



Nanoparticle Growth Induced by Coalescence in Colloidal System

Edson R. Leite, E.J.H. Lee, F.M. Pontes, T. R. Giraldi, E. Longo

*CMDMC – LIEC – Chemistry Department – UFSCar-São
Carlos, SP - BRAZIL*

J.A. Varela

CMDMC – LIEC - I.Q. – UNESP-Araraquara, SP -BRAZIL

Outline:

1 – Introduction

Ostwald ripening X Coalescence

Target

2 – Experimental Procedure

Synthesis and characterization

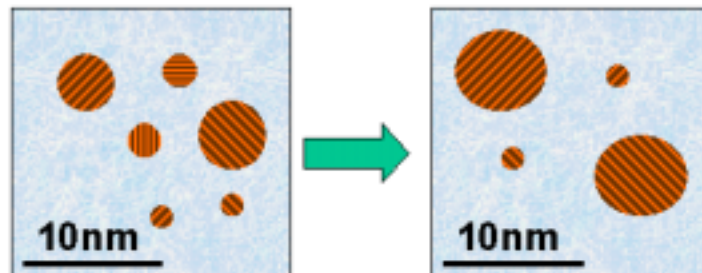
Theoretical Calculation

3 – Results and Discussion

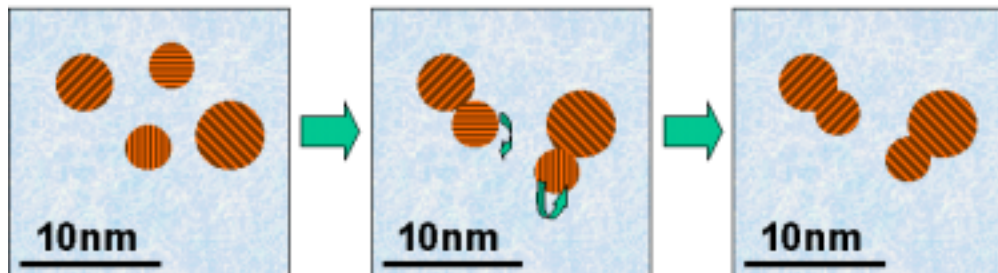
4 - Summary

1 – Introduction

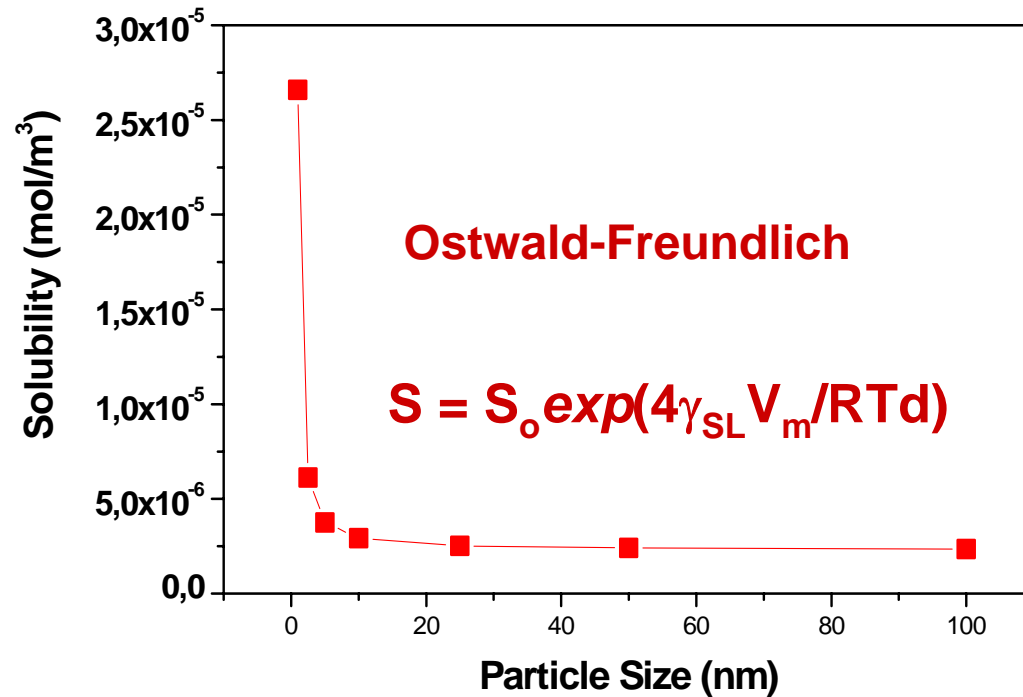
(a) Ostwald ripening



(b) Grain-rotation-induced grain coalescence (GRIGC)



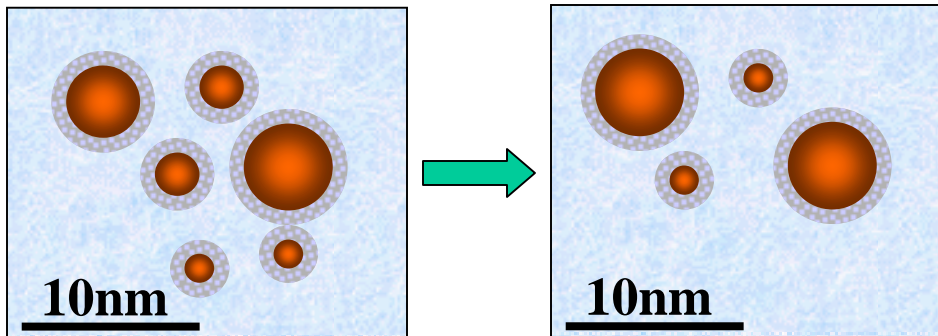
1 – Introduction – Ostwald ripening



In the Ostwald ripening mechanism, the atoms from one particle undergo dissolution and are then transferred to another particle;

There is a net atomic transport from the particles with sizes smaller than the average value to larger particles;

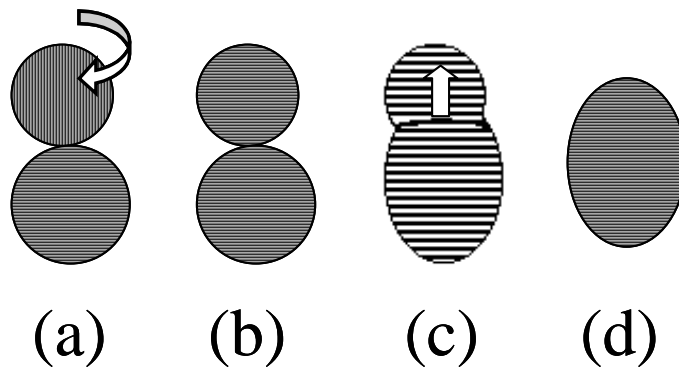
Particles smaller than the average value will shrink or even disappear.



