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► **To cite this version:**

Benoît Pichon, Yoshikazu Suzuki, Marie-Hélène Berger. Seeded growth of iron oxide onto titanate nanowires. *Funtai Oyobi Funmatsu Yakin* ==, 2009, 56, pp.640-644. 10.2497/jjspm.56.640 . hal-00794665

**HAL Id: hal-00794665**

**<https://minesparis-psl.hal.science/hal-00794665>**

Submitted on 22 Feb 2018

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## Paper

## Seeded Growth of Iron Oxide onto Titanate Nanowires

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Received July 9, 2009

## SYNOPSIS

The combination of different inorganic structures enables the preparation of multifunctional hybrid materials. The control on the formation of low dimensional nano-objects with specific morphologies and sizes is also a determinant factor to define specific properties. In this aim, the influence of the basic medium on hydrothermally prepared titanate nanowires was studied. The presence of Na<sup>+</sup> or K<sup>+</sup> counter ions dramatically influenced the preparation of nanoparticles or nanowires of TiO<sub>2</sub> and titanate. In a second time, hybrid materials were prepared by the impregnation of the titanate nanowires by a solution of iron chloride followed by the addition of NaOH to induce the formation of iron oxide onto titanate nanowires by the co-precipitation method.

## KEY WORDS

layered titanate, nanoparticles and nanowires, iron oxide, hydrothermal synthesis, impregnation

## 1 Introduction

In the past decades, the development of nanotechnologies resulted from a dramatic increase on the control of physical properties of materials. Low dimensionality objects with finely tailored composition and geometric parameters like specific morphology and size at the nanometer level have already been shown to be very suitable for the preparation of new and innovative technological devices<sup>1)</sup>. A new opening in the field of material chemistry becomes more and more the design of multifunctional nano-objects which enable the simultaneous combination of optoelectronics, magnetic and/or catalytic properties. Multi-component nanoheterostructures, which can be considered as hybrids and consist in the permanent assembly of at least two inorganic structures appeared to be very suitable materials<sup>2-4)</sup>. In addition, the enhancement of the structural and topological properties of such nano-objects allows improving their technological potential. The fine control of the joint material section also represents an important parameter because of exchange coupling or electronic communication effects. Metal oxides are very attractive to design new material because of their multiple properties in the solid state at the nanometer scale. Very well known strategies consist in the preparation of core-shell structures based on derivative iron oxide spinel structures and silica<sup>5-8)</sup> or in the decoration of nano-objects like spheres or tubes by metal oxide organic

clusters<sup>9)</sup>.

The association of semiconductor and magnetic heterostructures represents a high and interesting challenge because of the exploitation of technologically valuable multifunctional capabilities. Titanium oxide and iron oxide are very attractive because of the multiple possibilities to control their structure, size and morphology which define their physical properties. Titanate and titania one-dimensional (1D) materials represent very attractive materials for photo-electro conversion applications such as dye-sensitized solar cells (DSC)<sup>10)</sup> and photocatalysis<sup>11)</sup>. Magnetite (Fe<sub>3</sub>O<sub>4</sub>) is magnetic and conductive that makes it very suitable for application in magneto-transport applications<sup>12)</sup> and magnetic resonance imaging (MRI). The combination of both photo-catalysis and magnetic properties gives rise to a large panel of applications in the environmental and medicinal domains<sup>13-15)</sup>. The processing of such nano-objects into thin films enable many of those applications. Recently, we reported on the preparation of titanate<sup>16,17)</sup> and iron oxide<sup>18)</sup> nano-objects into thin films by the Layer by Layer and the Langmuir-Blodgett techniques.

In this paper, we report on the growth of iron oxide on titanate nanowires. A preliminary step consists in the impregnation of titanate nanowires using an aqueous solution of iron (II) and (III) chloride. The iron-coated

nanowires were immersed in a basic medium to initiate the growth of iron oxide by the co-precipitation method.

