## Self-supported helical oxide arrays templated by pore-swollen chiral mesoporous silica<sup>†</sup>

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## Self-supported helical architectures of $Ia\bar{3}d$ In<sub>2</sub>O<sub>3</sub> and $Fd\bar{3}m$ Co<sub>3</sub>O<sub>4</sub> are fabricated for the first time using the pore-swollen chiral silica as template.

Size- and shape-controlled nanostructural metal oxides have continuously captured research interests in the past few years due to their unique properties and potential applications in 'nanodevices'.1 However, to fabricate ordered 3D hierarchically structured metal oxides,<sup>2</sup> which might exhibit special advantages in adsorption, separation, and heterogeneous catalysis, is still a challenging mission. Among the diverse synthetic themes, significant progress has been achieved with the nanocasting route,3 which produces morphologycontrolled and stable nanostructured integrity more readily than traditional soft-templating approach. Nanoparticles, nanowires/rods, and nanostructured networks of metal oxides could be selectively formed in the void of ordered porous carbon and silica materials.<sup>4</sup> The mesoporous silica with helical pores and helical morphology, discovered recently,<sup>5</sup> provides the possibilities of producing metal oxides with unique 3D chiral ordered architecture by the nanocasting method. Thus in this work, for the first time, chiral mesoporous silica with tuned pore sizes is synthesized. Selfsupported chiral architectures of  $Ia\bar{3}d$  In<sub>2</sub>O<sub>3</sub> and  $Fd\bar{3}m$ Co<sub>3</sub>O<sub>4</sub> are then fabricated using the enlarged channels of chiral mesoporous silica as the template.

The chiral mesoporous silica is synthesized following a typical procedure previously reported<sup>5b</sup> with cetyltrimethylammonium bromide (CTAB) as the template, sodium silicate as the silica precursor, and ethyl acetate as the pH adjusting reagent. Using trimethylbenzene (TMB) as the pore-swelling reagent,<sup>6</sup> the mesoporous silicas with pore sizes enlarged from 2.0 to 3.0 and even 4.3 nm (Fig. 1A) are prepared. The XRD reflections (Fig. 1A, inset) could all be indexed as 2D hexagonal p6mm symmetry. A twisted hexagonal rod-like morphology with an outer diameter of ca. 140-160 nm and a length of ca. 600 nm is observed in the FESEM image for the chiral mesoporous silica (Fig. 1B, Fig. S1 and S2<sup>+</sup>). Two kinds of chiral channels can be found in the mesoporous silica samples (Fig. S1<sup>†</sup>). But the left-/right-handed ratio proves to be about 1:1 by counting the characteristic morphologies of 500 randomly chosen crystallites in the FESEM images.



**Fig. 1** (A) Pore size distribution (inset: XRD patterns) of helical silica with a pore size of 4.3 (a), 3.0 (b), and 2.0 nm (c); (B) FESEM image (inset: hexagonal cross-section); (C) HRTEM image; and (D) magnification of selected region in (C) of helical silica.

The HRTEM micrographs (Fig. 1C and 1D and Fig. S2<sup>†</sup>) show clear and well-ordered fringes corresponding to the (100) plane equidistantly along the axis of the nanobar, characteristic of chiral channels.

After the CTAB template in the mesoporous channels is effectively removed (Fig. S3†) by a microwave digestion<sup>7</sup> method, indium or cobalt nitrate is used as the precursor to impregnate the mesoporous silica in ethanol. Then the nitrates are transformed to oxides by calcination. The pore volume (Table 1) of the mesoporous silica with pore sizes of 4.3, 3.0, and 2.0 nm is estimated to decrease by 66, 57, and 45% due to the In<sub>2</sub>O<sub>3</sub> encapsulation, and by 76, 58, and 33% because of the Co<sub>3</sub>O<sub>4</sub> encapsulation. This means that the pore volume

 Table 1
 Textural properties of metal oxide/silica composites

Sample	Pore size					
	4.3 nm		3.0 nm		2.0 nm	
	$S_{\rm BET}{}^a$	$V_{\rm p}^{\ b}$	$S_{\rm BET}{}^a$	$V_{\rm p}^{\ b}$	$S_{\rm BET}{}^a$	$V_{\rm p}^{\ b}$
Silica	1100	1.15	1181	0.98	775	0.49
In <sub>2</sub> O <sub>3</sub> /silica	389	0.39	370	0.42	209	0.27
Co <sub>3</sub> O <sub>4</sub> /silica	273	0.27	364	0.41	234	0.33
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<sup>*a*</sup> BET specific surface area,  $m^2 g^{-1}$ . <sup>*b*</sup> Total pore volume,  $cm^3 g^{-1}$ .