1 – Introduction – GRIGC

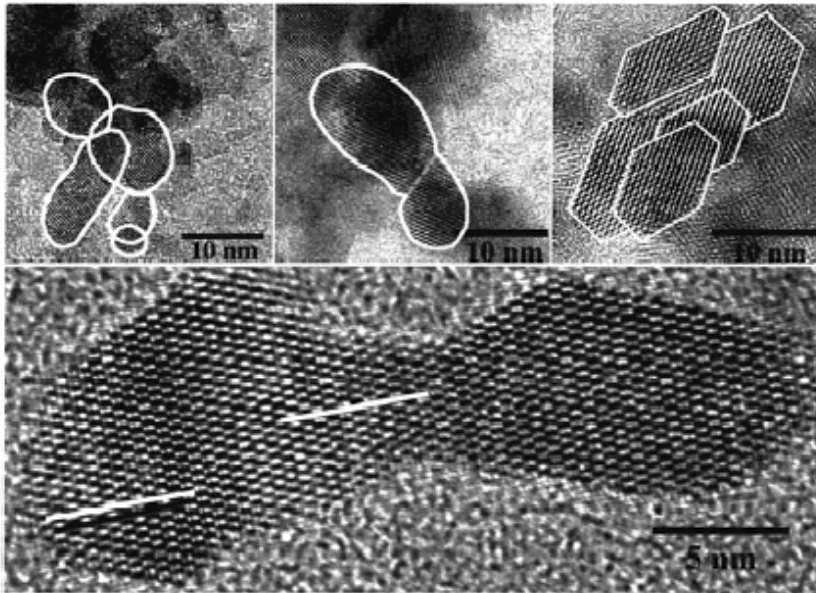
Moldovan and co-workers (*D. Moldovan, V. Yamakov, D. Wolf, and S.R. Phillport, Phys. Rev. Lett., 89, 206101-1 (2002)*) **recently studied the grain growth process of nanocrystalline materials and proposed a new growth mechanism: grain-rotation-induced grain coalescence.**

According to this model, the rotation of grains among neighboring grains results in a coherent grain-grain interface (the grains assume the same crystallographic orientation), which leads to the coalescence of neighboring grains via the elimination of common grain boundaries, thus forming a single larger grain.

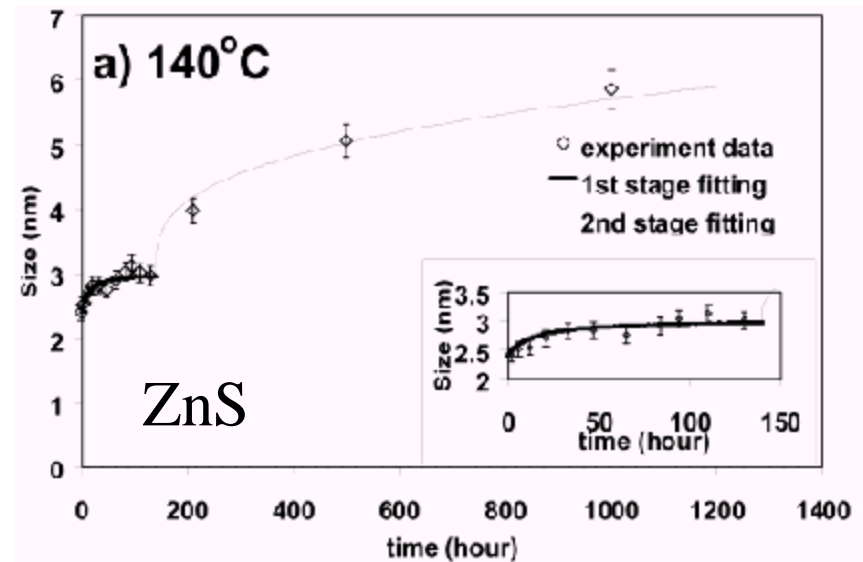


1 – Introduction – GRIGC

This process had already been observed in colloidal systems under special conditions (usually under hydrothermal condition) and was dubbed coarsening by oriented attachment (L. Penn, and J.F. Banfield, *Geochimica et Cosmochimica Acta*, 63, 1549 (1999); R.L. Penn, and J.F. Banfield, *Science*, 281, 969 (1998); J.F. Banfield, S.A. Welch, H. Zhang, T.T. Ebert, and R.L. Penn, *Science*, 289, 751 (2000)).



R.Lee Penn et al. - *J. Phys. Chem. B*, 105, 2177 (2001)



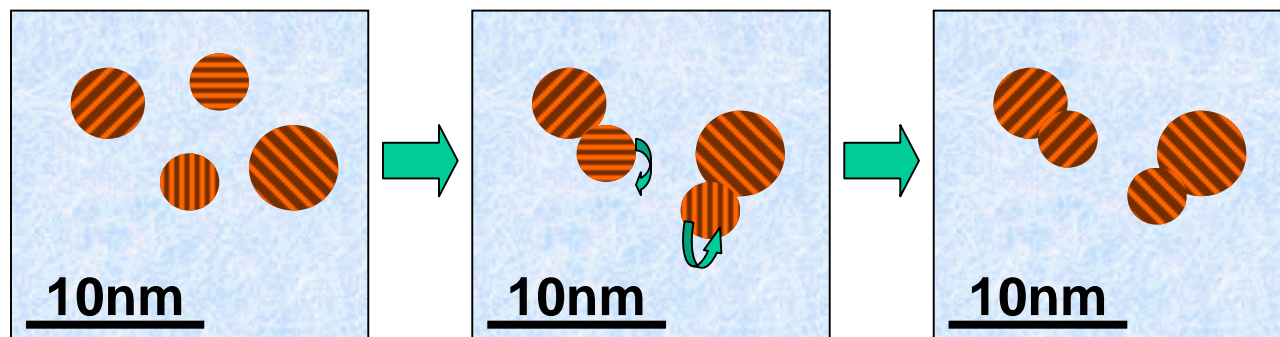
F. Huang et al. – *Nanoletters*, 3, 373 (2003)

1 – Introduction – Target

We believe that this growth mechanism (GRIGC) can take place in colloidal systems at room temperature.

