Synthesis of oxide nano-particles with a continuous hydrothermal production process under supercritical conditions.

F.Demoisson*, M.Ariane and F. Bernard

Laboratoire Interdisciplinaire Carnot de Bourgogne (ICB)
Département Nanosciences - Equipe MaNaPI : "Matériaux Nanostructurés: Phénomènes à l'Interface"
UMR 5209 CNRS/Université de Bourgogne
9 Avenue Alain Savary
BP 47 870   21078 DIJON Cedex (France).
Tel : (33) 03 80 39 59 06
Fax : (33) 03 80 39 61 67
E-mail : Frederic.Demoisson@u-bourgogne.fr

Synthesis crystalline ZnO, ZrO_2 and TiO_2 nano-particles were carried out under supercritical water conditions from metallic salts ($Zn(NO_3)_2$, $ZrO(NO_3)_2$) and organometallic (ALT*) as precursors. At room temperature, metallic salt and with or without hydroxide aqueous solution (KOH) were pressurized to 30 MPa. Then, the reactant(s) was/were rapidly heated to 550-673 K by mixing with the supercritical water in a tubular reactor. Residence time is about 4 s. Production of nanosize particles with an uniform size distribution ($\leq$ 20 nm) showed highly crystalline phases identified by XRD and TEM observations.

* bis(ammonium lactato)titanium dihydroxide: $(CH_3CH(O)CO_2NH_4)2Ti(OH)_2$

Keywords: *ZnO, ZrO_2, TiO_2, continuous hydrothermal synthesis, supercritical water, nano-particles.*

INTRODUCTION

Nanotechnology is defined as a technology to use materials whose dimension is in the range from 0.1 to 100 nm and thus physical and chemical properties are usually improved from bulk one. Nanoparticles are considered as essential materials in Nanotechnology. Physical and chemical properties of nanoparticles can be varied by changing their size and morphology. Especially the size of the particles reflects leads to an increase of the ratio surface to volume. The size effect, in particular the quantum size, is mainly considered to describe physical properties (the quantum size effect appears where the normal bulk electronic structure is replaced by a series of discrete electronic levels).While the surface induced effect plays an important role for chemical processing [1]. However in the size effect, when the size of nanoparticles is lower than critical wavelength of light (less than 100 nm), a useful property as transparent which can be applied in packaging, cosmetics and coating will be appeared [2].
  Metal oxide nanoparticles are usually used in a variety of applications including sensors, varistors, pigments, fillers, electrography and medical materials. Nanoparticles can be produced by several techniques such as precipitation, spray pyrolysis, thermal decomposition and hydrothermal synthesis. In particular, supercritical Water Hydrothermal Synthesis (scWHS) is an environmentally process for the production of potentially valuable metal oxide nanoparticles (ZnO, TiO_2, …) usually applied in the domains of the Nanotechnology. Currently, most scWH syntheses are performed in batch reactor. However, the main drawback of this closed reactor is the thermal inertia which must resist to the combined effect of the temperature (T > 374°C) and the pressure (P > 22.1 MPa). These limits can be removed in a

continuous synthesis process which can also synthesize larger quantities of nanopowders than in a batch reactor. In this context, the MaNaPI team of the Laboratoire Interdisciplinaire Carnot de Bourgogne (ICB) has developed a continuous hydrothermal production process of oxides and hydroxides nanoparticles synthesized in supercritical conditions. In the proposed method with a flow type tubular reactor, metal salt aqueous solution was mixed with high temperature water to increase the solution temperature rapidly up to the supercritical state. Because of the high reaction rate of hydrothermal synthesis and low solubility of metal oxides, extremely high super saturation degree is attained just after the mixing point. This leads to the formation of nanometer size particles [3-5].

This paper presents some examples of synthesis crystalline ZnO, ZrO_2 and TiO_2 nano-particles which were carried out under supercritical water conditions from metallic salts ($Zn(NO_3)_2$, $ZrO(NO_3)_2$) and organometallic (ALT*) as precursors.

MATERIALS AND METHODS

Materials. Zinc nitrate ($Zn(NO_3)_2$), zirconyl nitrate ($ZrO(NO_3)_2$), potassium hydroxide (KOH) salts and bis(ammonium lactato)titanium dihydroxide ($CH_3CH(O)CO_2NH_4)2Ti(OH)_2$ organometallic were used as starting materials and were purchased from Sigma Aldrich. Deionized water was used for hydrothermal synthesis.

