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TITANATE-BASED NANOTUBES

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Introduction

- Carbon nanotubes (CNT) were discovered in 1991
- Since than nanotubes of numerous inorganic compounds were synthesised:

  - layered d-metal dichalcogenides MX_2 (M = Mo, W; Ta; X= S, Se)

  - other type of chalcogenides: InS, ZnS, Bi_2S_3, TiS_2, $TiSe_2$, CdS, CdSe, Ag_2S,

  - boron nitride (BN), carbide (BC_x) and carbonitride ($B_xC_yN_z$)

  - semiconducting materials, such as: SiGe, InGe/GaAs, InGaAs/GaAs, SiGe/Si and InGeAs/GaAs

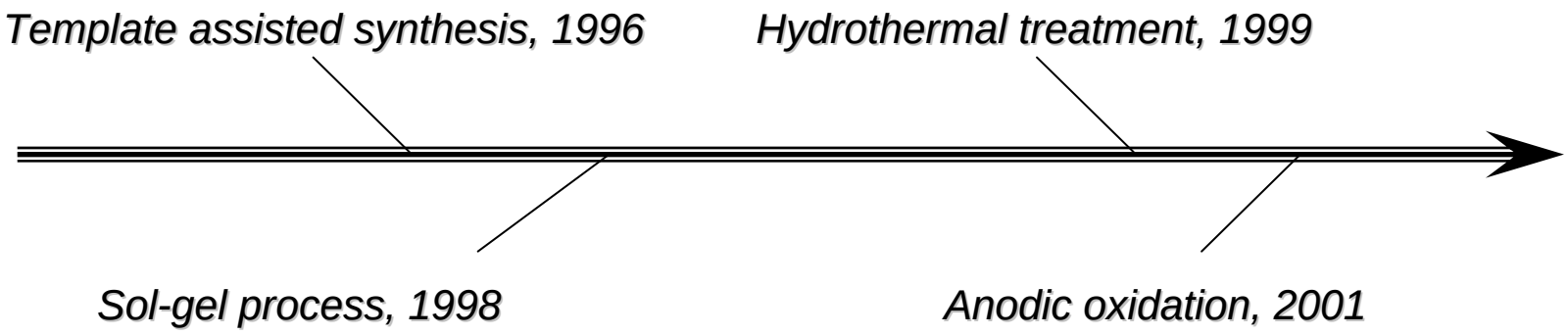
  - nanotubes of metals: Co, Sb, Se, Bi,

  - **p-**, **d-, f-metal** (Al, **Si,** Ge, **Ti,** Nb, Ta, Zr, V, Mo, Dy, Tb) **oxides**