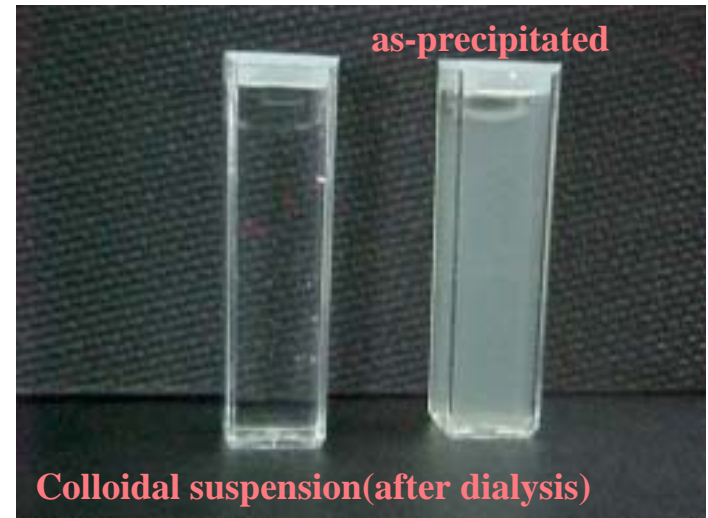
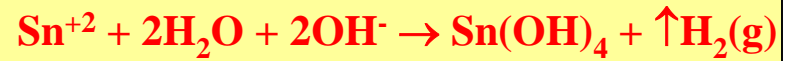
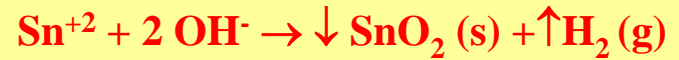
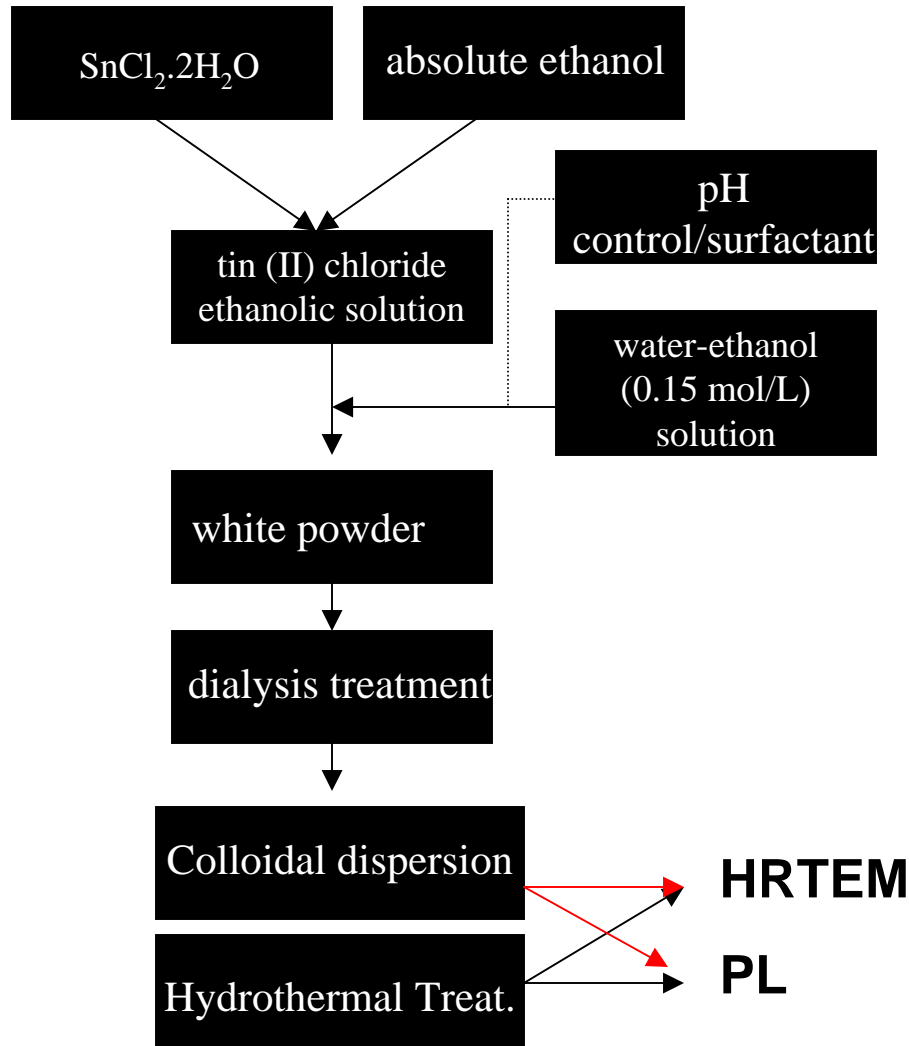
#The jiggling of nanoparticles by the Brownian motion can allow adjacent particles to collide and rotate to find a low-energy configuration, resulting in a coherent grain-grain boundary. This phenomenon can occur even during particle deposition.

#Here, we give experimental evidence that the GRIGC mechanism is an important crystal growth process in colloidal tin oxide (SnO_2) nanocrystal at room temperature.



2 – Experimental Procedure

Synthesis and characterization



2 – Experimental Procedure

Synthesis and characterization

quantum-confinement

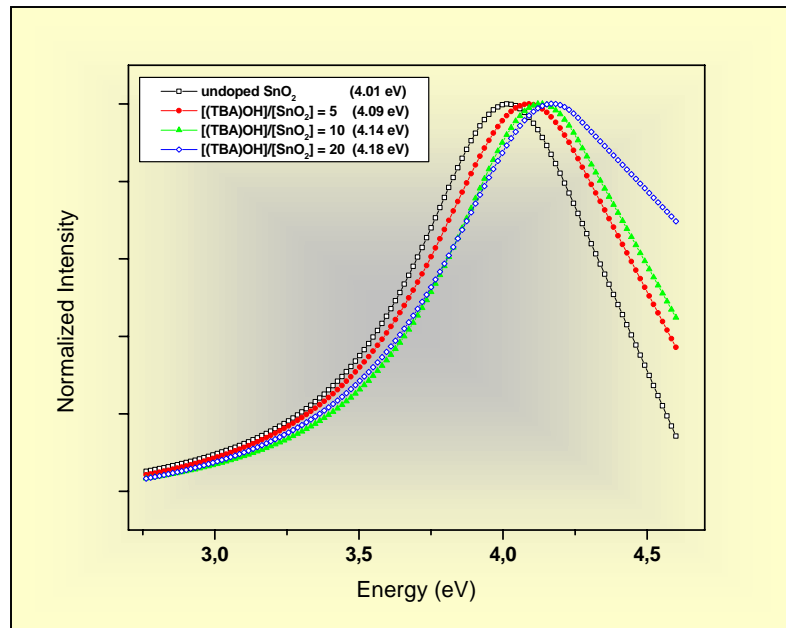
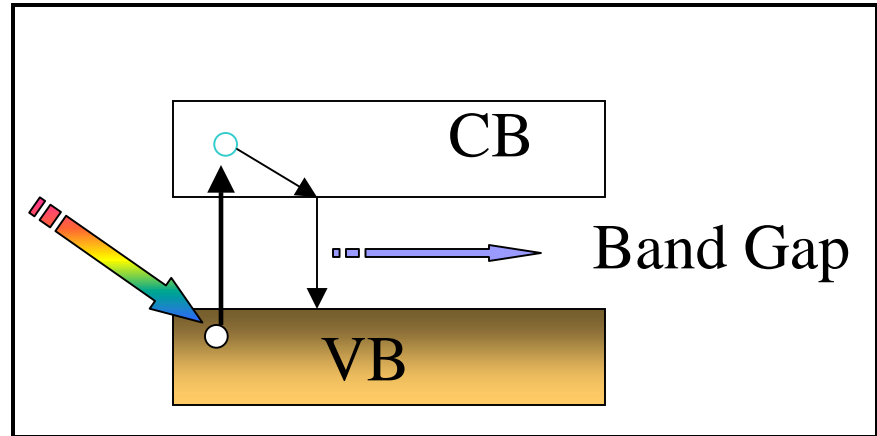
$$\Delta E = (\hbar^2/2m_e^*)(\pi^2/d^2)$$