Procedure. In the continuous hydrothermal synthesis process apparatus (Figure 1), reactive solutions and deionized water were fed using high-pressure pumps. Pressure was regulated thanks to the back pressure regulator, located at the outlet, and kept constant in the whole apparatus. Deionized water was preheated to a temperature that was above the desired temperature in the pre-heater. The three streams were then combined in a tubular reactor (patent pending [6]). This last was optimized with the help of a commercially available CFD package (FLUENT® 6.3). CFD models of the mixing zone of a previous reactor are presented in Figure 2. The residence time in the reactor depended on pump flows (~ a few seconds). Once leaving the reactor, the solution was rapidly quenched in a cold bath. Two filters made of 7 μm and 2 μm porous stainless steel removed agglomerated particles. Then, the suspension was centrifuged and washed with deionized water under ultrasonication. The sol formed was freeze-dried to conserve a well-dispersed nanopowder. This apparatus allowed performing very fast reactions (residence times were only a few seconds in the reactor). Supercritical conditions leading to instantaneous formation of a large number of hydroxide nuclei, short residence times were of great interest to reduce particle growth. Therefore, nanopowders were synthesized with a production of around 10 to 15 g/h. Note that, a new filtration system allows to produce 60 g/h of dry powder. A large set of experimental conditions could be used from soft chemistry to supercritical conditions. All operating parameters (temperature, pressure, concentration of reactive solutions, residence time, pH...) could be adjusted independently showing that this process was very flexible. Indeed, thanks to the preheated water flow (which was heated above the desired temperature), the temperature of the solution after the mixing zone could be set to the desired temperature, depending on the pumps flows. Moreover close to the H_2O critical point, minor variations of temperature and pressure could generate large changes of solvent properties allowing an adjustment of reaction medium.
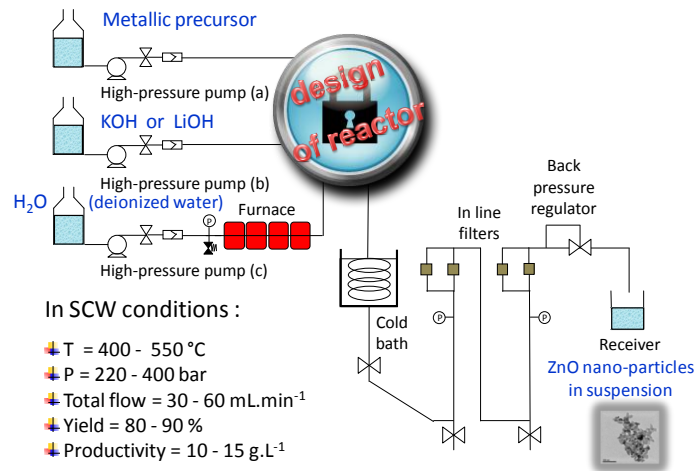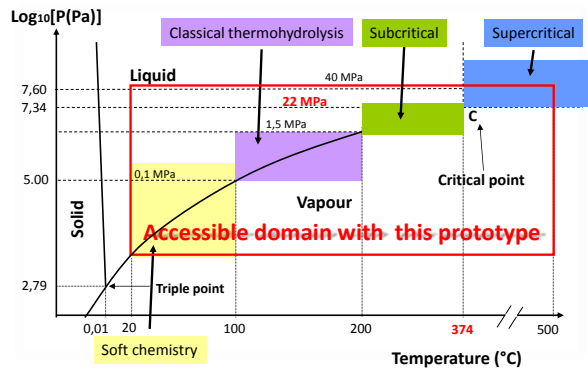
Figure 1: Continuous hydrothermal production process of oxide and hydroxide nanoparticles synthesized in sub and supercritical conditions. State diagram of water viewing the accessible domain of synthesis available using this device.
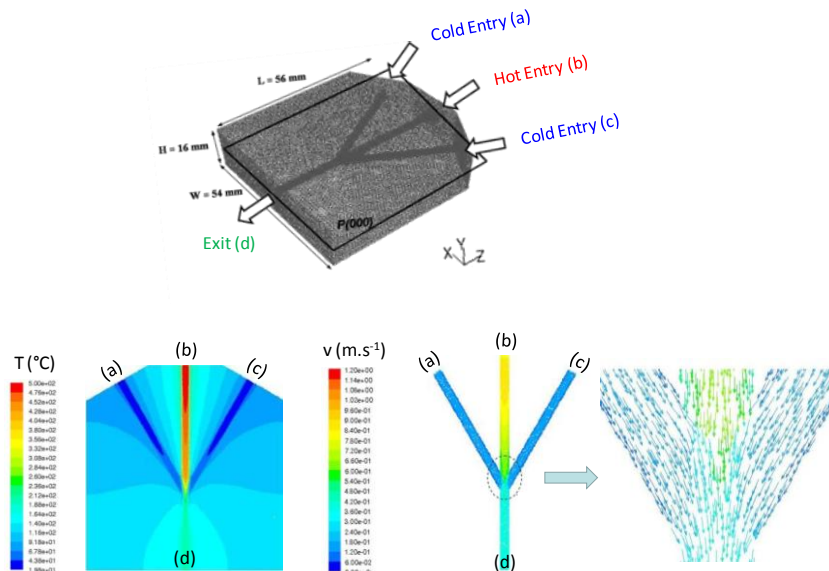