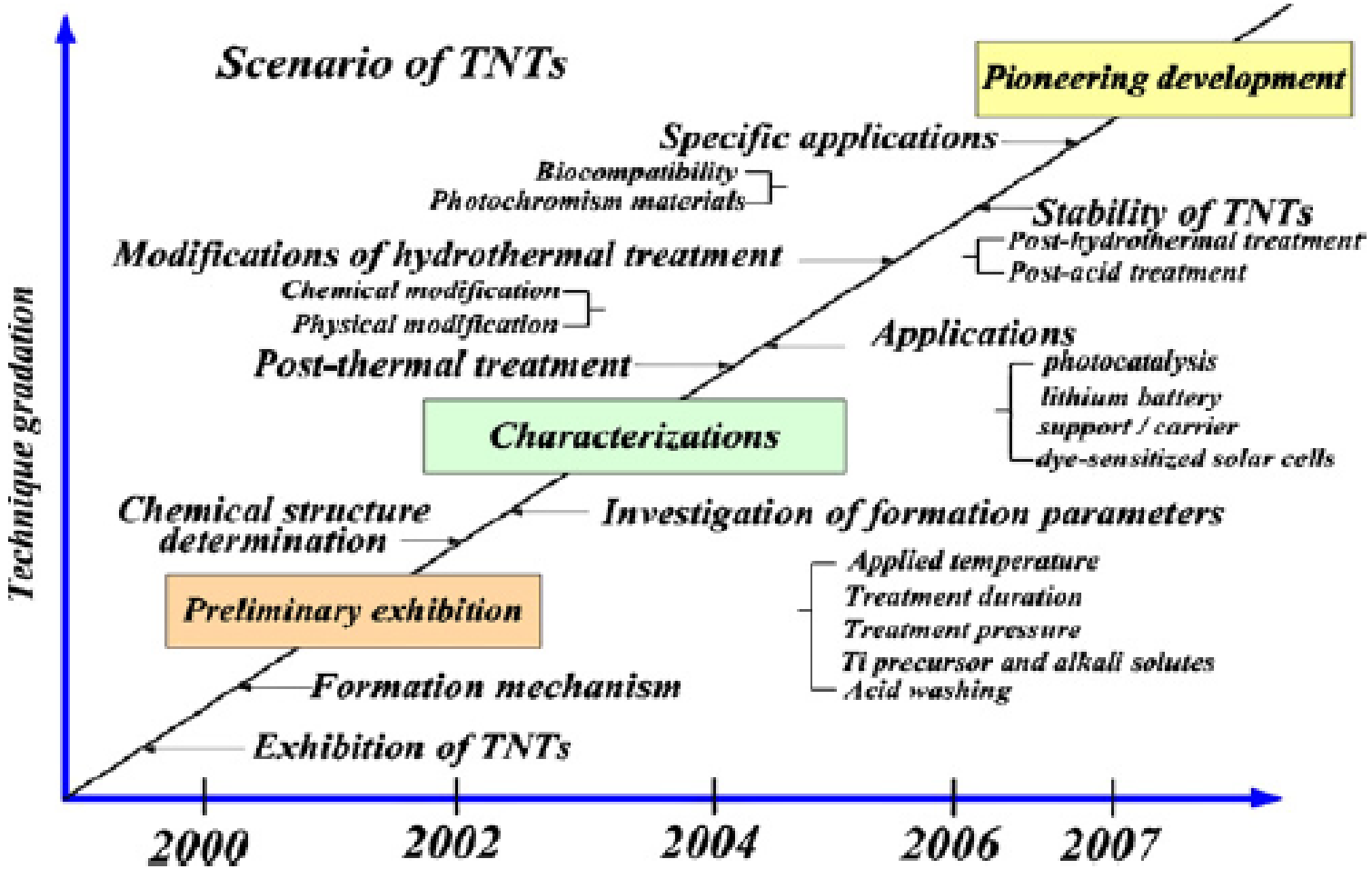
Introduction

- The major advantage of TiO_2 nanotubes is the opportunity to obtain tubes with 10nm diameter and high specific surface areas. On these materials, **can be immobilized enzymes, microorganisms, drugs,** leading to interesting **nanocomposites for biocatalytic applications**
- In their use as hydrogen sensors, the TiO_2 nanotubes possess such excellent **photocatalytic properties** that they are able to self-clean from contamination with exposure to ambient UV light.
- Furthermore materials with high porosity in the sub-micron renge are of great interest for **application in organic electronics, microfluidics, molecular filtration, drug delivery**, and **tissue engineering**.
- Other recent applications include their successful use in **dye sensitized heterojunction solar cells**, where in comparison to nanoparticulate systems the use of the nanotube improves photogenerated charge carrier lifetimes by well over an order of magnitude.

Evolution of TiO_2 nanotubes preparation methods



Titania based Sol-Gel Nanotubes by hydrothermal method



Aim

- Preparation of titanate-based nanotubes, by chemical methods (hydrothermal treatment and sol-gel route)
- Study of the experimental parameters' influence on structure, morphology and properties
- Applications for photocatalitic processes and bioremediation

Background

- Titanate-based nanotubes architecture, obtained by hydrothermal treatment demonstrates that, this **single step** procedure, in a closed system, yields **high degree of crystalinity** and defines a **pure phase structure**
- Research was oriented on 6 directions:

1. influence of the TiO_2 precursor
2. influence of preparation/synthesis parameters and post-hydrothermal treatment (as washing, separation)
3. physical and chemical modifications (sonication, doping)
4. post-treatments (drying, thermal treatment)
5. material characterization and reaction mechanism
6. applications

Sample preparation

- PRECURSORS:

  TiO_2 P25 Aeroxide Degussa and amorphous sol-gel TiO_2

- EXPERIMENTAL SET-UP:

1. TiO_2 precursor was dispersed in of 10M NaOH solution by sonication

2. the slurry was transferred into 20 ml Parr Instruments pressure vessel, sealed and heated at 140°C for various times (24, 48, 72, 96 hours)

3. the precipitate was separated by centrifugation then washed by filtration with distilled water, 0.1N HCl solution, alternatively, until pH ~6

4. the sample was dried at 110°C, 12 h, in air

Sample characterization

- PRECURSORS:

  TiO_2 P25 Aeroxide: by TEM, SAED, FT-IR and DTA/TG

  TiO_2 sol-gel: by TEM, SAED, FT-IR and DTA/TG

- NANOTUBE SAMPLES

Samples **D*h*-*T*** and Samples **SG*h*-*T***,

where **D**-Degussa, **SG**-sol-gel, ***h***-time, ***T***-temperature

were characterized:

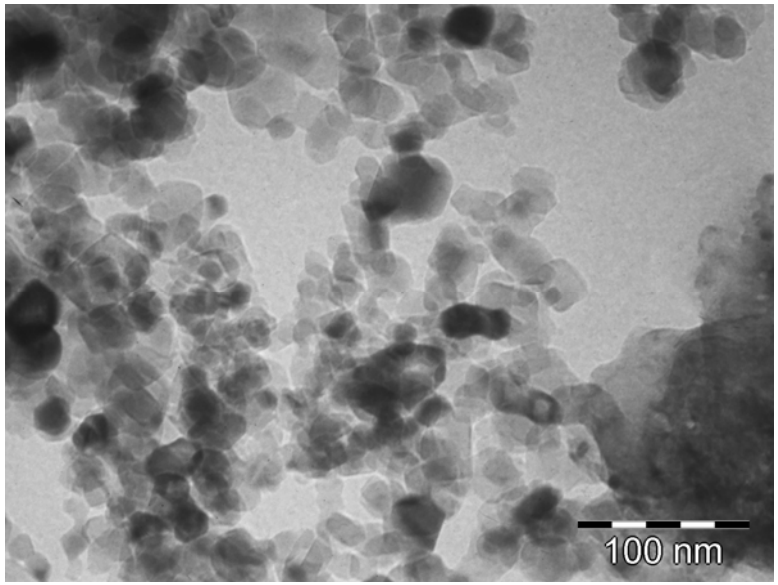
by TEM

Sample D72-110 was supplementary characterized by EDAX

Precursors

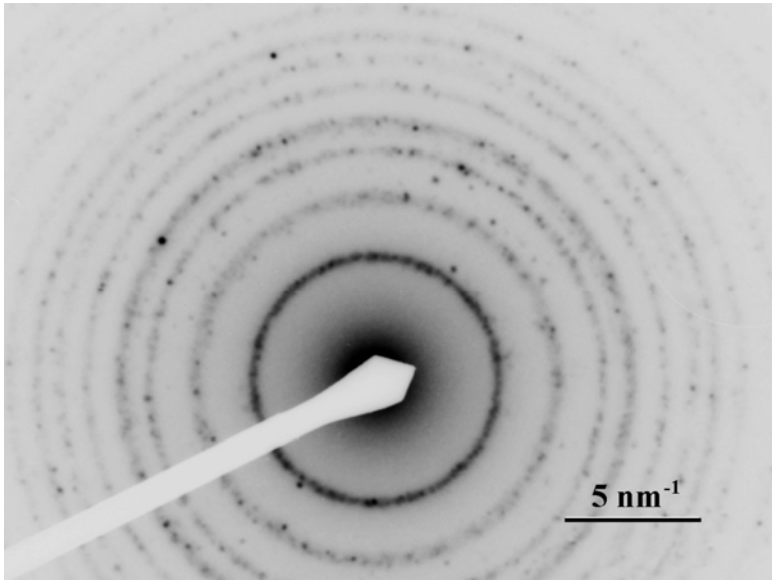
TiO_2 P25 (Degussa)