$$\Delta E = E_n - E_b, E_b = 3.6\text{eV}$$

$$m_e^* = 0.27m_e$$

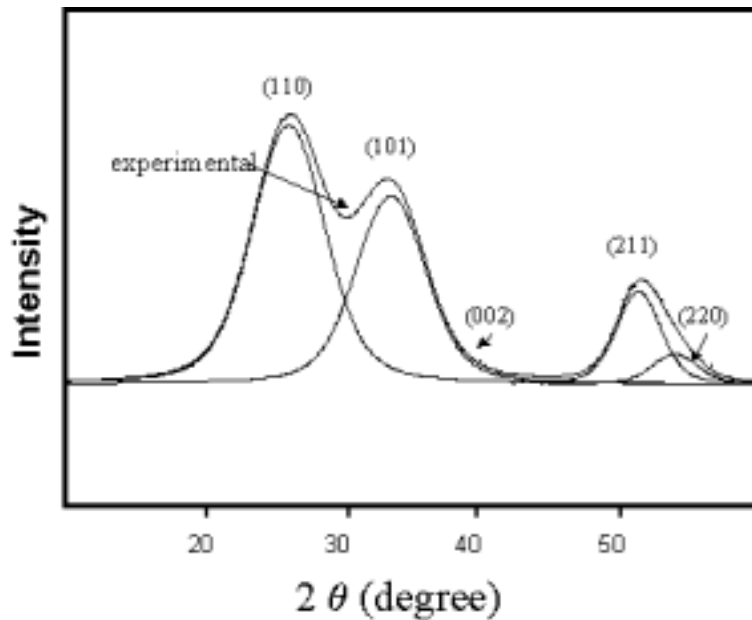
(m_e = electron mass)

and \hbar is the Planck constant

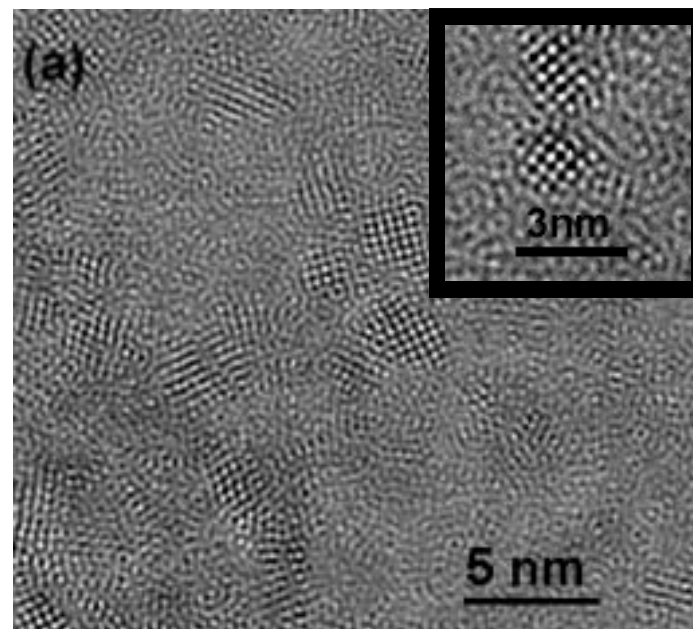


2 – Experimental Procedure

Synthesis and characterization



XRD analysis

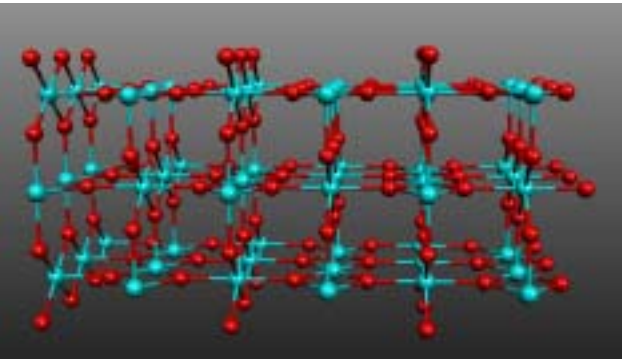


HRTEM characterization

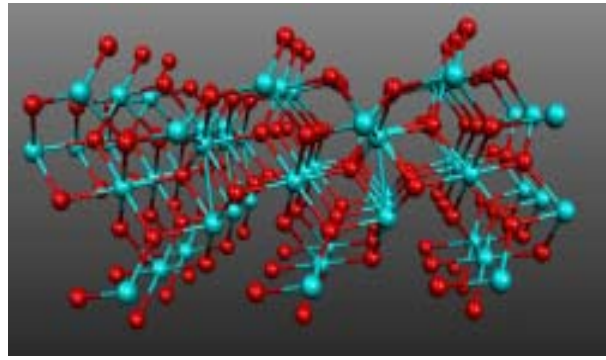
2 – Experimental Procedure

Theoretical Calculation

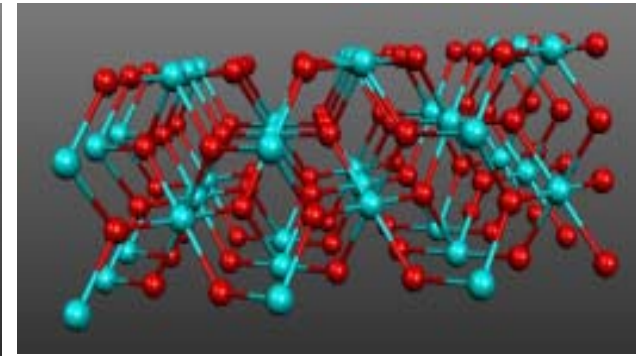
We calculated the specific surface energy and its relative stability in several directions, using the crystalline orbital program **Crystal-98** (V. R. Saunders, R. Dovesi, C. Roetti, M. Causà, N. M. Harrison, R. Orlando and C. M. Zicovich-Wilson, *CRYSTAL98 User's Manual* (University of Torino, Torino, 1998)).