Figure 2: CFD simulation (FLUENT$^{®}$ 6.3): design of a previous reactor, CFD models of the mixing zone: temperature and velocity fields.

Characterization. SCW end-products were investigated by X-ray diffraction (XRD) measurement using a Siemens D5000 powder diffractometer. The instrumental broadening correction was determined from a SiO_2 standard reference material from Brucker. Pseudo-voigt peak profile analysis, using the Halder Wagner and the Le Bail methods [7-8] was performed to determine both the average crystallite size and crystallographic imperfections (methods including all the diffraction reflections for the calculation). The lattice parameters of the powders were deduced from XRD line positions using a least-squares refinement method. The size and shape of the nanoparticles were studied by using the transmission electron microscopy. TEM experiments were conducted on a JEOL JEM-2100 LaB6 microscope operating at 200kV equipped with a high tilt pole-piece achieving a point-to-point resolution of 0.25 nm.

RESULTS

Zinc Oxide (ZnO).

Zinc oxide (ZnO) nanoparticles were synthesized at 673 K and 30 MPa with a zinc nitrate concentration of 0.06 mol.L^{-1} in basic condition ([KOH]= 0.24 mol.L^{-1}). The total flow was set up at 60 mL.min^{-1}.

XRD pattern of the resulting material is presented in Figure 3. The synthesis conducted from $Zn(NO_3)_2$ led to a pure and well crystallized ZnO phase. The XRD peaks can be attributed to a wurtzite ZnO structure and the larger XRD peaks indicates a small size of the ZnO crystallites.
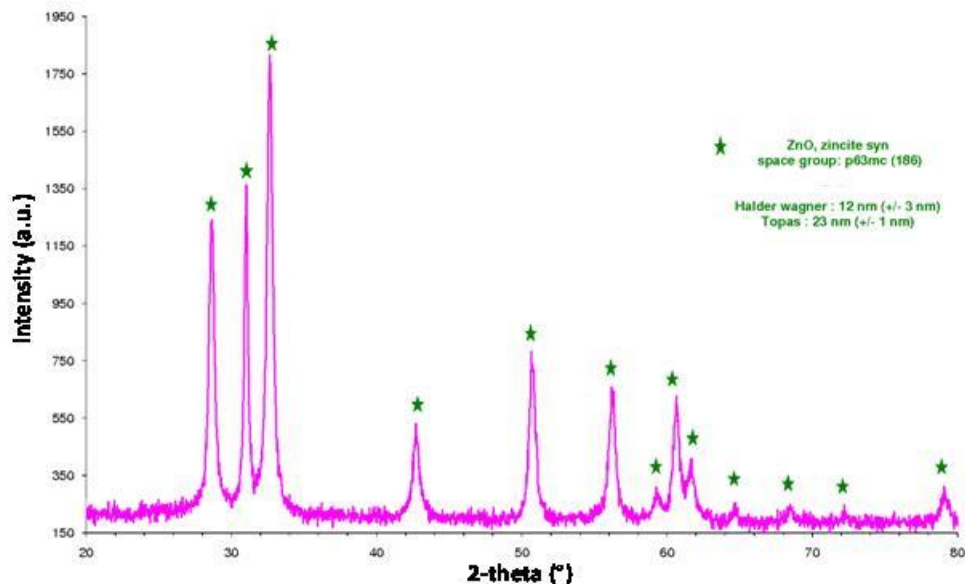