TEM



Crystallites size range 15-50 nm; Average size ~27 nm, determined on 137 particles

SAED

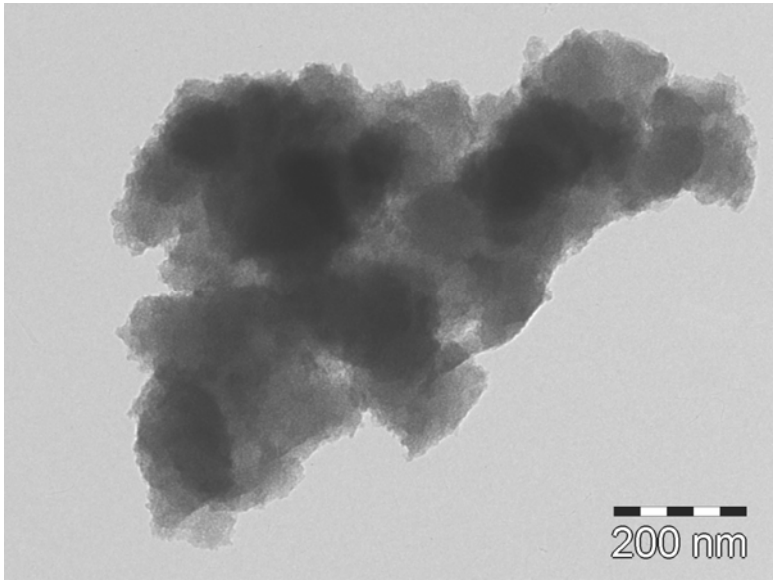


Crystalline phases of anatase and rutile (larger particles)

Precursors

TiO_2 (sol-gel route)

TEM



Particle aggregates;
Micron and submicrometer size;
High density of nanometer size pores

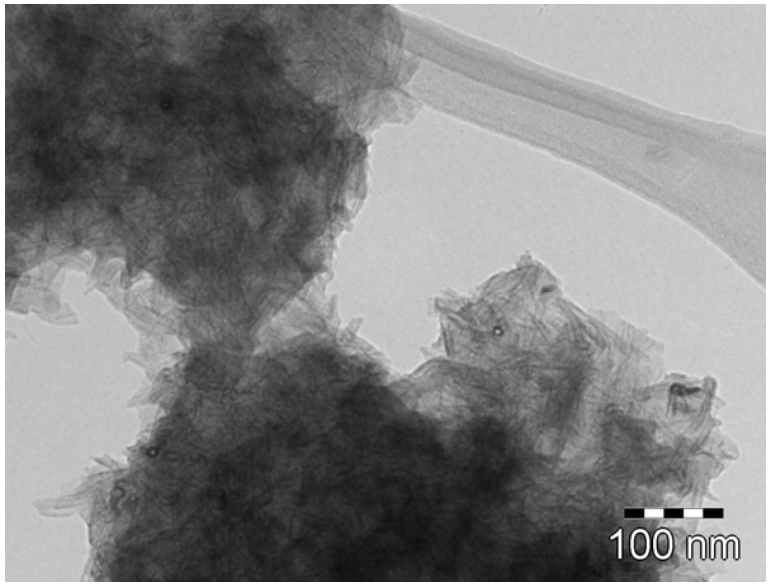
SAED

Amorphous structure

Sample D24-110

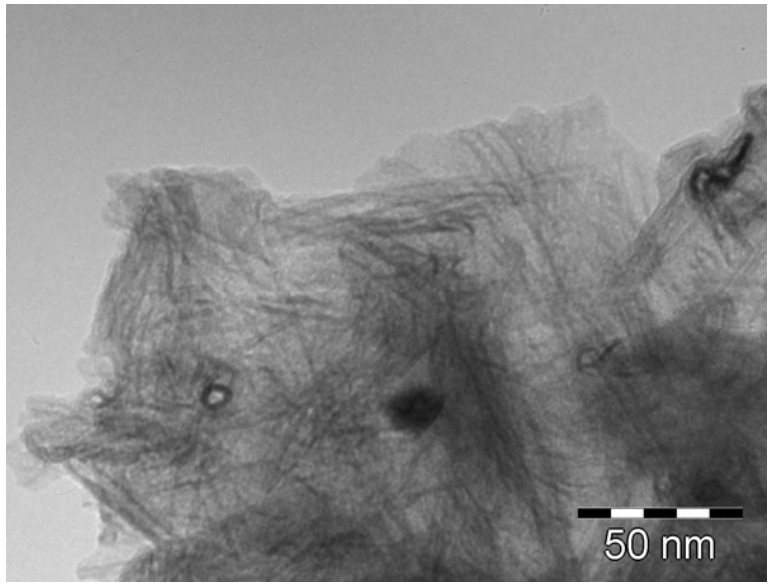
HT T(°C)=140°C; t(h)=24h

TEM



Nanotubes aggregate;
Aggregates are compact and few nanotubes are outside, isolated