## 2 Experimental Procedure

### 2.1 Synthesis of TiO<sub>2</sub>-derived nanoparticles and nanowires by hydrothermal synthesis

First of all, we present the syntheses of TiO<sub>2</sub>-derived nano-objects prepared by an hydrothermal synthesis which was adapted from our previous reports<sup>19,20</sup>. Nanoparticles and nanowires were prepared from a commercial anatase TiO<sub>2</sub> powder (ST-01, Ishihara Sangyo Ltd.). 10 M alkali solutions were prepared by dissolving NaOH (20 g) for nanoparticles and KOH (28 g) for nanowires in 44 mL Milli-Q water and inserted in Teflon-lined autoclaves of 50 mL. The ST-01 powder (2 g) was added to those solutions and stirred for 5 min for dissolution. The autoclaves were both heated at 120 °C under static conditions for 48 h. After cooling to room temperature, both suspensions were washed by water to proceed to the exchange of Na<sup>+</sup> and K<sup>+</sup> ions. First of all, the solution with diluted around ten times with water to reduce the pH and reached around 1 M solutions. The alkali solutions were neutralized by the addition of 1 L of a 2M HCl solutions. The white powder was then collected by using a glass filter. It was dispersed in 1 L of a 1 M HCl solution and stirred for 1 h and filtered again. This procedure was conducted twice to remove Na<sup>+</sup> and K<sup>+</sup> ions. Wet powders were collected after filtration to prevent the aggregation of those nanoparticles and nanowires.

### 2.2 Impregnation and synthesis of iron oxide in TiO<sub>2</sub>-derived nanowires

Nanowires (200 mg) were dispersed in a 40 mL of an aqueous solution of FeCl<sub>3</sub>·9H<sub>2</sub>O (860 mg, 2.65 mmol) and FeCl<sub>2</sub>·4H<sub>2</sub>O (160 mg, 0.804 mmol) and stirred for 17 h at room temperature under N<sub>2</sub> bubbling to prevent the oxidation of Fe<sup>2+</sup> ions. The as obtained paste-like mixture was then centrifuged and the precipitate was dispersed in a 20 mL of a 5N NH<sub>4</sub>OH solution and stirred for 3 h at room temperature. The mixture was then heated at 95 °C for 150 min under static conditions. The nanowires were washed three times with water under centrifugation. The powder was finally dried in air.

### 2.3 Characterization

The structure of both nanowires and nanoparticles was studied using a D5000 Siemens diffractometer (Cu-K $\alpha$  radiation, operated at 40 kV and 30 mA). The pristine and coated TiO<sub>2</sub>-derived compounds were characterized by high resolution transmission electron microscopy (HRTEM) using JEOL JEM-2010F and FEI Tecnai F20ST microscopes

operating both at 200 kV. The latter was also used to study the chemical composition of the samples by electron-energy-loss spectroscopy (EELS) and to record Energy Filtered-TEM (EF-TEM images).

## 3 Results and discussion

### 3.1 Influence of the experimental parameters on the morphology of the TiO<sub>2</sub> nano-objects

The growth of TiO<sub>2</sub>-derived nano-objects depends mainly on the experimental conditions. Transmission electronic microscopy (TEM) shows a dramatic influence of the base and the counter ion, Na<sup>+</sup> or K<sup>+</sup> (Fig. 1). In the current experimental condition, NaOH led to the preparation for nanoparticles which are difficult to observe separately because of their strong aggregation upon drying (Fig. 1 (a)). Their shape is not well-defined and they have very high size dispersion from 5 to 35 nm. In contrast, KOH lead to nanowires which also tend to aggregate but display lower size dispersion, especially according to their diameter, from 10 to 20 nm and a length of about several hundreds of nanometers (Fig. 1 (b)). Fig. 1 (c) is an image at higher magnification which suggests the nanowires to result from the assemblies of nanoparticles and so, to be polycrystalline. The high resolution image in Fig. 1 (d) demonstrates the nanowires are highly structured and confirm they are polycrystalline. We can observe an interspacing distance close to 3.52 Å between *hkl* planes, which seemingly corresponds to the (101) planes of anatase, according to the JCPDS file No. 21-1272.

The structure of both nanoparticles and nanowires was investigated more precisely by X-ray diffraction (Fig. 2). Broad peaks were observed for both samples but do not refer to the same crystal structure. For the nanoparticles (Fig. 2 (a)), the diffractogram displays peaks which can all be indexed to anatase according to the JCPDS file No. 21-1272. However, for nanowires (Fig. 2 (b)), peaks can be tentatively indexed to one of layered hydrogen titanate structure approximated as H<sub>2</sub>Ti<sub>2</sub>O<sub>5</sub>·H<sub>2</sub>O according to the JCPDS No. 47-0124 (Note that another titanate, such as H<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>·xH<sub>2</sub>O is also a candidate<sup>19</sup>). In addition, for nanoparticles which can be assimilated to spheres, the full width at half maximum corresponds to their range of size deduced from TEM measurements. One peak at 2 $\theta$  = 31 ° still remains undetermined and may be corresponds to some impurities. On the other hand, the XRD pattern of nanowires displays fewer peaks and large humps (15-35, 40-45 and 56-62 degrees) which correspond to some amorphous compounds.