Figure 3: XRD pattern of the as-synthesized ZnO prepared in H_2O-supercritical conditions (673 K - 30 MPa) from zinc nitrate $Zn(NO_3)_2$ ([ ] = 0.06 mol.L^{-1}) as precursor in basic condition ([KOH]= 0.24 mol.L^{-1}).

The Halder Wagner and Le Bail methods conclude to an average particles diameter of 12 ± 3 nm and 23 ± 1nm respectively in agreement with TEM results presented in Figure 4. TEM and High-resolution transmission (HRTEM) images show ZnO nanocrystallines with an average particle size of 20 ± 6 nm. Note that a very well homogeneous distribution of particle

size is obtained. The HRTEM image clearly shows a single crystalline structure. The coexisting cation from the basic salt (KOH and LiOH) and the coexisting anion from zinc salt $(Zn(CH_3COO)_2, ZnSO_4, Zn(NO_3)_2)$ seem to considerably influence the size and the morphology of the nanomaterial during the growing step [9] (data not shown).

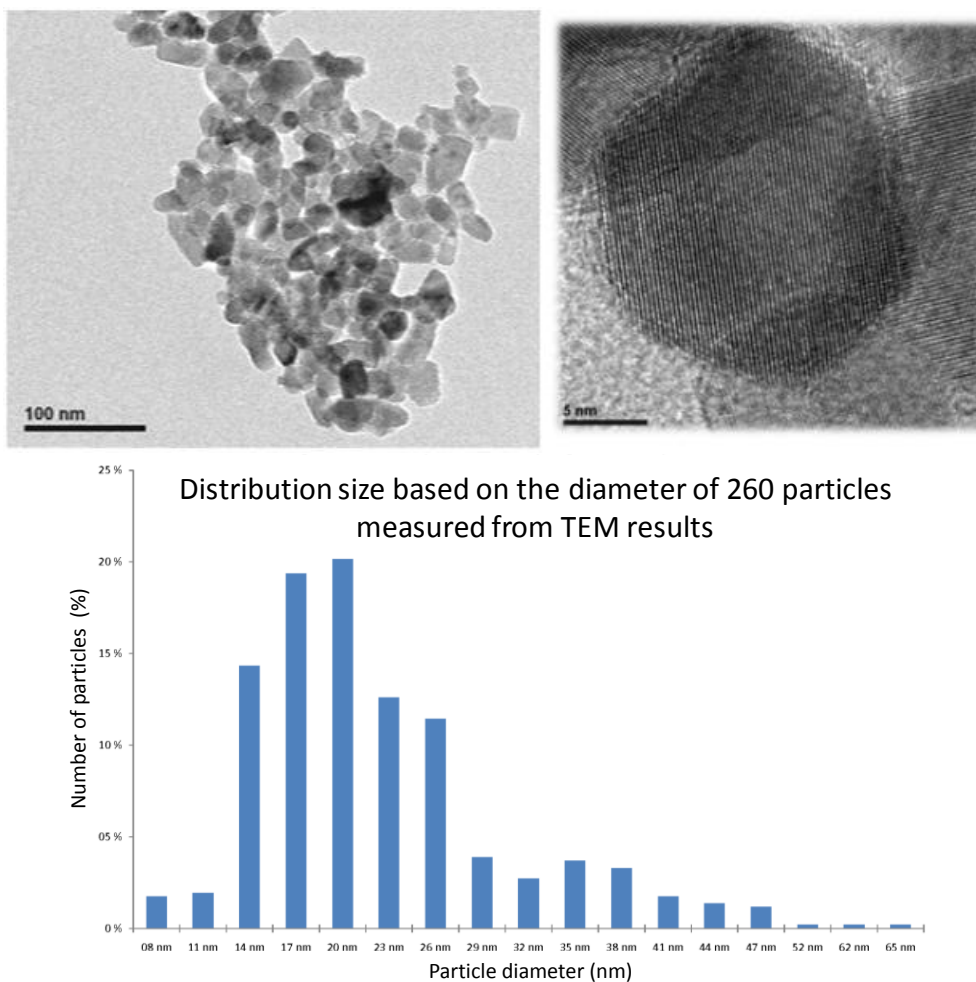**Figure 4**: (HR)TEM images of the as-synthesized ZnO prepared in H_2O-supercritical conditions (673 K - 30 MPa) from zinc nitrate $Zn(NO_3)_2$ ([ ] = 0.06 mol.L^{-1}) as precursor in basic condition ([KOH]= 0.24 mol.L^{-1}).