TEM - detail

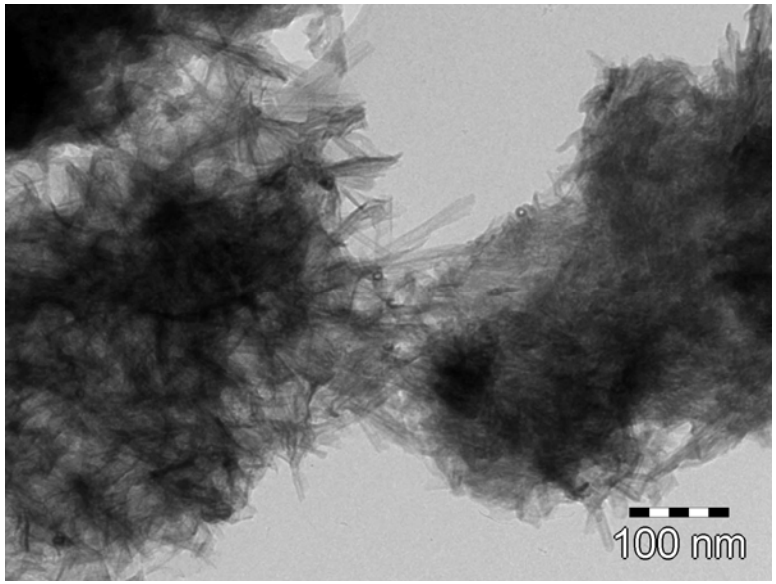


Nanotubes are trapped into an amorphous phase network

Sample D48-110

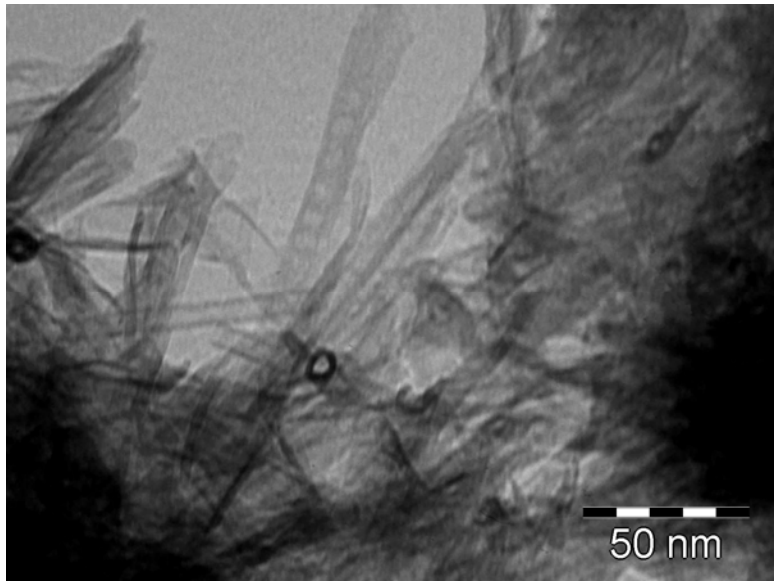
HT T(°C)=140°C; t(h)=48h

TEM



Two aggregates types:
Nanotubes aggregates and amorphous phase aggregates

TEM - detail

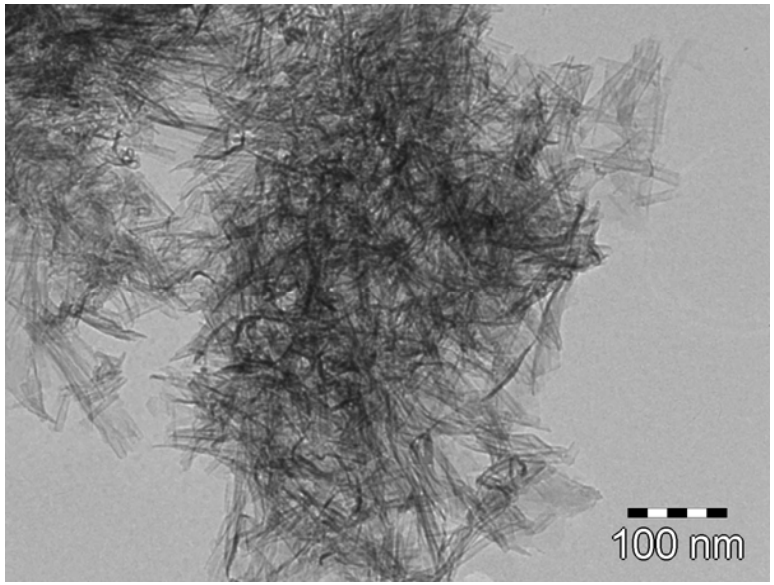


Nanotubes are trapped into an amorphous phase network

Sample D72-110

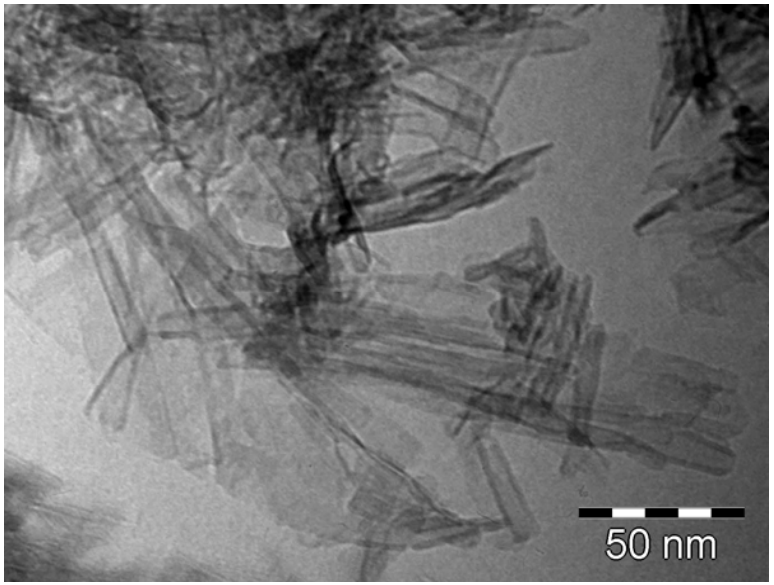
HT T(°C)=140°C; t(h)=72h

TEM



Nanotubes aggregates;
Nanosheets are also present;
Aggregates are less compact;
Amorphous phase dissapeared