(110)



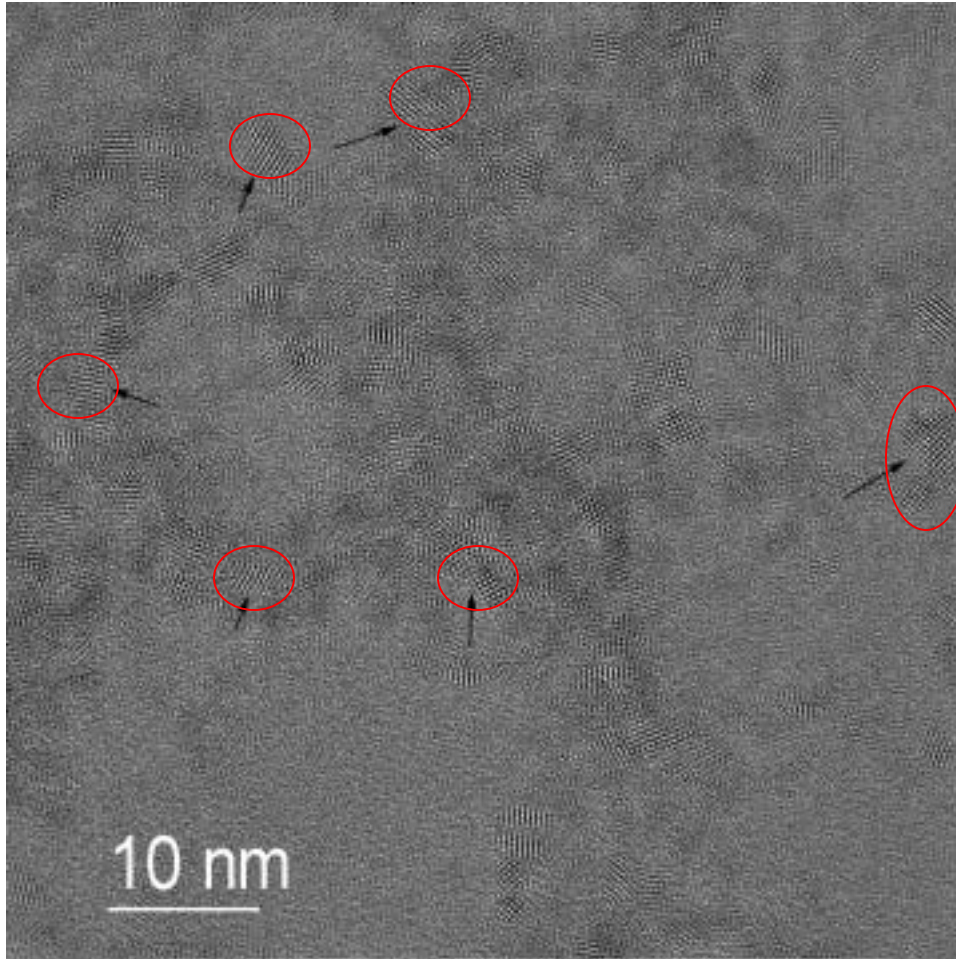
(101)



(001)

3 – Results and Discussion

Room Temperature

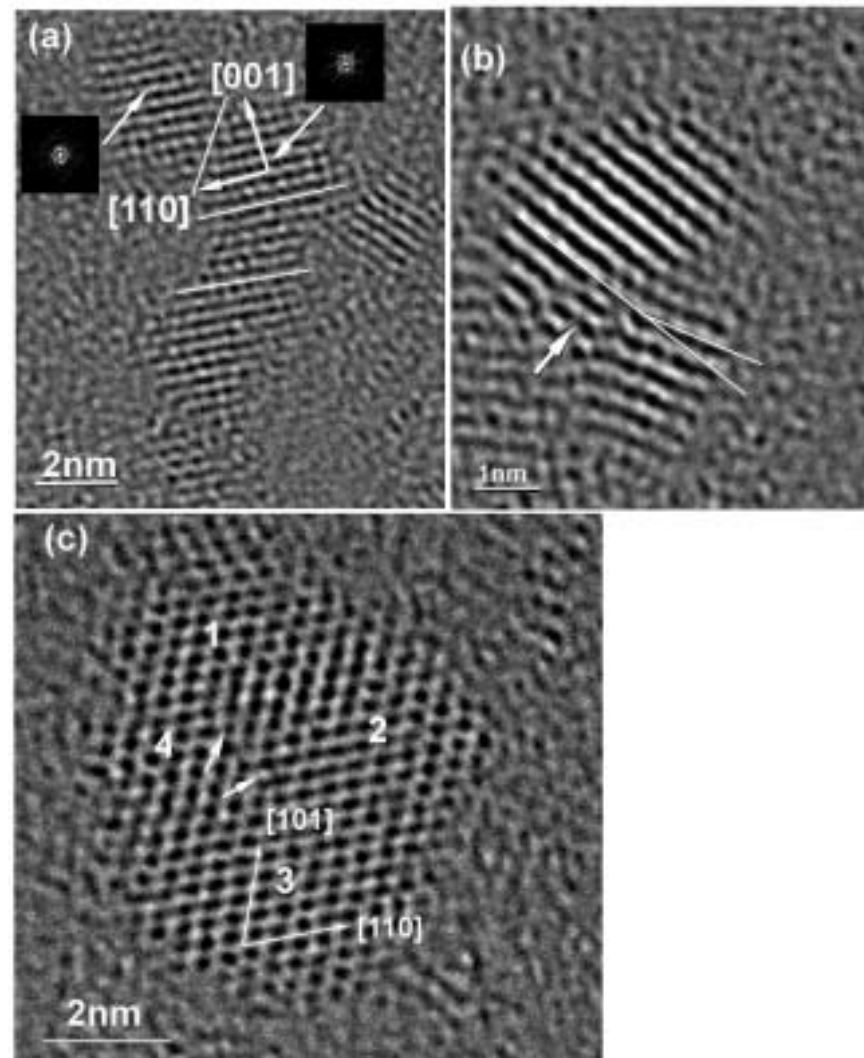


HRTEM image shows randomly oriented particles, as well as several clusters and chains formed by grains with the same crystallographic orientation .

The presence of clusters and chains is quite frequent, suggesting the large-scale formation of such morphologies.

3 – Results and Discussion

Room Temperature



#Figs. (a) and (c) provide strong evidence that coalescence occurs when two or more grains assume the same orientation, resulting in a single crystalline cluster or chain.

#Observation of the coalescence process in a system not subjected to heat treatment suggests that this growth mechanism presents a very low activation energy or even a zero kinetic barrier.