Zirconuim Oxide (ZrO$_2$).

Zirconium oxide (ZrO_2) nanoparticles were synthesized at 773 K and 30 MPa with a zirconyl nitrate concentration of 0.05 mol.L^{-1} without addition of base (from [10-12]). The total flow was set up at 30 mL.min^{-1}.

XRD pattern of the resulting material is presented in Figure 5. The synthesis prepared from $ZrO(NO_3)_2$ led to a mixed pure and well crystallized ZrO_2 phases. The XRD peaks can be attributed to a tetragonal and a monoclinic ZrO_2 structures and the presence of larger XRD peaks indicates a small size of the ZrO_2 particles. The crystallographic form of ZrO_2 depended directly on the reaction medium. Indeed, the thermohydrolysis of this precursor usually led to the tetragonal ZrO_2 phase, whereas using basic conditions (KOH addition) an amorphous

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phase was formed which was the orthorhombic ZrO_2 phase after a heat-treatment at 550 °C during 6 h [13].
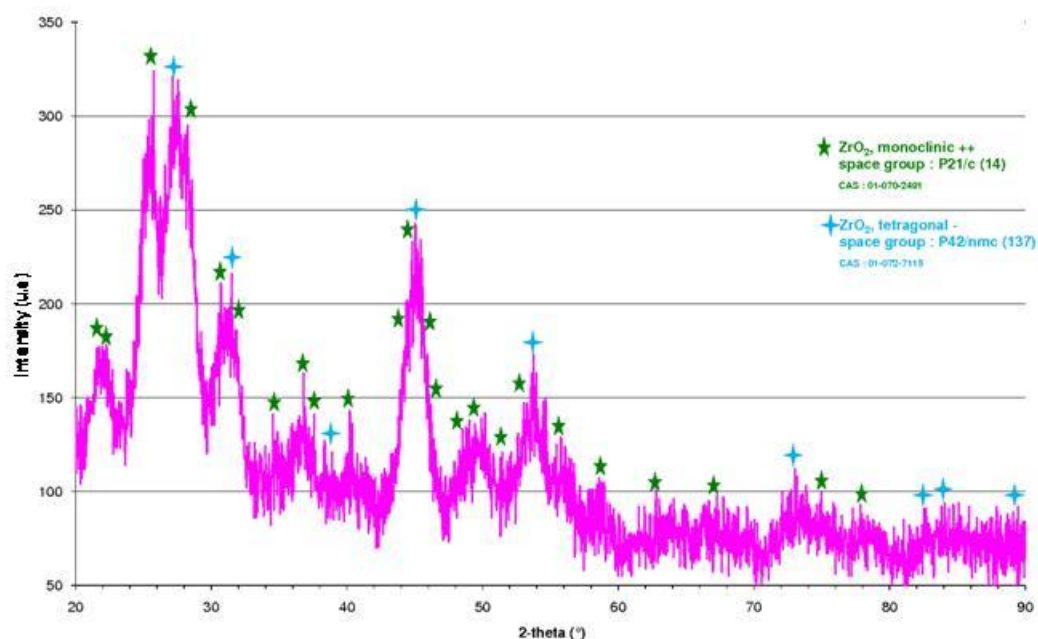

Figure 5: XRD pattern of the as-synthesized ZrO_2 prepared in H_2O-supercritical conditions (773 K - 30 MPa) from zirconyl nitrate $ZrO(NO_3)_2$ ([ ] = 0.05 mol.L^{-1}) as precursor.