TEM - detail

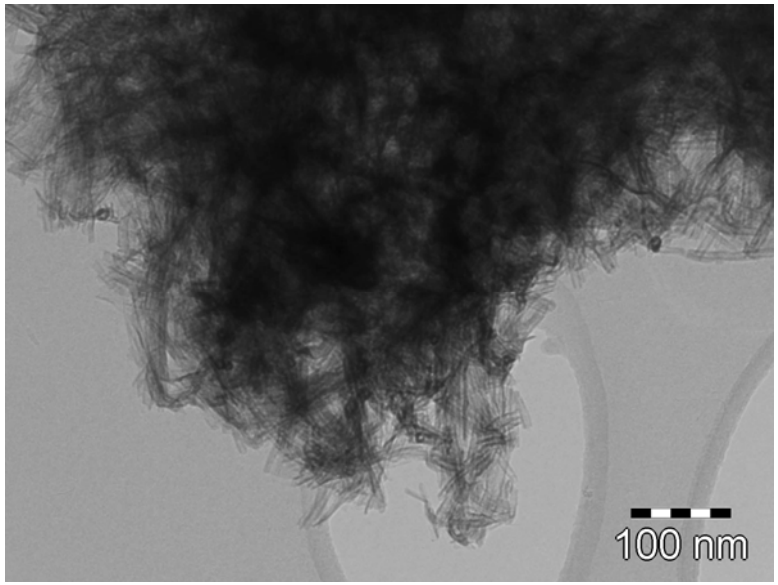


Best nanotubes yielding

Sample D96-110

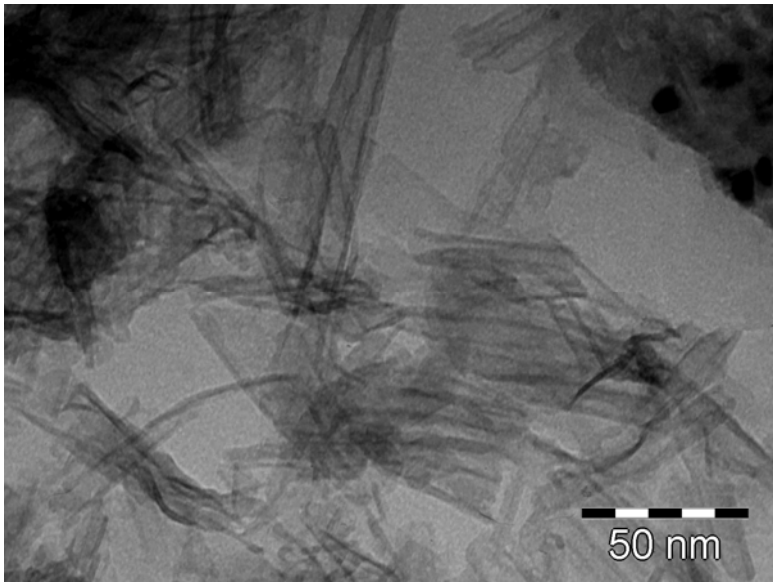
HT T(°C)=140°C; t(h)=96h

TEM



Aggregates are more compact than D72-110

TEM - detail

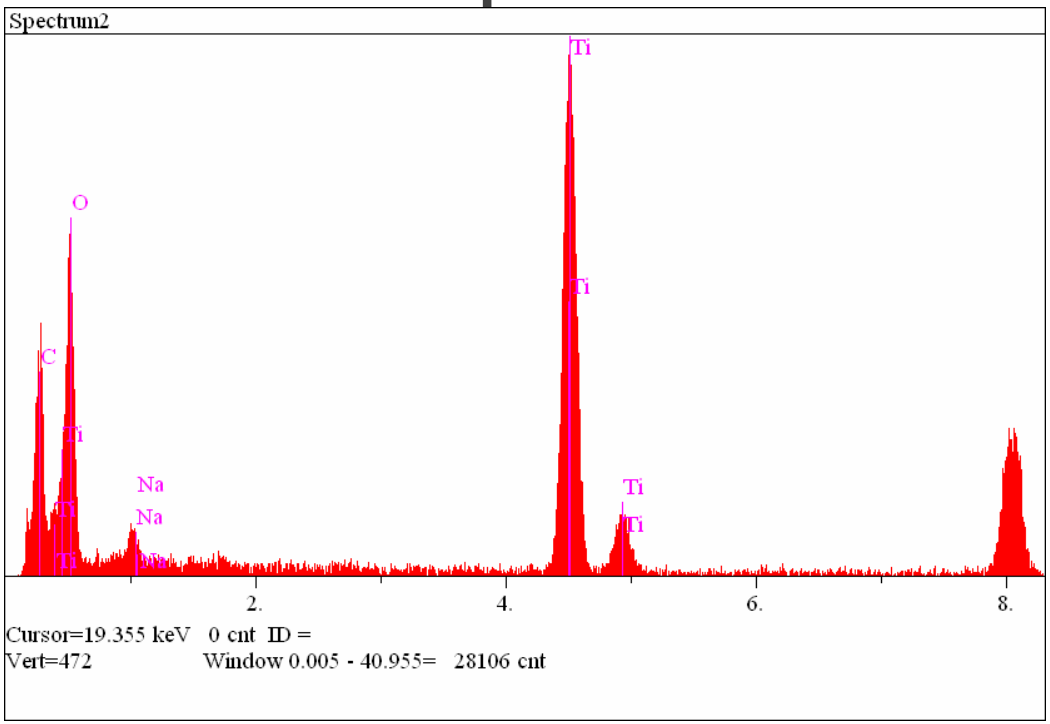


Nanosheets became major phase; Nanotubes are secondary phase

Sample D72-110

HT T(°C)=140°C; t(h)=72h

EDAX spectrum

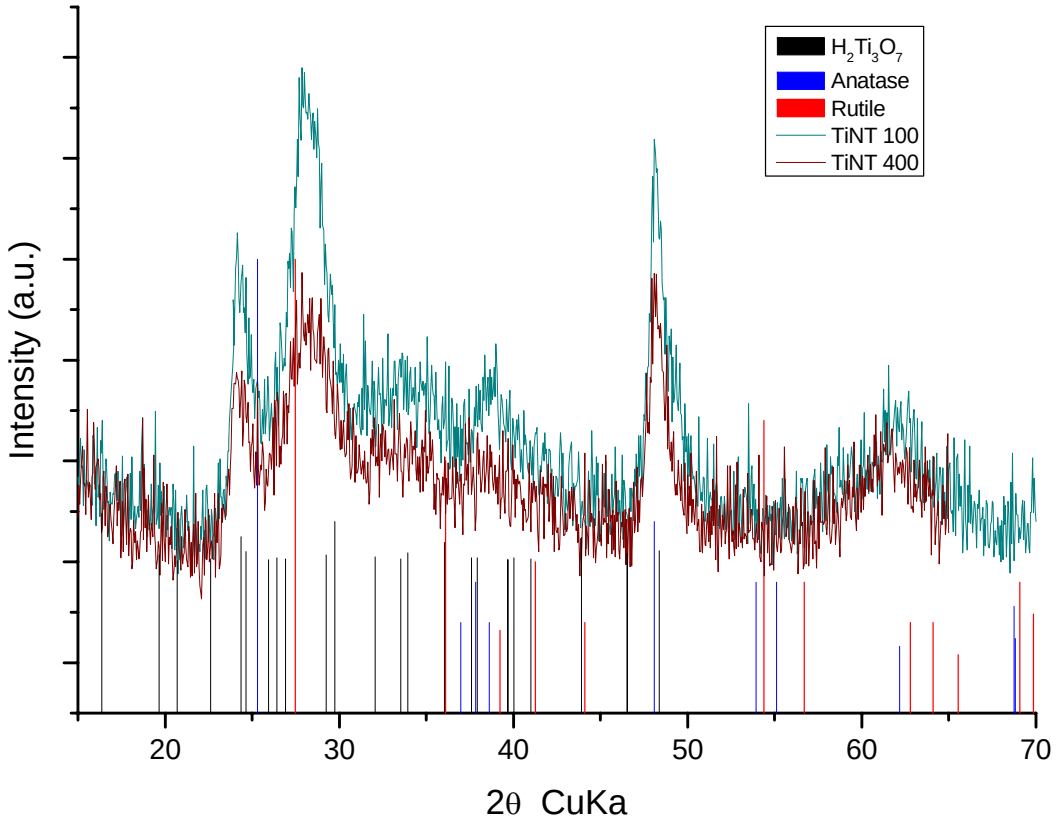


Sodium is still present in nanotubes' chemical composition;
