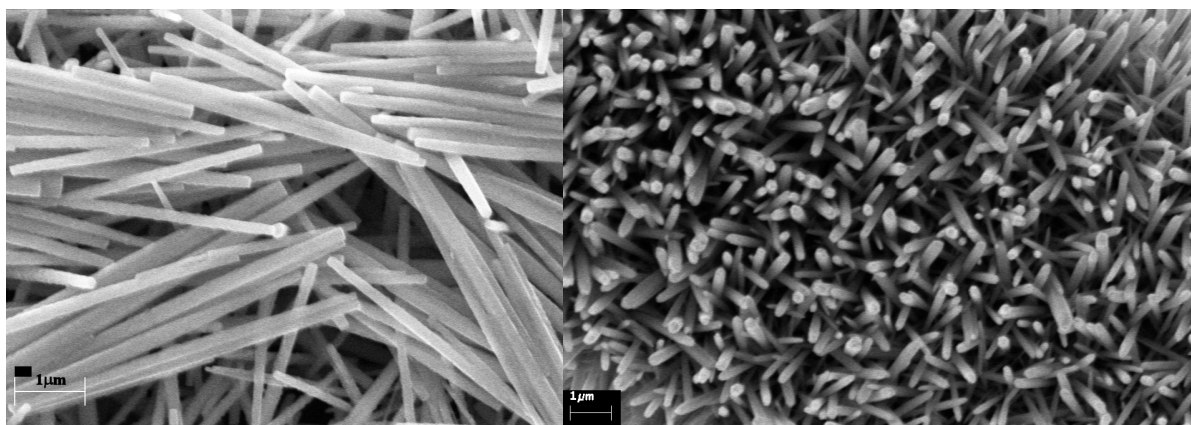


Figure 2. FEG-SEM micrographs of zincite ZnO nanoparticulate thin film consisting of nanorods; with parallel(left) and perpendicular (right) orientation onto the substrate.

In addition to nanoparticulate thin films, highly ordered microparticulate thin films of zincite ZnO consisting of three-dimensional arrays of perpendicular length tailored hexagonal microrods have also been produced and are shown in figure 3. The rods are crystalline and elongated along the c-axis of the wurtzite crystal structure (hexagonal system, crystal class 6_{mm} , space group $P6_3mc$). The thin films materials were produced by taking advantage of the structural anisotropy of wurtzite, that is to say, there is no center of inversion in this crystal structure and therefore an inherent asymmetry is present which allows the anisotropic growth of the crystal along the [001] direction. Such purpose-built material has been designed to study the influence of the rod length on the photoelectrochemical properties and electron transport of ZnO electrodes in the UV region [17] as well as to develop ZnO and dye-sensitized ZnO photovoltaic cells [18-20].

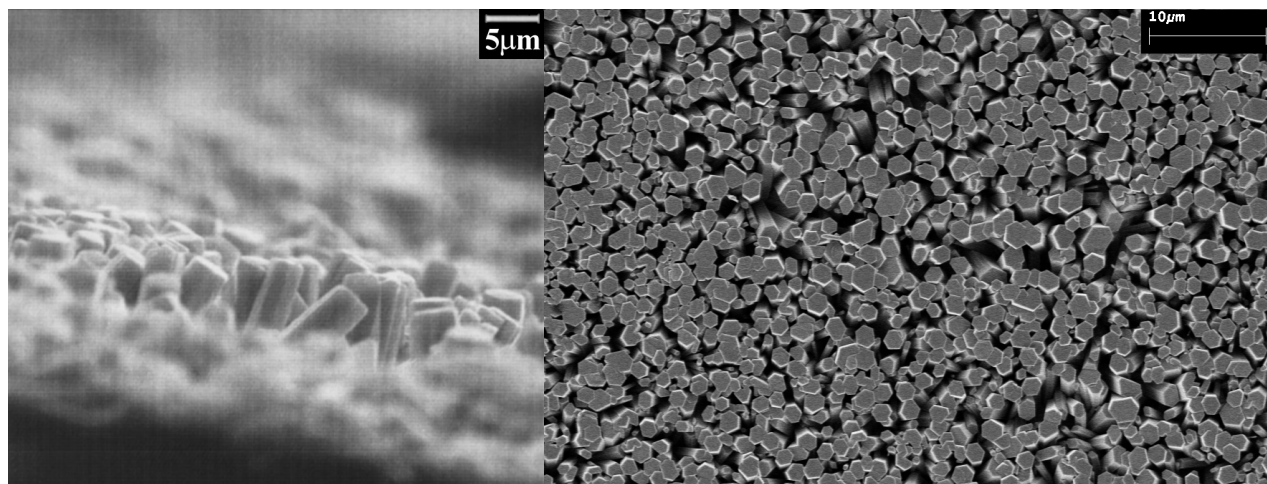


Figure 3. FEG-SEM cross section (left) and top view (right) micrographs of microparticulate thin films consisting of zincite ZnO microrods grown normal to the conductive substrate surface.