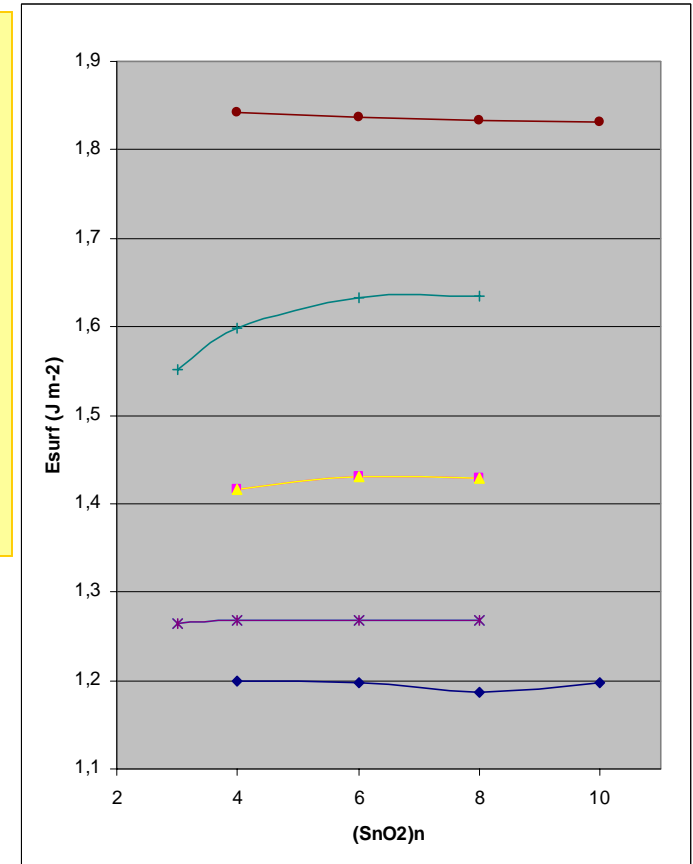
#Slight misorientations (indicated by arrows) are visible in the images of a cluster composed of several primary SnO₂ nanocrystals (at least four nanocrystals) shown in Fig. (c). These misorientations or defects originate from imperfect attachment among several nanocrystals, resulting in edge and screw dislocations. The imperfectly oriented attachment may produce different kinds of defects .

It is interesting to observe, in Fig. (b), that a tilt between the grains suffices to prevent coalescence. In fact, Fig.(b) shows the initial stage of the grain growth process.

3 – Results and Discussion

Theoretical Analysis

| Surface | Specific Surface Energy (J/m ²) |
|-------------|---|
| (110) | 1.2 |
| (010),(100) | 1.27 |
| (101) | 1.43 |
| (001) | 1.84 |



3 – Results and Discussion

Theoretical Analysis

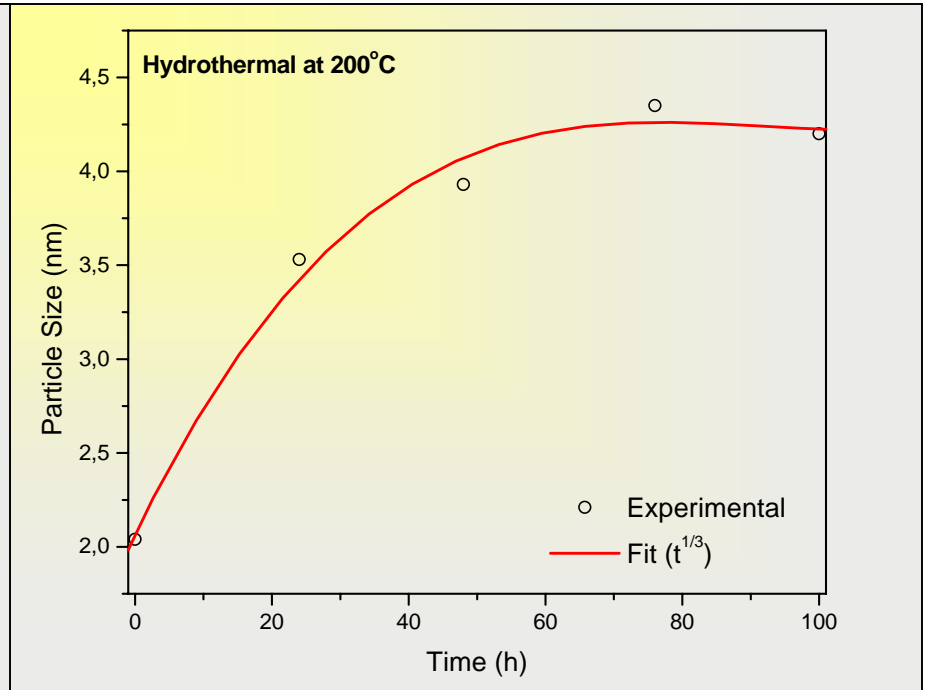
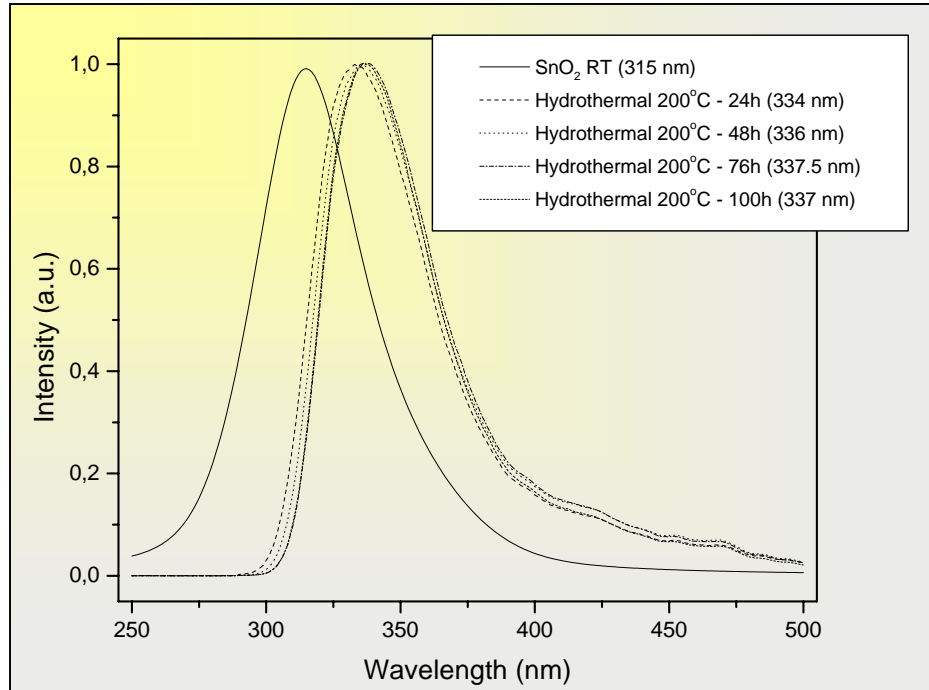
Based on this theoretical study, one can predict preferential growth along the [001]. An anisotropic growth may occur even in the [101] direction. For example, the surface energy of the (001) surface is 1.53 times greater than the (110) surface, while the (101) surface presents a surface energy only 1.19 times that of the (110) surface. This analysis suggests that growth in the [001] direction will result in particles with a higher aspect ratio than the growth in the [101] direction.

Our HRTEM results revealed the formation of chains and primary particle clusters resulting in a single large crystalline nanocrystal. The chain morphology showed preferential growth in the [001] direction, while the clusters grew preferentially in the [101] direction.

These results, which indicate that the GRIGC mechanism occurs typically on high surface energy planes, are congruent with the theoretical calculations.