Quantitative analysis is difficult because of sample morphology;
$Na_2Ti_3O_7$ composition may be suggested, according to literature

Samples D24-110 and D24-400

HT T(°C)=140°C; t(h)=24h

XRD

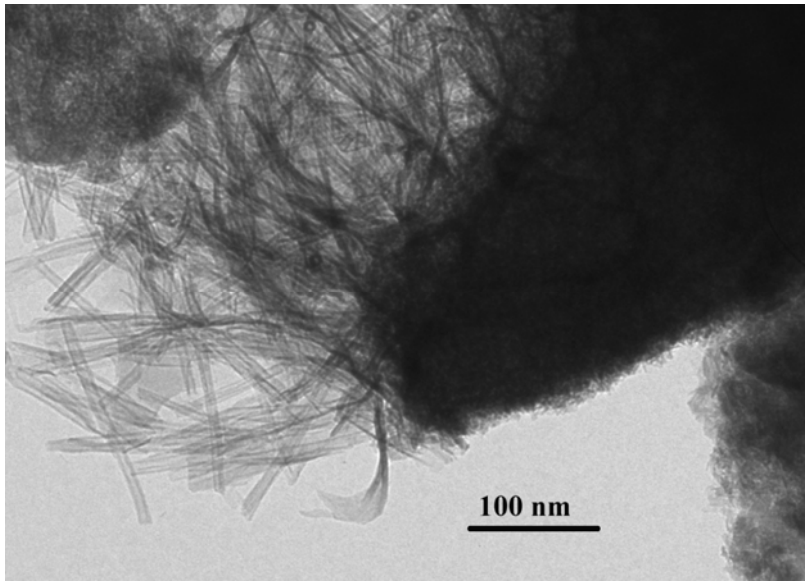


The as synthetized nanotubes, obtained by hydrothermal treatment, starting from P25 Aeroxide, didn't present a defined crystalline structure.
Based on XRD patterns, the chemical formula of the samples can be $Na_xH_2Ti_3O_7 \cdot nH_2O$, where x depends on washing solution pH.

Sample SG24-110 (without centrifugation)