Given that such microparticulate thin films are well-defined and highly oriented both crystallographically and macroscopically, the study of its electronic structure by polarization dependent XAS has been investigated and compared to the spectra of an isotropic particulate thin film sample made of monodisperse spherical particles of ZnO.

The polarization dependent x-ray absorption measurements of the anisotropic microrod array as well as the isotropic mesospherical array at grazing and normal incidence are shown in figure 4. The vertical dashed lines are drawn for the guidance of the eyes. The variations in the spectral shape continue up to 30 eV above the absorption threshold. The resolved absorption features are indicated as a1 to a8. Up to feature a1, no polarization dependence is observed in the x-ray absorption spectra for either sample. However, for the ZnO microrods (bottom spectra), strong anisotropic effects are observed at higher photon energies. Measuring at grazing incidence geometry ($\theta = 10^\circ$), where the absorption features a3, a5, and a8 are stronger, the excitation to the state along the c-axis of the wurtzite structure is enhanced. At normal incidence geometry ($\theta = 90^\circ$), where the absorption features a2, a4, and a7 are stronger, the excitation to the in-plane state is enhanced. No significant change is observed for the isotropic samples of ZnO consisting of spherical particles. However, all the absorption features are averaged out and observed in the XAS spectra measured with either geometrical detection.

In order to fully demonstrate the orbital character and symmetry as well as their contribution to the conduction band of this post transition metal oxide, full-potential calculations of orbital-resolved x-ray absorption of a periodic crystal of ZnO have been carried out which includes the Zn 3d orbitals as part of the valence states. Indeed, an excellent agreement is found between the theory and the experimental findings giving a clear picture of the orbital-symmetry resolved conduction band and bulk properties of the ZnO microrods [21].

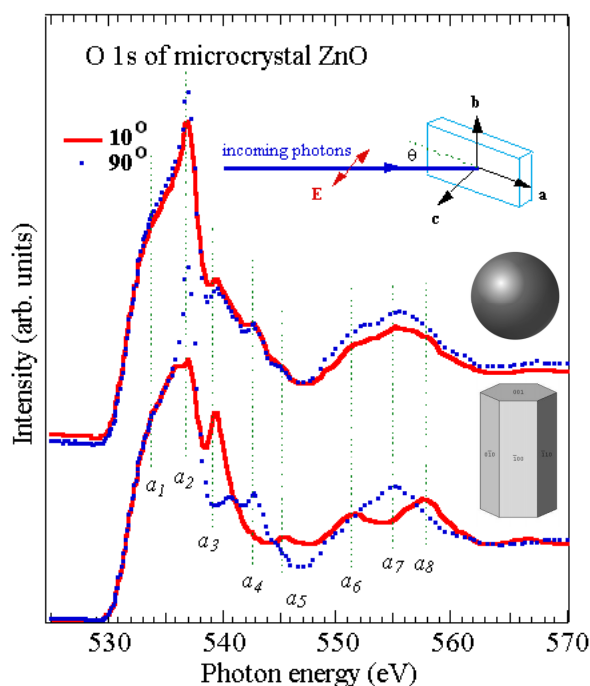


Figure 4. O K-edge Polarization dependent x-ray absorption spectra of microstructured particulate thin films of crystalline zinc oxide (ZnO, zincite) consisting of monodisperse spherical particles (top spectra) and perpendicularly oriented microrods (bottom spectra). The inset illustrates the XAS experimental geometry, where a and b axes define the sample-surface plane, c axis is along the growth direction of the ZnO rods, E is the polarization of incoming photons, and θ represents the incident angle to the sample surface: 10° ($E \parallel c$, solid lines) and 90° ($E \perp c$, dots).