### 3.2 Growth of iron oxide from TiO<sub>2</sub>-derived nanowires



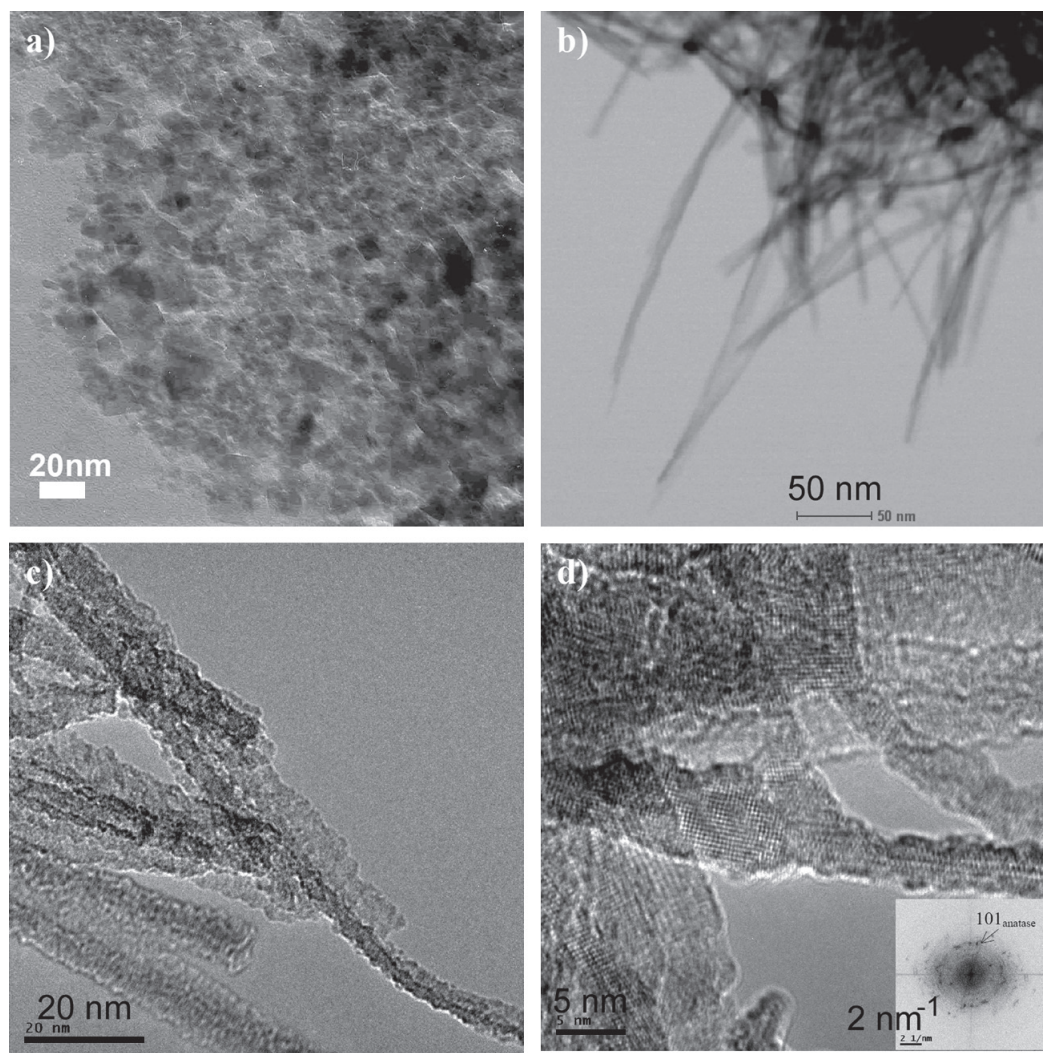


Fig.1 TEM analysis of a) nanoparticles obtained in the presence of NaOH and b, c, d) nanowires obtained in the presence of KOH. d) is a high resolution image of the nanowires and associated Fast Fourier Transform. Most of the intense spots are located on a circles of  $1/0.35 \text{ nm}^{-1}$  in diameter that originates from (101) planes of anatase.