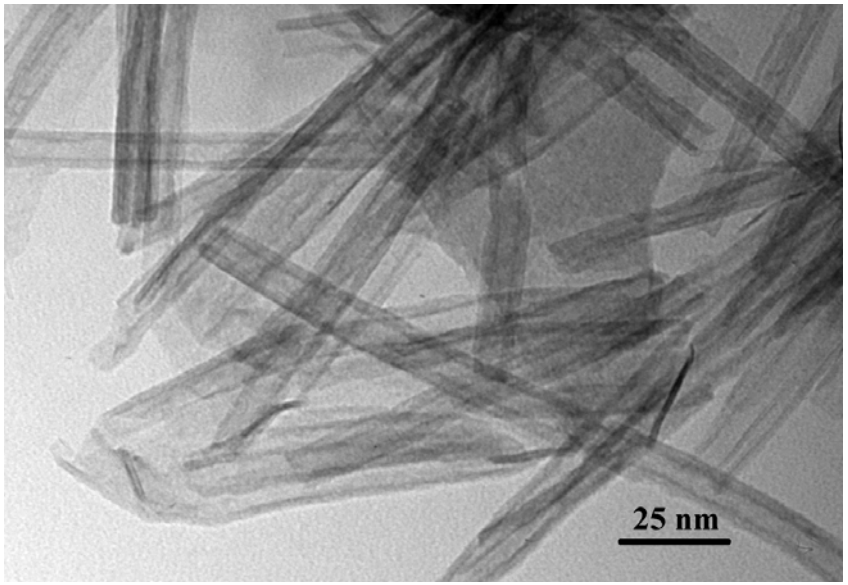
HT T(°C)=140°C; t(h)=24h

TEM



Nanoparticles aggregates with nanotubes growing on their surface

TEM - detail

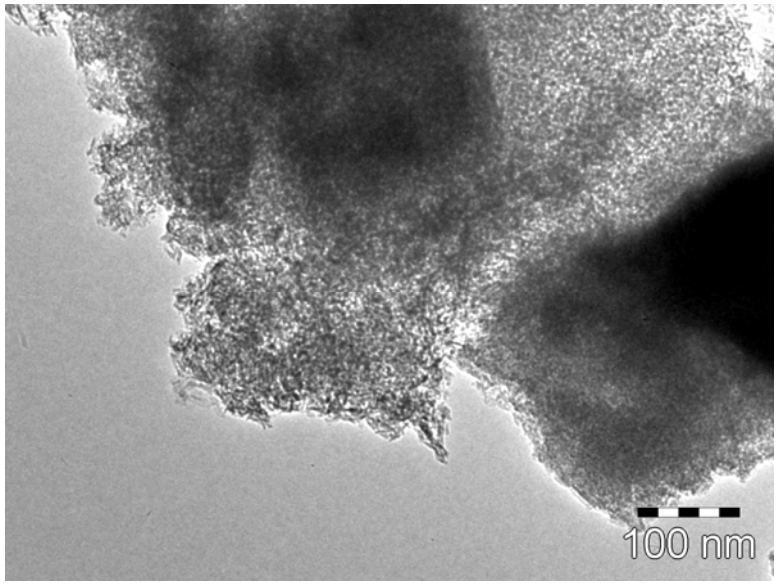


Outer diameter Ø=10-12nm;
Wall thickness 3-4nm

Sample SG24-110 (with centrifugation)

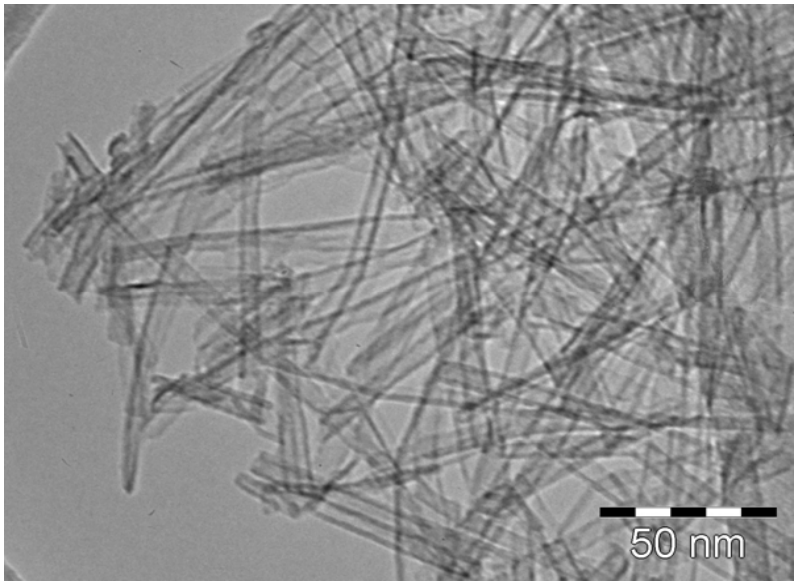
HT T(°C)=140°C; t(h)=24h

TEM



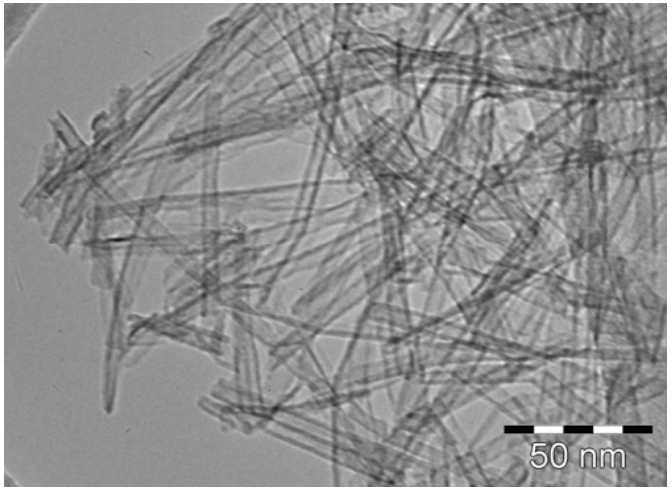
Nanosheets and nanotubes aggregates;
Nanosheet – major phase

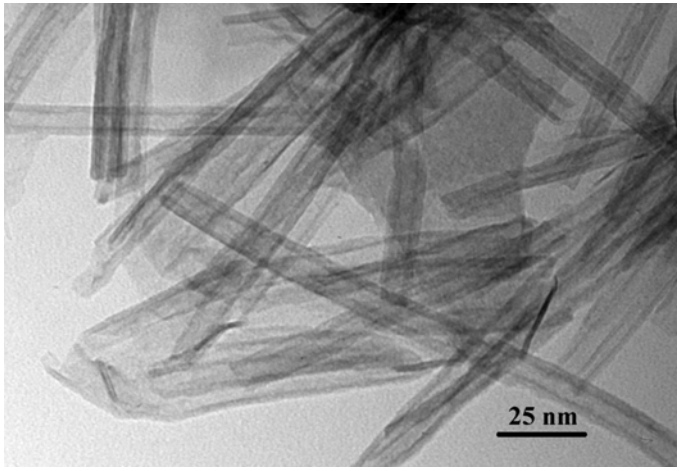
TEM - detail



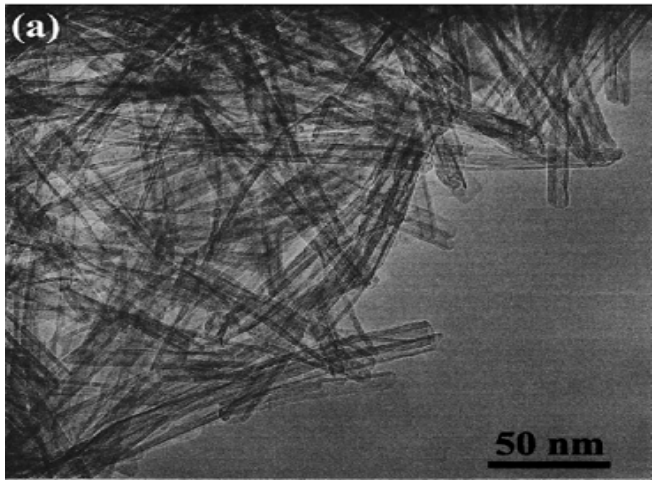
Outer diameter Ø=8-9nm;
Wall thickness 2nm;
Lengths 200nm