CONCLUSION

The ability to produce, at low cost, anisotropic nanoparticles and to control their orientation onto a substrate in order to generate well-controlled nano and microstructured particulate thin films, will contribute to create a novel generation of smart and functional nanomaterials. Simultaneously, it will contribute to reach better fundamental understandings of their physical properties. We have measured the polarization dependent XAS spectra of ZnO with isotropic and anisotropic morphology grown by controlled aqueous chemical growth and strong anisotropic effects have been observed on the c-elongated microrod sample. It clearly demonstrates that designing materials with the appropriate morphology, size and orientation, i.e. *purpose-built materials*, enables to reach comprehensive knowledge of the electronic structure of particulate metal oxides thin films.

ACKNOWLEDGEMENTS

This work was supported by the Swedish Natural Science Research Council (NFR), the Swedish Research Council for Engineering Sciences (TFR), and the Göran Gustafsson Foundation for Research in Natural Science and Medicine. The experimental work at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory was supported by the U. S. Department of Energy, under contract No. DE-AC03-76SF00098.

REFERENCES

1. L. Vayssieres, A. Hagfeldt and S.-E. Lindquist, *Pure Appl. Chem.* **72(1-2)**, 47-52 (2000).
2. L. Vayssieres, Ph.D. Dissertation, Université Pierre et Marie Curie (Paris), 1995.
3. L. Vayssieres, C. Chaneac, E. Tronc and J.-P. Jolivet, *J. Colloid Interface Sci.* **205(2)**, 205-212 (1998).
4. L. Vayssieres, N. Beermann, S.-E. Lindquist and A. Hagfeldt, *Chem. Mater.* **13(2)**, 233-235 (2001).
5. L. Vayssieres, J.-H. Guo and J. Nordgren, in *Anisotropic Nanoparticles: Synthesis, Characterization and Applications*, edited by L. A. Lyon, S. J. Stranick, C. D. Keating, P. C. Searson, (*Mater. Res. Soc. Symp. Proc.* **635**, Warrendale, PA, 2001), pp. C781-786.
6. L. Vayssieres, J.-H. Guo, J. Nordgren, *J. Nanosci. Nanotech.* **1(4)**, (2001) in press.
7. L. Vayssieres et al. manuscript to be published.
8. L. Vayssieres, K. Keis, S.-E. Lindquist and A. Hagfeldt, *J. Phys. Chem. B* **105(17)**, 3350-3352 (2001).
9. L. Vayssieres, K. Keis, A. Hagfeldt and S.-E. Lindquist, *Chem. Mater.* **13(12)**, (2001) in press.
10. L. Vayssieres, presented at the 8th International conference of composite engineering (ICCE8), Tenerife, Canary Islands, Spain, 2001 (unpublished).
11. L. Vayssieres, A. Hagfeldt and S.-E. Lindquist, patent pending.
12. J. H. Kennedy and K. W. Frese, *J. Electrochem. Soc.* **125**, 709 (1978).
13. N. Beermann, L. Vayssieres, S.-E. Lindquist and A. Hagfeldt, *J. Electrochem. Soc.* **147(7)**, 2456-2461 (2000).
14. J.-H. Guo, L. Vayssieres, C. S  the, S. Butorin and J. Nordgren manuscript to be published.
15. M. H. Huang et al. *Science* **292**, 1897-1899 (2001); *Adv. Mater.* **13(2)**, 113-116 (2001).
16. Y. C. Kong, D. P. Yu, B. Zhang, W. Fang, and S. Q. Feng, *Appl. Phys. Lett.* **78(4)**, 407-409 (2001).
17. K. Keis, L. Vayssieres, S.-E. Lindquist and A. Hagfeldt, *J. Phys. Chem. B* submitted.
18. J. Zhong, A. H. Kitai, P. Mascher, W. Puff, *J. Electrochem Soc.* **140(12)**, 3644-3649 (1993).
19. K. Keis, L. Vayssieres, S.-E. Lindquist, A. Hagfeldt, *J. Electrochem. Soc.* **148(2)**, A149-155 (2001); *Nanostruct. Mater.* **12(1-4)**, 487-490 (1999).
20. K. Tennakone, G. R. R. A. Kumara, I. R. M. Kottegoda, V. P. S. Perera, *Chem. Commun.* 15-16 (1999).
21. J.-H. Guo, L. Vayssieres, C. Persson, R. Ahuja, B. Johansson and J. Nordgren submitted to *Phys. Rev. Lett.*