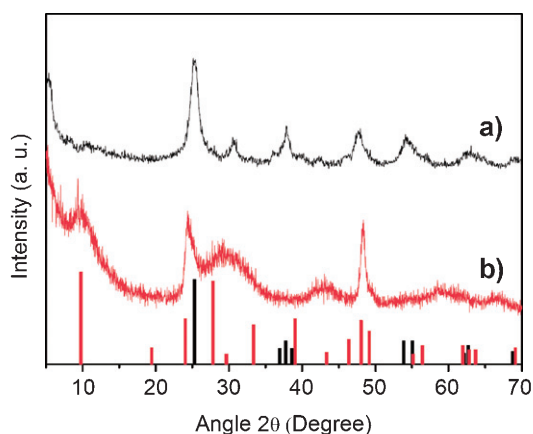


Fig.2 X-ray diffraction patterns of  $\text{TiO}_2$ -derived nanomaterials: (a) nanoparticles and (b) nanowires. Bottom bars are references of anatase (black bars) and a layered titanate  $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$  (red bars). (Peaks around 5 degree is attributed to the incident beam effect of diffractometer).

The formation of iron oxide onto the nanowires was investigated by high-resolution TEM (Fig. 3) and Energy Filtered TEM (EF-TEM, Fig. 4) using EELS peaks (Fig. 5). From a high-resolution TEM figure (Fig. 3 (a)), nanowires with a particle of  $\sim 10 \text{ nm}$  in diameter were observed. The HR-TEM and its Fast Fourier Transform (FFT) showed the particle has a lattice fringe of  $\sim 2.1 \text{ \AA}$ , which can be attributable to the magnetite 400 reflection. The inverse FFT of Fig. 3 (b) clearly demonstrated the particle at the center of image consisted of the material with  $\sim 2.1 \text{ \AA}$  lattice fringe.

Although some relatively-larger iron-oxide nanoparticles ( $10\text{--}20 \text{ nm}$ ) were separately found (Fig. 4 (a)), iron signals spread on whole nanowires (Fig. 4 (c)). This EF-TEM image implies iron-oxide nanoparticles were homogeneously coated on titanate nanowires.

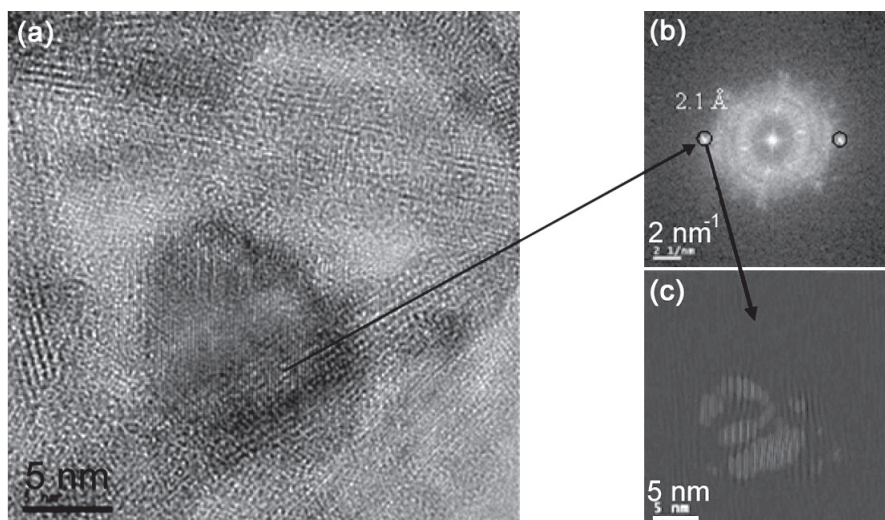


Fig.3 Titanate nanowires with iron oxide particles: (a) High-resolution TEM image. (b) Fast Fourier Transform (FFT) of Fig. 3 (a) indicating the spot of 2.1 Å (attributable to the magnetite 400 reflection). (c) Inverse FFT of Fig. 3 (b), which demonstrates the particle at the center of image (of ~ 10 nm in diameter) might be composed of magnetite.

