Electronic Supplementary Material (ESI) for Dalton Transactions. This journal is © The Royal Society of Chemistry 2014

SUPPORTING INFORMATION

SI 1: Different synthesis ways of titanate nanoribbons

There are many ways to synthesize titanium oxides nanoribbons. The general term "titanium oxide" is used to define simple and mixed titanium oxides. It should be remembered that mixed titanium oxide, often called titanate, are composed of titanium ions involved into a polyhedron of coordination with the formation of iono-covalent bonds with oxygen ions. This assembly plays the part of anion which combines with another cation. In 2002, titanate nanoribbons were synthesized for the first time by a hydrothermal treatment of a pulverulent TiO₂ precursor in a strongly basic medium [31]. An aqueous solution of NaOH with adjustable concentration and TiO₂ particles were introduced in an autoclave in which they underwent a thermal treatment between 180 and 240°C for 24 or 48 hours. This approach enables to get titanate nanoribbons with a width varying from 30 to 500 nm and a length of several tens micrometers or so. In 2004, a simple and convenient procedure for the synthesis of titanium oxide nanowires was demonstrated by Jiang et al. [33]. In this work, a tetraalkoxyltitanium solution, $Ti(OR)_4$ (with R = - C_2H_5 , -iso- C_3H_7 , or-n- C_4H_9), was added to ethylene glycol and heated in an oil bath to 170°C for 2 hours under vigorous stirring and nitrogen flow. During the reaction, the alkoxide was transformed into a glycolate complex chain that subsequently crystallized into uniform nanowires with a width of 50 nm and a length up to 30 µm. These nanostructures were named nanowires. Nevertheless, the characterizations didn't enable to confirm the cylinder-shape of nanoparticles and their dimensions better match the nanoribbons ones [25]. It is likely that the synthesis led in fact to the formation of nanoribbons. The same year, Wei et al. [34] managed to develop titanates nanowires from Na2Ti3O7 titanate layers in an HCl aqueous solution heated at 170°C for 7 days in an autoclave. This reaction, based on the cationic exchange of Na⁺ by H⁺, led to the formation of nanowires more than one hundred micrometers long, having width lying between 20 and 100 nm and with a chemical composition close to H₂Ti₃O₇. Once again, although the author used the word "nanowires", the dimensions and the morphology of the nanoparticles correspond to those of nanoribbons. More recently Yu et al. [35] used an electrospinning process to synthesize titanium oxide nanoribbons whose width was about 450 nm and whose length reached several tens micrometers or so. Using this method, highly ordered nanoribbons arrays were obtained when applying the appropriate voltage, environmental relative humidity and spinneret geometry.

SI 2: Different TiO₂ precursors used for the synthesis of titanate nanoribbons



Figure 11: TEM images of different TiO_2 precursors used to synthesize titanate nanoribbons: (a) 5-10 nm anatase, (b) 10-15 nm anatase, (c) P25 (anatase + rutile) and (d) rutile.

	Ø TEM (average size ± standard deviation)	Ø Raman (± 10%)	Ø XRD (± 5%)	S BET (± 5%)	
Anatase TT350°C	7 ± 1 nm	8 nm	7,3 nm	253 m ² .g ⁻¹	
Anatase TT470°C	$13 \pm 2 \text{ nm}$	11 nm	13,1 nm	72 m ² .g ⁻¹	
P25	$25 \pm 4 \text{ nm}$	26 nm	26 nm	25 m ² .g ⁻¹	
Rutile	$175 \pm 27 \text{ nm}$	-	175 nm	6,5 m ² .g ⁻¹	

Table 2: Lattice structure, crystallite size and specific surface area of the TiO_2 precursors used for the synthesis of titanate nanoribbons. The Raman size is determined using the phonon confinement model and XRD size by Halder and Wagner method (profile fitting program Fityk [58]).

SI 3: Curve fitting of photoemission peaks obtained by XPS analysis of titanate nanoribbons

Full widths at half-maximum were fixed for the fitting procedure: 1.7 eV for $Ti^{4+} 2p_{3/2}$ and 2.4 eV for $Ti^{4+} 2p_{1/2}$, 1.8 eV for O^{2-} , 2 eV for OH⁻, and 2.5 eV for H₂O component of O1s peak. The contribution of sodium Auger peak was not taken into account in the calculation of concentration components. This explains the small gap between the whole contribution of oxygen and the concentration sum of its components. The carbon 1s peak (284.5 eV) allows correction of charge effects. FWHM of its components were fixed at 1.8 eV for C-C and C-H bonds, 1.9 eV for C-O bonds and 2 eV for C=O and O-C=O functions. According to measurements performed on standards, the concentration error is lower than 5%. This error is lower than 2% when repeating the measurements. From this point of view, the comparison between samples is very accurate.



