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Fast preparation of highly ordered nonsiliceous mesoporous materials *via* mixed inorganic precursors†

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Employing metal alkoxide as the main inorganic precursor and anhydrous metal chloride as the pH 'adjustor' and hydrolysis-condensation 'controller', very fast preparation of ordered nonsiliceous mesoporous materials has been demonstrated.

Nonsiliceous mesoporous materials usually show special electronic, magnetic and catalytic properties compared with pure siliceous counterparts. For example, titania has extraordinary photocatalytic properties and has attracted much attention and contribution.[1–10] Mesoporous titania, up to now, has been prepared through various methods.[1–5,8,9] The most striking example was reported by Yang *et. al.*[2] However, this synthesis of mesoporous titania always meets several problems which can not be neglected, *e. g.* the synthetic period is long (always more than one week) and the structural regularity is always less ordered which may be caused by the high acidity of the mother solution. Sanchez[3] *et al.* addressed these problems by ammonia post-treatment. Here we present for the first time a very effective, fast and easy approach to synthesize highly ordered, pore size tunable mesoporous titania of both hexagonal and cubic mesophases *via* mixed inorganic precursors.This methodology is also suitable for the preparation of ordered mesoporous zirconia and alumina and is also demonstrated in this work.

For the preparation of highly ordered mesoporous titania, the mixed inorganic precursors were titanium alkoxide (titanium ethoxide, titanium isopropoxide or titanium n-butoxide) and titanium chloride ($TiCl_4$). In a typical synthesis, 1 g of Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, M_{av} = 5800, Aldrich) or 1.2 g of Pluronic F108 ($EO_{132}PO_{60}EO_{132}$, M_{av} = 14600, Aldrich) was dissolved in 20 g of ethanol or tetrahydrofuran (THF), then 0.6 g of $TiCl_4$ and 2.5 g of titanium isopropoxide were added in that order to the solution and the mixture was further stirred for 2 h. The pH value of the mother solution was *ca.* 1.2. Then the mother solution was transferred to petri-dishes and underwent solvent evaporation. Alternatively, mesoporous titania film can be prepared by dip-coating of the mother solution. After gellation at 40 °C for only 1 day, the template was removed by microwave assisted extraction (ESI†) or calcination at 350 °C in air.

X-Ray diffraction patterns of mesoporous titania prepared from the mixed inorganic precursors method and by using P123 and F108 as the templates are shown in Fig. 1. The as-made products (templated by P123) show several well-resolved peaks, and combined with the results from transmission electron microscopy (TEM) (see below), these peaks can be indexed to (100), (110) and (200) Bragg reflections of *p6m* space group. After template removal by microwave extraction, the structural regularity declined slightly. After calcination of those samples, the d_{100} value decreased, and this is due to structural shrinkage. F108 is also efficient in the assembly of mesoporous titania. Though the XRD pattern (Fig.1 inset) is less resolved, combined with the TEM images, we conclude that F108 can direct 3D caged mesostructures (possible *Im3m* space group).

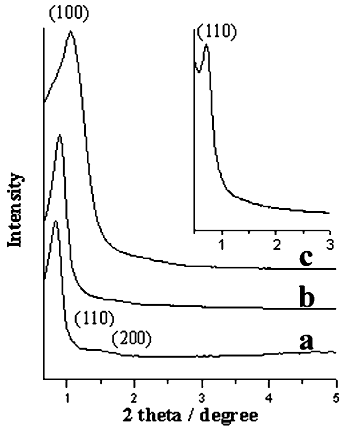

Fig. 1 XRD patterns of (a) as-made, (b) microwave extracted, (c) calcined mesoporous titania templated by P123 and calcined sample templated by F108 (inset).

FTIR curves show no distinct absorption peaks attributed to C–H stretching and bending modes, suggesting that the bulk of the templates have been removed by calcination and microwave extraction.

Fig. 2 shows the TEM images of calcined mesoporous titania templated by P123 and F108 (inset). The images show highly ordered hexagonal and rectangular (inset) patterns in large domains, typical of two dimensional hexagonal and 3D cubic mesostructure. The electron diffraction pattern (camera length, 20 cm) of the calcined samples show several diffraction rings, suggestive of semi-crystallized wall structures. Moreover, energy dispersive X-ray spectroscopy (EDX) measurements reveal no detectable chloride ions which is indicative of complete elimination of Cl^- upon calcination.

N_2 adsorption–desorption isotherm curves of the calcined mesoporous titania templated by P123 and F108 feature a steep

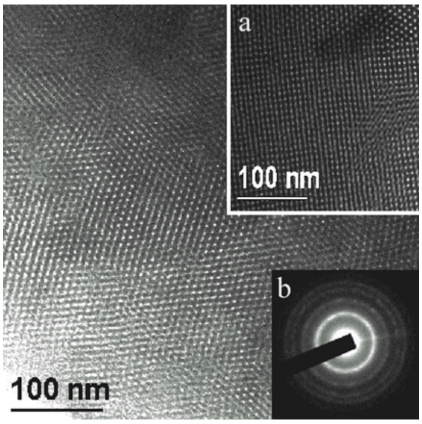

Fig. 2 TEM images of calcined mesoporous titania viewed from [110] plane (template, P123) and inset a, [110] plane (template, F108). Inset b shows the electron diffraction pattern (camera length, 20 cm) of the same hexagonal area.