3 – Results and Discussion

Hydrothermal Treatment



3 – Results and Discussion

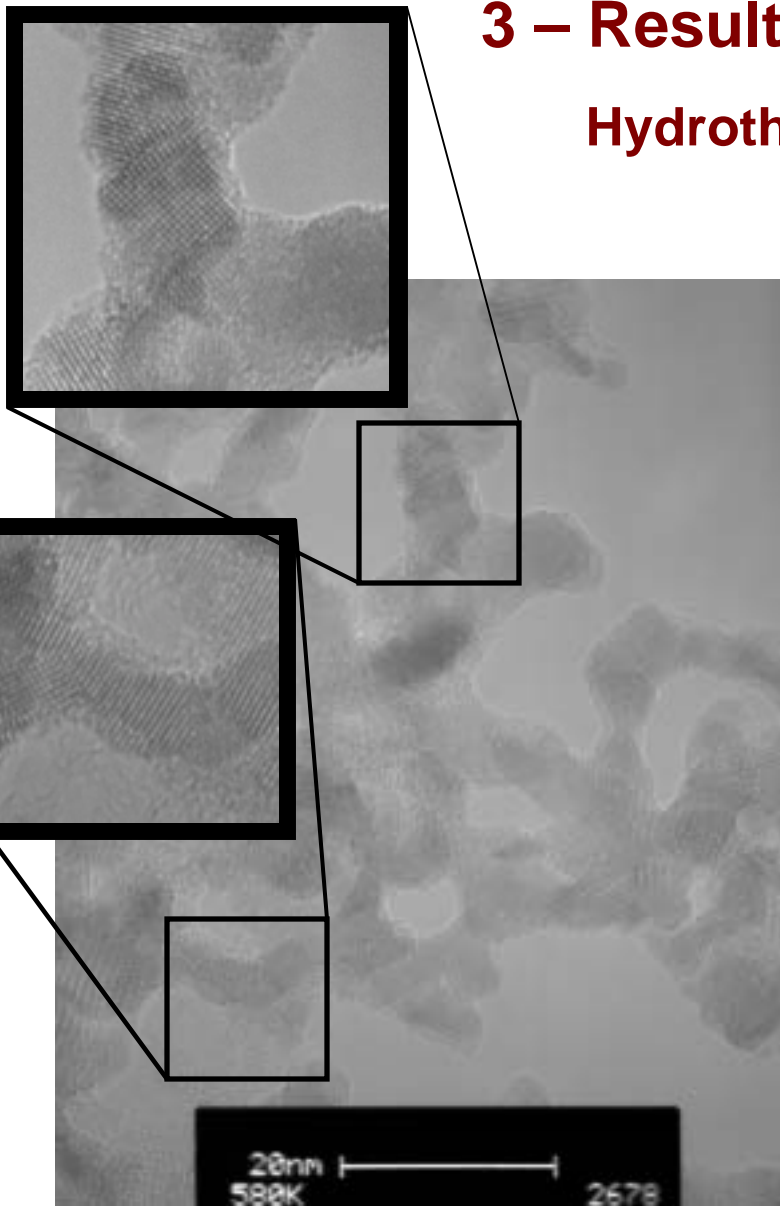
Hydrothermal Treatment

The growth kinetics under hydrothermal treatment showed that the grain size is proportional to $t^{1/3}$ (*);

This time dependence can suggest a OR mechanism (diffusion control);

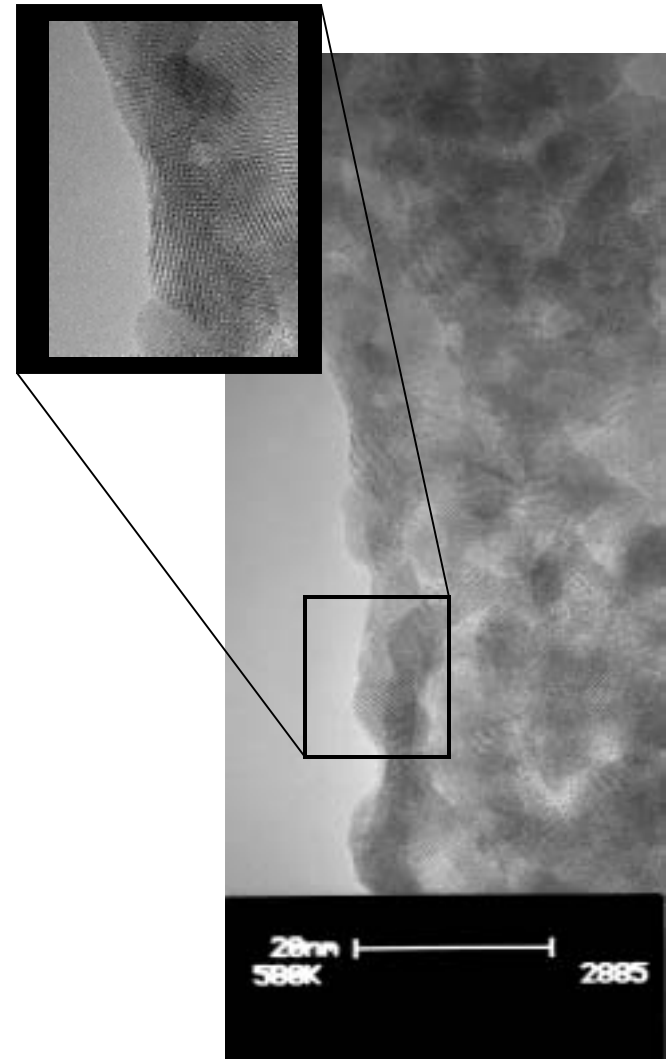
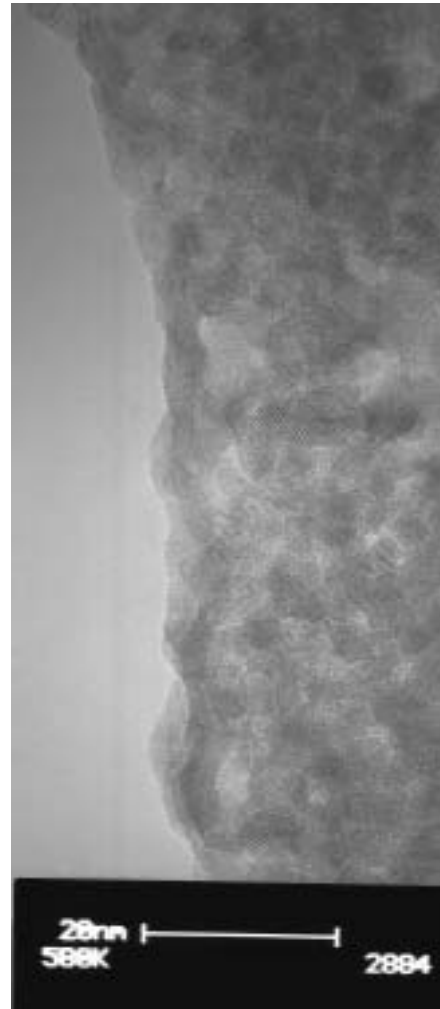
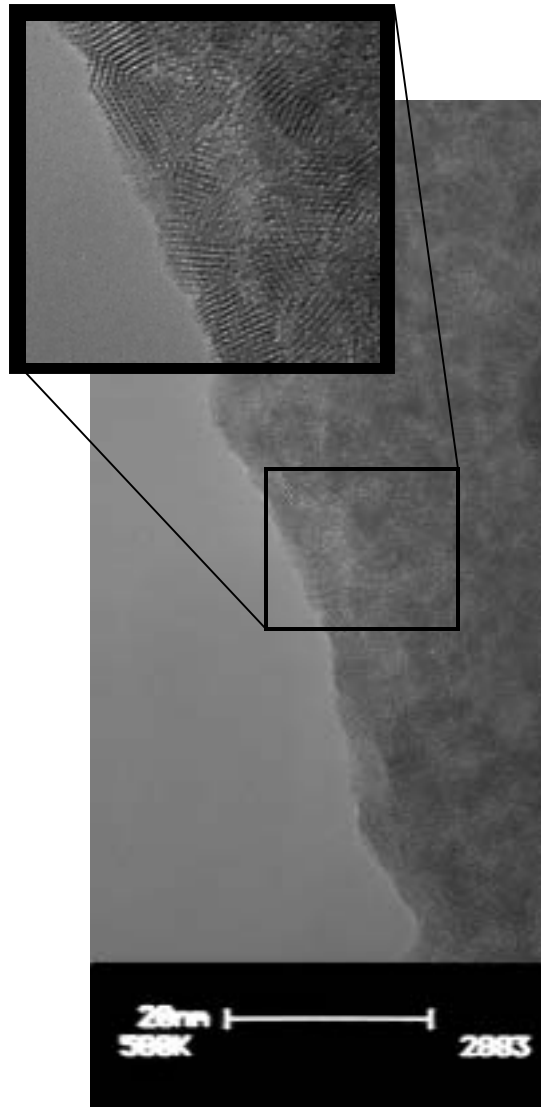
However the HRTEM analysis suggest a GRIGC process