About the morphology, TEM images presented in Figure 6 show spherical-like ZrO_2 with a homogeneous distribution of average particle size of 7 ± 1 nm.
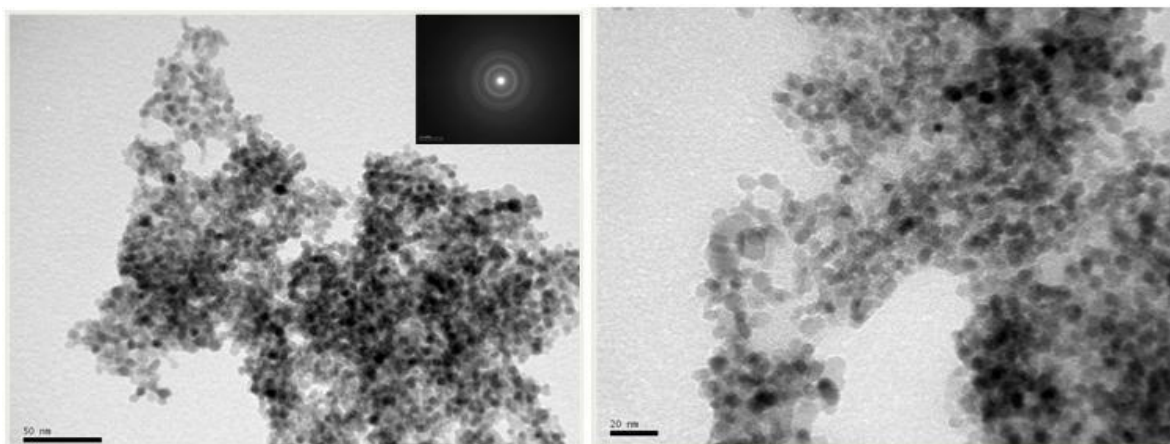

Figure 6: TEM images of the as-synthesized ZrO_2 prepared in H_2O-supercritical conditions (773 K - 30 MPa) from zirconyl nitrate $ZrO(NO_3)_2$ ([ ] = 0.05 mol.L^{-1}) as precursor.

Titanium Oxide (TiO$_2$).

Titanium oxide (TiO$_2$) nanoparticles were synthesized at 673 K and 30 MPa with a bis(ammonium lactato)titanium dihydroxide (ALT) concentration of 0,104 mol.L^{-1} (from [14-15]). The total flow was set up at 30 mL.min^{-1}.

XRD pattern of the resulting material is presented in Figure 7. The synthesis performed from ALT led to a pure and well crystallized TiO$_2$ phase.
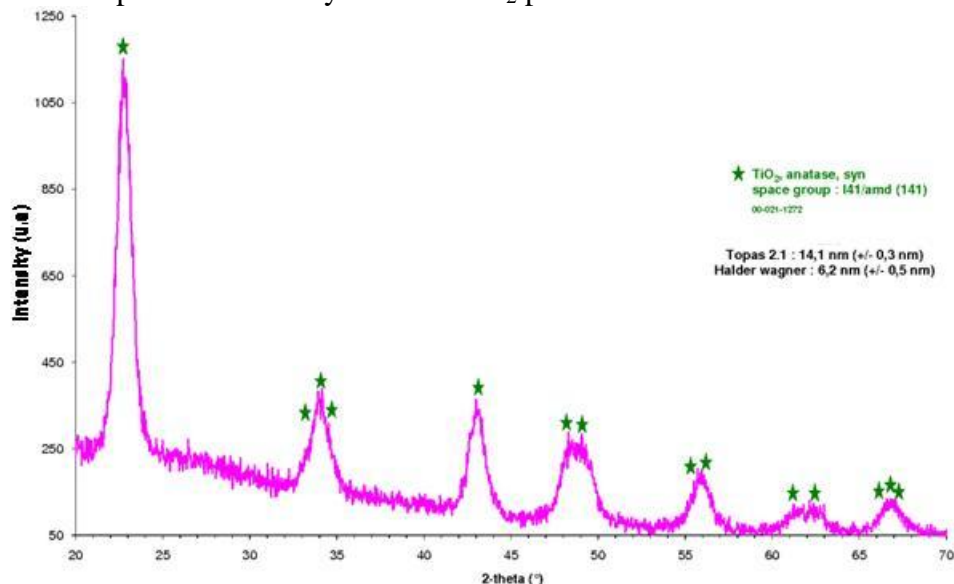

Figure 7: XRD pattern of the as-synthesized TiO$_2$ prepared in H$_2$O-supercritical conditions (673 K -30 MPa) from ALT ([(CH$_3$CH(O)CO$_2$NH$_4$)2Ti(OH)$_2$] = 0,104 mol.L^{-1}) as precursor.