Figure 12: Example of curve fitting of (a) oxygen 1s level and (b) carbon 1s level of titanate nanoribbons synthesized by hydrothermal treatment (440 mg TiO₂, 110 mL soda solution 10M, ultrasound treatment (30 minutes, 375 Watt), 180°C, 20 hours, 7 bar, 150 rpm) from P25 TiO₂ precursor.

SI 4: Curve fitting of the first characteristic peaks of the XRD patterns of the nanoribbons synthesized by hydrothermal treatment for different TiO₂ precursors



Figure 13: Fit of the first characteristic peaks of the XRD patterns of the nanoribbons synthesized by hydrothermal treatment (440 mg TiO₂, 110 mL soda solution 10M, ultrasound treatment (30 minutes, 375 Watt), 180°C, 20 hours, 7 bar, 150 rpm) for different TiO₂ precursors: 5-10 nm anatase, 10-15 nm anatase, P25 and rutile, according to pseudo-Voigt functions.

SI 5: Undesired nanoparticles formed during the synthesis of titanate nanoribbons by hydrothermal treatment



Figure 14: (a-b) TEM images and (c) SAD picture of undesired nanoparticles formed during the synthesis of titanate nanoribbons by hydrothermal treatment (440 mg P25 TiO₂, 110 mL soda solution 10M, ultrasound treatment (30 minutes, 375 Watt), 180° C, 20 hours, 7 bar, 150 rpm).

SI 6: Formation of a super-structure



Figure 15: Small angle part of the XRD patterns of the nanoribbons synthesized by hydrothermal treatment (440 mg TiO₂, 110 mL soda solution 10M, ultrasound treatment (30 minutes, 375 Watt), 180° C, 20 hours, 7 bar, 150 rpm) for 5-10 nm anatase TiO₂ precursor.

Peak position (nm)	2 nd order harmonic (nm)	3 rd order harmonic (nm)	4 th order harmonic (nm)	5 th order harmonic (nm)	
3.31	1.57	1.05	0.79	0.66 🗖	
1.86	0.95	0.62 🔺	0.48	0.38	
0.94	0.47 ★	0.31	0.23	0.19	
0.91	0.45 •	0.30	0.22	0.18	
0.66 🗕	0.33	0.22	0.17	0.13	
0.62	0.31	0.21	0.16	0.12	
0.47 ★	0.23	0.16	0.12	0.09	
0.45 •	0.22	0.15	0.11	0.09	

 Table 3: Summary table of the different peaks and their second to fifth order harmonics.

SI	7:	Che	emic	al	compositio	on	of	tita	nate	e nanoril	obons
syn	thesi	zed	by	hy	drothermal	tr	eatm	ient	of	different	TiO ₂
pre	curse	ors									

	Anatase 5-10 nm	Anatase 10-15 nm	P25 26 nm	Rutile 178 nm	
Carbon (± 1%)	23	13	14	16	
Sodium (± 1%)	6	6	5	6	
Oxygen (± 1%)	57	50	48	50	
Titanium (± 1%)	14	31	33	27	
Na ⁺ /Ti ⁴⁺	0.43	0.19	0.15	0.22	
O ²⁻ /Ti ⁴⁺	2.71	1.1	1	1.07	
C-C and C-H (± 10%)	13	7	8	7	
C-O (± 10%)	8	4	4	6	
C=O and O-C=O (± 10%)	2	2	2	3	
O ²⁻ (± 10%)	38	34	33	29	
OH ⁻ and C=O (± 10%)	10	8	9	11	
H ₂ O and C-O (± 10%)	6	5	4	7	

Table 4: XPS atomic chemical species ratio of nanoribbons synthesized by hydrothermal treatment (440 mg TiO₂, 110 mL soda solution 10M, ultrasound treatment (30 minutes, 375 Watt), 180 °C, 20 hours, 7 bar, 150 rpm) from different TiO₂ precursors: 5-10 nm anatase, 10-15 nm anatase, P25 and rutile.

SI 8: Formation of nanotubes during hydrothermal treatment



Figure 16: TEM pictures of (a) nanotubes formed after 4 hours of reaction and (b) nanotube fragments formed after 8 hours of reaction.

SI 9: Titanate nanoribbons after ultrasound treatment



Figure 17: TEM pictures of (a) dislocated and (b) torn nanoribbons after ultrasound stick treatment (1 min, 750W)