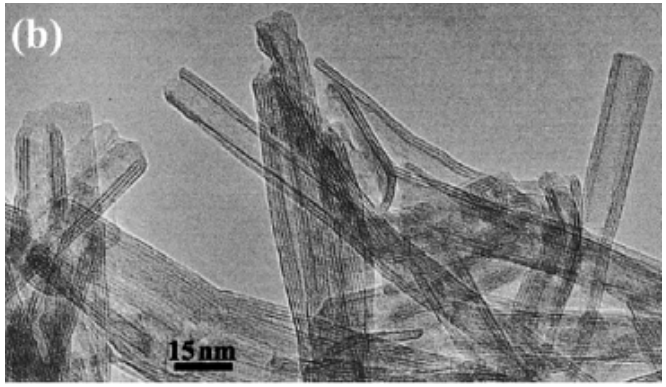
Comparison between synthesized and literature reported TiO_2 nanotubes





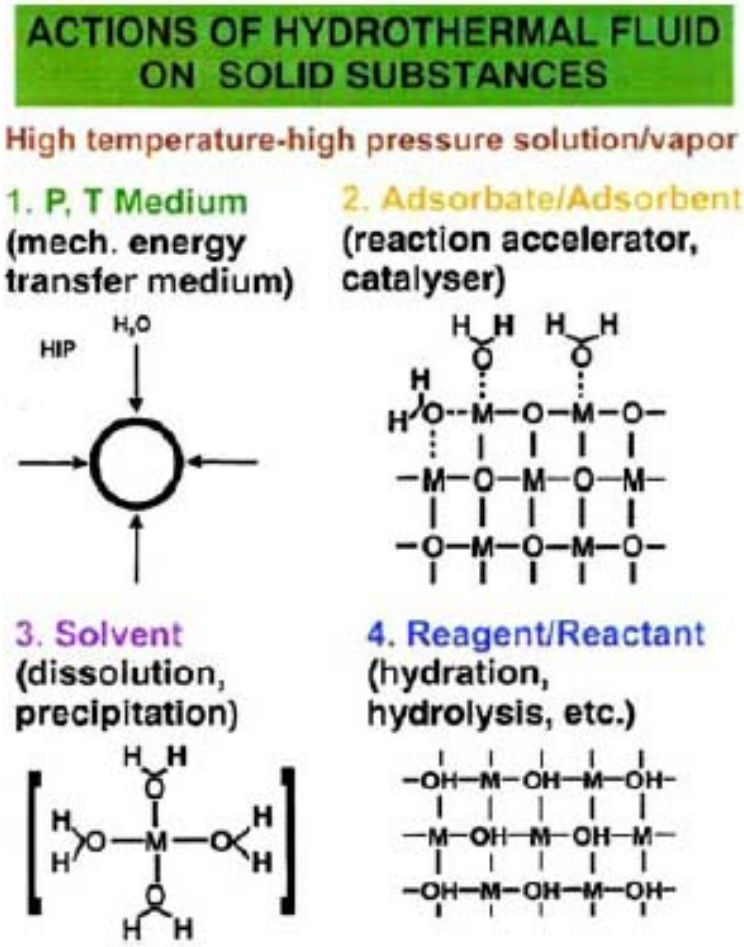
Synthesized TiO_2 nanotubes





Literature data: F. Krumeich et all.
J. Am. Chem. Soc. ***121*** *(1999) 8324*

Possible mechanism of nanotube formation



In solution processing the key parameter is the solvent.
In case of hydrothermal processing the solvent plays multiple roles and its role has to be understood clearly in order to work out a mechanism for materials processing under hydrothermal conditions.

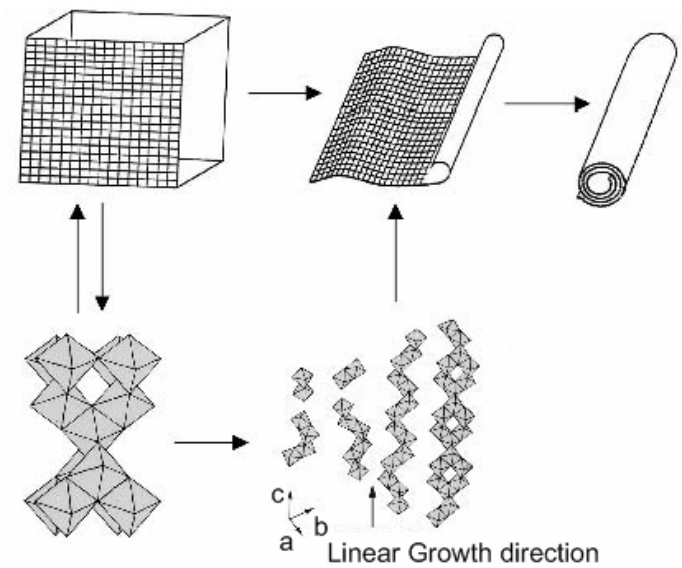
Possible mechanism of nanotube formation

The formation mechanism takes places in three stages during hydrothermal treatment:

1. The 3D structure of the precursors (crystalline or amorphous) transforms under alkaline attack in 2D lamellae structure

2. The boundaries of the lamellae (nanosheets) have free bonds and the free energy, under alkaline medium disturb this 2D structure by bending, driven by the tendency to saturate these free bonds.

3. The tube structure, 1D, is forming by rolling the nanosheets and saturation of the free bonds from the nanosheets boundary



The modeling of the nanotube formation from nanopowders is under evaluation

CONCLUSIONS

There were obtained, by hydrothermal treatment, under alkali attack, 1D tubular nanosized structure

The amorphous sol-gel precursor could be much efficient as precursor than crystalline P25 Aeroxide because it skips the dissolution stage of the crystalline phase and it has high reactivity

The best nanotube ratio has been obtained for 72 hours hydrothermal treatment when starting from P25 Aeroxide Degussa

The structure and chemical composition could be assigned to sodium titanate based on EDAX and XRD analysis

Acknoledgment

The research was realized in the frame of PNII National Program by the NANOTUBOX project, under contract No.71-109/2007