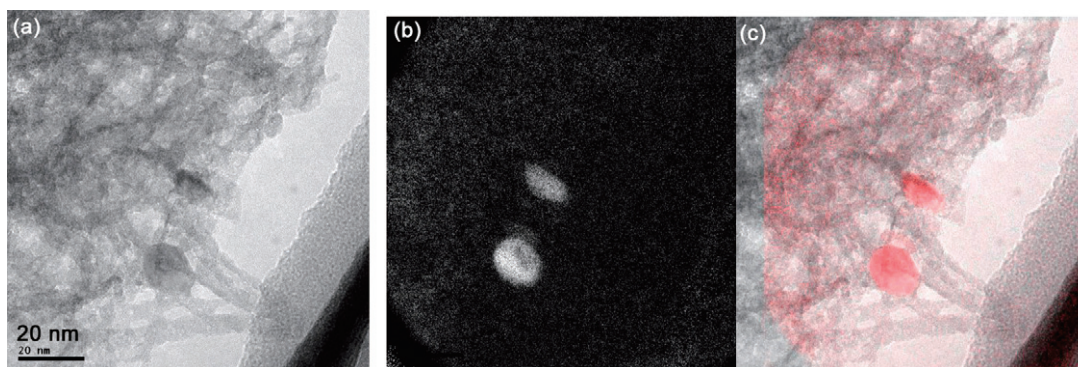


Fig.4 EF-TEM images of the nanowires. (a) Zero Loss filtered image, (b) EF-TEM image on the L3L2 absorption edge of Fe, and (c) superimposed image of (a) + (b).

#### 4 Conclusions

The basic medium, i.e. the counter ion dramatically influence the formation of nanoparticles and nanowires of titanium oxide upon the hydrothermal synthesis. The purity and the crystallinity of the compounds were also affected. However, iron chloride can be grafted onto the surface of TiO<sub>2</sub> nanowires and co-precipitated in basic medium to give rise to the formation of iron oxide clusters. Work is in progress to precise the formation and to identify the crystalline structure of such cluster onto TiO<sub>2</sub> nano-objects.

#### Acknowledgements

This study was supported by the Collaboration Agreement between Strasbourg University and Kyoto University. A part of this work was also financially supported by Grant-in-Aid for Science Research No. 19685020 For Young Scientist: Category A.

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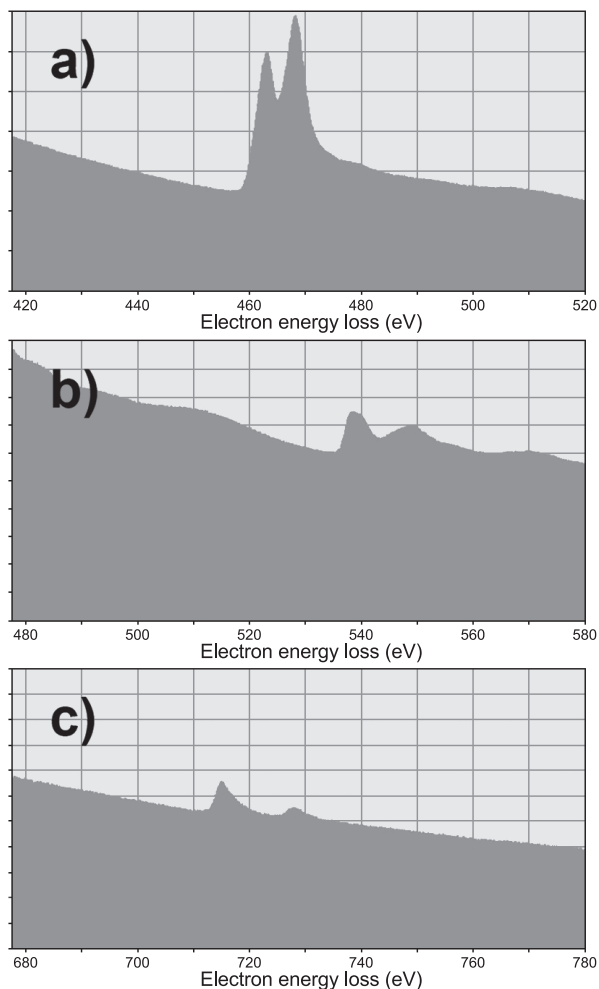


Fig.5 EELS spectra of a) Ti L3L2, b) O K, and c) Fe L3L2 absorption edges.

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