(*) a more detailed analysis will be performed in order to confirm this time dependence



3 – Results and Discussion

Solid State Growth- *In-Situ* Growth Analysis



4 - Summary

#The synthesis method reported in this work is a suitable chemical route to prepare, at room temperature, SnO₂ nanocrystals (particle size ranging from 1-3nm) with no thermal or hydrothermal treatment. In this process, SnCl₂.2H₂O was used as precursor, allowing for easier elimination of Cl⁻ by dialysis.

We have shown that the GRIGC mechanism occurs in SnO₂ nanocrystals at room temperature. Observing this mechanism at room temperature may elucidate, for instance, the presence of dislocations usually found in nanocrystals (see Figures).

We have experimental evidences showing that the GRIGC mechanism occurs during hydrothermal treatment and in solid state.

Acknowledgment:

#FAPESP   , CNPq and CAPES

Dr. A. Beltrán and Dr. J. Andres (Departament de Ciències Experimentals -Universitat Jaume I, Castelló (Spain))



www.mrs.org/meetings/spring2004/

CALL FOR PAPERS

ABSTRACT DEADLINES: **October 20:** for abstracts sent via fax or mail
November 3: for abstracts sent via the MRS Web site

MRS Symposium S: Nanostructured Materials in Alternative Energy Devices

Most of today's energy needs are met by fossil fuels of finite reserves. Fossil fuels may be abandoned much sooner in favor of renewable and clean energy sources as soon as these become more attractive alternatives (environmentally and economically). Key performance issues to be overcome for new energy conversion and storage technologies remain device efficiency, and energy and power density. Projects based on nanoscale materials can offer new or improved performance in devices involving electrochemical reactions and heterogeneous catalysis such as fuel cells, photovoltaics, and batteries. Nanoscale structures can dramatically alter surface reaction rates and electrical transport, resulting in improvements in energy storage, conversion, and generation. Successful design of nanoscale materials and related alternative energy devices could lead to a wide range of new technologies. This symposium aims to discuss the most recent and relevant results pertaining to electrochemical and catalytic properties of nanomaterials, as applied to alternative energy devices.

Contributions are solicited in, but not limited to, the following areas:

- Impact of the nanostructured materials in alternative energy devices
- Nanostructured materials for lithium-ion batteries: synthesis, characterization, and properties
- Nanostructured materials for solar cells: synthesis, characterization, and properties
- Nanostructured and nanocomposite materials for fuel cells and hydrogen generation: synthesis, characterization, and properties
- Nanostructured materials for solid oxide fuel cells: synthesis, sintering, characterization, and properties

A joint session is anticipated with Symposium N: *Interfacial Engineering for Optimized Properties III*.

Invited speakers (tentative) include: **P. Barboux** (Ecole Polytechnique, France), **L.O. Bulhões** (Federal Univ. of São Carlos, Brazil), **F. Disalvo** (Cornell Univ.), **B. Dunn** (Univ. of California-Los Angeles), **D. Larcher** (Univ. of Picardie Jules Verne, France), **M. Graetzel** (Ecole Polytechnique Federal de Lausanne, Switzerland), **M. McGehee** (Stanford Univ.), **D.R. Rolison** (Naval Research Lab), **J. Owen** (Univ. of Southampton, United Kingdom), **J. Schoonman** (Delft Univ. of Technology, The Netherlands), **E. Traversa** (Univ. of Rome Tor Vergata, Italy), **H.L. Tuller** (Massachusetts Inst. of Technology), and **A. Zaban** (Bar-Ilan Univ., Israel).

Symposium Organizers

Edson Roberto Leite

Federal University of São Carlos, Dept. of Chemistry, via Washington Luis Km 235
CP-676, São Carlos, SP, 13565-905, Brazil
Tel 55-16-260-8214, Fax 55-16-261-5215, derl@power.ufscar.br

Jean-Marie Tarascon

Université de Picardie Jules Verne, Lab. de Réactivité et Chimie des Solides
33 rue St-Leu, F-80039 Amiens, France
Tel 33-3-2282-7571, Fax 33-3-2282-7590, jean-marie.tarascon@sc.u-picardie.fr

Yet-Ming Chiang

Massachusetts Institute of Technology, Dept. of Materials Science & Engineering
77 Massachusetts Ave., Cambridge, MA 02139
Tel 617-253-6471, Fax 617-253-6201, ychiang@mit.edu

Erik M. Kelder

Delft University of Technology, Delft Inst. for Sustainable Energy
Laboratory for Inorganic Chemistry, Julianalaan 136, 2628BL Delft, The Netherlands
Tel 31-15-278-2647, Fax 31-15-278-8047, e.m.kelder@tme.tudelft.nl

For additional meeting information, visit the MRS Web site at www.mrs.org/meetings/ or contact:



Member Services

Materials Research Society

506 Keystone Drive, Warrendale, PA 15086-7573 • Tel 724-779-3003 • Fax 724-779-8313 • info@mrs.org