The XRD peaks can be attributed to an anatase TiO$_2$ structure and the presence of larger XRD peaks indicates a small size of the TiO$_2$ particles. The Halder Wagner and Le Bail methods conclude to an average particles diameter of 6.2 ± 0.5 nm and 14.1 ± 0.3 nm respectively.
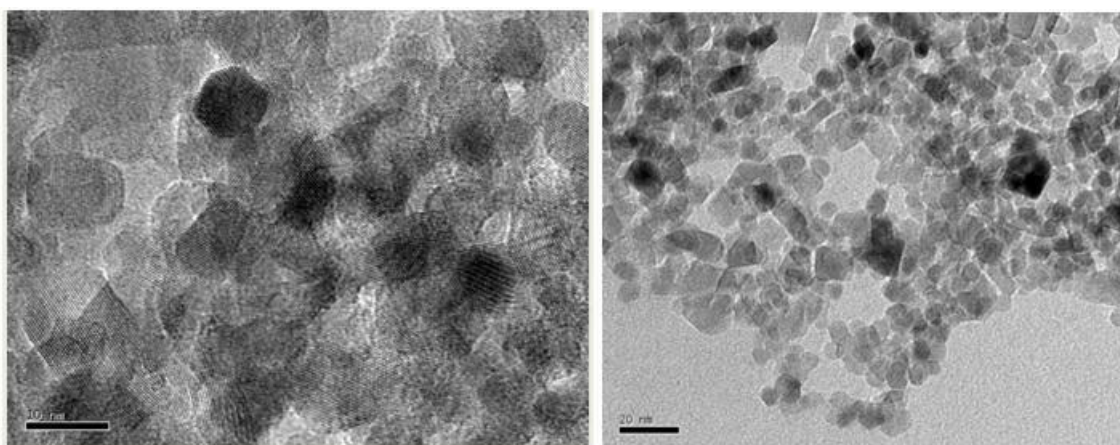

Figure 8: (HR)TEM images of the as-synthesized TiO$_2$ prepared in H$_2$O-supercritical conditions (673 K -30 MPa) from ALT ([(CH$_3$CH(O)CO$_2$NH$_4$)2Ti(OH)$_2$] = 0,104 mol.L^{-1}) as precursor.

The thermohydrolysis of ALT allowed the formation of pure crystalline anatase TiO_2 without any adjuvant (neither acidic nor alkali solution). Moreover, through a better control of the hydrolysis, a very narrow particle size distribution was clearly revealed by TEM. TEM and High-resolution transmission (HRTEM) images in Figure 8 show TiO_2 nanocrystallines with an average particle size of 8 ± 2 nm in agreement with the Halder Wagner method. Note that a very well homogeneous distribution of particle size and the HRTEM image clearly shows a single crystalline structure.

CONCLUSION

In summary, this work presents an environmental friendly and simple continuous process to rapidly synthesize very well crystallized nanoparticles under supercritical water (SCW) conditions. Indeed, well-crystallized ZnO, ZrO_2 and TiO_2 powders with very well homogeneous distribution of nanoparticle size (< 20 nm) have been successfully prepared with a production of around 10 to 15 g/h. Other synthesis of ZnO powder (data not shown) have been conducted with different coexisting cation from the basic salt (NaOH and LiOH) and coexisting anion from the zinc salt from zinc salt ($Zn(CH_3COO)_2$, $ZnSO_4$). The resulting materials suggested that the zinc species and environment are the crucial factors on the morphology and the size of nanoparticles. The understanding of size-dependent physical and chemical properties of these nanomaterials will be the following step of this work in order to control the size and the morphology of nanoparticles.

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