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† Electronic supplementary information (ESI) available: microwave extraction, N_2 sorption curves and UV–VIS spectra. See http://www.rsc.org/suppdata/cc/b2/b205006d/

Table 1 Physicochemical properties of mesoporous titania synthesized *via* mixed inorganic precursors

Sample		Inorganic precursors	Surfactant	BET surface areas ($m^2\ g^{-1}$)		Pore volumes[a] ($cm^3\ g^{-1}$)	Pore size[a] (nm)	Gelation time[b]
				Extracted	Calcined			
Titania	T1	$Ti(OC_3H_7)_4$, $TiCl_4$	P123	178	223	0.28	4.1	1 d
	T2	$Ti(OC_3H_7)_4$, $TiCl_4$	B50–6600	148	167	0.26	5.5	1 d
	T3	$Ti(OC_3H_7)_4$, $TiCl_4$	Brij97	204	275	0.21	2.6	1 d
	T4	$Ti(OC_3H_7)_4$, $TiCl_4$	CTAB		214	0.14	1.9	1 d
	T5	$Ti(OC_2H_5)_4$, $TiCl_4$	P123	171	236	0.27	4.0	1 d
	T6	$Ti(OC_4H_9)_4$, $TiCl_4$	P123	139	174	0.21	4.1	2 d
	T7	$Ti(OC_3H_7)_4$, $TiCl_4$	F108	152	205	0.36	6.3	1 d
Zirconia	Z1	$Zr(OC_3H_7)_4$, $ZrCl_4$	P123	141	163	0.21	4.2	5 h
Alumina	A1	$Al(OC_4H_9)_3$, $AlCl_3$	P123	156	208	0.59	10.6	2 h

[a] The data of calcined samples (BJH model). [b] The gelation times for mesoporous titania, zirconia and alumina according to Ref. 2 are 7 d and 7 d, respectively.

rise in adsorption at 0.5 ~ 0.7 relative pressure (P/P_o) region (ESI†) and the pore size distributions are rather narrow and at the mean values of 4.1 and 6.3 nm (calculated by BJH model), respectively. The surface area and the total pore volume are 150–250 $m^2\ g^{-1}$ and 0.20–0.40 $cm^3\ g^{-1}$, respectively, comparable to the results reported by Yang *et al.*[2] The pore size of the one dimensional channel can be tuned by using various amphiphiles, namely B50-6600, Brij 97 and CTAB (see Table 1), and that of three dimensional cavity can be tuned by using F 98, Brij 700 and Brij 35 (not shown here).

By comparing with synthesis from a single titanium source, namely $TiCl_4$,[2] the reason for the ease of fast preparation of highly ordered mesoporous titania which is demonstrated in this work can be elucidated. The dissolution of $TiCl_4$ in EtOH is violently exothermic and generates a large amount of HCl which causes the solution to become highly acidic (the pH value is far below zero), thus the preparation of mesoporous titania bulk materials through rapid solvent evaporation strategy is problematic: (a) the gellation process is restrained so that the synthetic period is long, (b) the elimination of the chloride ions is incomplete even upon calcination,[2,3] (c) the 'crown-ether–titanium oligomers' complexation[2] may be weak (probably influenced by high acidity), namely weaker inorganic–organic interactions, thus causing poor structural order. In our work, with titanium alkoxide used as the main titanium source, and titanium tetrachloride serving as the pH 'adjustor' and hydrolysis–condensation 'controller', the above problems can be overcomed since the pH value of the mother solution is significantly and *controllably* reduced (highly ordered mesostructure formed when the pH value is 1–2). Compared with single $TiCl_4$, the Ti–O–Ti bridges may partially result from the condensation between Ti–Cl and Ti–OR formations (see Scheme 1), The added metal alkoxide serves as extra oxygen donors, therefore the cross-linkage of inorganic framework may be easier and better in this case. The better cross-linkage can also be reflected by the UV–VIS spectra (see ESI†). Both as-made film and mother liquor prepared from single $TiCl_4$ have higher onset values (nm) compared with those from mixed titanium precursors. We postulate that the titanium species in both mother liquor and as-made film can be formulated as $TiO_{2-x-y}Cl_{2x}(OR)_{2y}$ oligomers, and since chlorine has lower metallic coordination spheres compared with oxygen ligands,[3] thus the lower content of Cl, the higher value of $(2-x-y)$, namely the higher degree of crosslinkage. The differences of onset values are direct results of the differences of the oligomer compositions (the charge transfer is influenced by the coordination micro-environments). In sum, The whole preparation process is in a more *controllable* and *adjustable* manner, and highly ordered mesophase is easily formed.

$$\equiv M-Cl \;+\; \equiv M-O-R \longrightarrow \equiv M-O-M\equiv \;+\; R-Cl$$

Scheme 1 Possible condensation reaction of mixed inorganic precursors under nonaqueous condition.

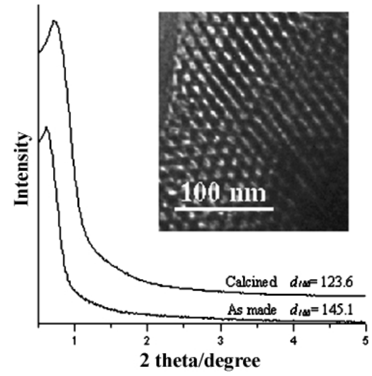

Fig. 3 XRD patterns and TEM image of mesoporous alumina prepared from $AlCl_3$ and $Al(OC_4H_9)_3$ blends in THF media.

This methodology can also be generally applied in the syntheses of ordered mesoporous zirconia and alumina. The XRD patterns and TEM image show the efficient assembly of mesoporous alumina (sample A1, Fig. 3). Other mesoporous transition metal oxide may be prepared in the similar way as long as proper metal chloride and metal alkoxide are obtainable.

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