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occupied by the metal oxides increases obviously with enlarged pore size. The higher oxide loading is proposed to benefit from the facile penetration of metal nitrates as precursors into larger channels of helical mesoporous silica. The TEM image of the  $In_2O_3$ /silica hybrid material (Fig. S4(a)†) illuminates the wellpacked  $In_2O_3$  (dark black) formed abundantly and homogeneously inside the 4.3 nm chiral channels. Due to high oxide loadings, a sharp decrease in the reflection intensity of the (100) plane is observed for both  $In_2O_3$ /silica and  $Co_3O_4$ /silica composites (Fig. S4(b)†), which is attributed to the decrease in the contrast between the walls and the pores as proposed previously.<sup>8</sup>

Etching the silica with an aqueous solution of NaOH gives  $Ia\bar{3}d$  In<sub>2</sub>O<sub>3</sub> (JCPDS No. 44-1087) and  $Fd\bar{3}m$  Co<sub>3</sub>O<sub>4</sub> (JCPDS No. 42-1467) as illustrated by the XRD patterns in Fig. 2. The



**Fig. 2** XRD patterns and HRTEM images of  $In_2O_3$  (left) and  $Co_3O_4$  (right) prepared in mesoporous channels of (a) 2.0, (b) 3.0, and (c) 4.3 nm.



**Fig. 3** Schematic diagram for the formation of self-supported chiral metal oxides: (a) chiral mesoporous silica with a pore size of 4.3 nm; (b) metal oxide/silica composites; (c) helical mesostructured metal oxides with self-supported architecture after etching the silica; and (d) the top view of the helical mesostructure consisting of 55 nanowires along the axis.

morphologies of both In<sub>2</sub>O<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub> rely highly upon the pore diameter of the helical mesoporous silica (Fig. 2). For the metal oxides templated by the silica with a pore size of 2.0 nm, scattered nanoparticles are mainly observed. When the pore size is enlarged to 3.0 nm, non-continuous oxide nanowires are formed, arrayed to a topical ordered structure. Swelling the pore size to 4.3 nm, continuous nanowires are fabricated into self-supported helical bundles for both In<sub>2</sub>O<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub>. The diameters of continuous nanowires are 3.6-4.0 nm, well in accord with the pore diameter of their silica template. The outer diameters of self-supported helical bundles of nanowires are estimated at around 120 nm for In<sub>2</sub>O<sub>3</sub> and 110 nm for Co<sub>3</sub>O<sub>4</sub>, consistent with the outer diameter scale of the silica rods (Fig. 1C). The fringes (marked by arrows), which are also observed in the silica template, appear along the axis of the nanorod. The nanocasted metal oxides have thus substantially reproduced the morphology of the silica template. The adequate filling of template pores with oxides ensures the formation of self-supported helical arrays. The formation mechanism of the self-supported helical framework is simulated in Fig. 3. The lattice (Fig. 2(c), insets) shows a spacing of 0.29 nm for In<sub>2</sub>O<sub>3</sub> and 0.47 nm for Co<sub>3</sub>O<sub>4</sub>, corresponding to the well-crystallized (222) and (111) planes of the  $Ia\bar{3}d$  and  $Fd\bar{3}m$  groups. The N<sub>2</sub> sorption measurements give BET surface areas of 95 m<sup>2</sup> g<sup>-1</sup> and 151 m<sup>2</sup> g<sup>-1</sup> for helical Co<sub>3</sub>O<sub>4</sub> and In<sub>2</sub>O<sub>3</sub> arrays, which are quite high for metal oxides. The narrow pore size distribution (Fig. 4) gives the maximum at 4.1 and 3.8 nm for self-supported Co<sub>3</sub>O<sub>4</sub> and In<sub>2</sub>O<sub>3</sub> helical arravs.

The optical properties of  $In_2O_3$  are illustrated in Fig. 5. The initial position for the sharp decline in the UV diffuse reflection spectrum is used to discuss the  $In_2O_3$  UV absorption features. It is estimated at ~305 nm (~4.07 eV) for the



Fig. 4 Pore size distribution of  $In_2O_3$  (A) and  $Co_3O_4$  (B) self-supported helical arrays.



Fig. 5 UV diffusion reflection (A) and photoluminescence (B) spectra of  $In_2O_3$  prepared in mesoporous channels of 2.0 nm (a), 3.0 nm (b), and 4.3 nm (c).

self-supported In<sub>2</sub>O<sub>3</sub> helical arrays (Fig. 5A(c)) by intersecting the tangents of the plain and decline parts. Compared with that of bulk In<sub>2</sub>O<sub>3</sub> (3.65 eV),<sup>9a</sup> the bandgap of the In<sub>2</sub>O<sub>3</sub> arrays shows an obvious blue shift, similar to that observed for nanodots (Fig. 5A(a)) and nanowires (Fig. 5A(b)). This could be rationally ascribed to the quantum confinement effect, as proposed previously.<sup>1c,9b</sup> Similar effects have also been observed for In<sub>2</sub>O<sub>3</sub> nanorods (300 nm),<sup>4a</sup> corundum-type In<sub>2</sub>O<sub>3</sub> nanocubes (*ca.* 300–310 nm),<sup>9c</sup> and nanoporous In<sub>2</sub>O<sub>3</sub> crystal clusters (220 nm).<sup>9b</sup> The energy shift could be calculated using eqn (1)<sup>1g</sup> if its dependence on particle size is assumed;

$$\Delta E = \frac{h^2}{8 \times (0.3m_0 + 0.6m_0)R^2} \tag{1}$$

where  $m_0$  is the free electron mass,  $\Delta E$  is the energy shift and R stands for the radius of the particles.  $\Delta E$  is calculated as 420 meV for the self-supported In<sub>2</sub>O<sub>3</sub> helical arrays. The average size of the corresponding In<sub>2</sub>O<sub>3</sub> particle is thus calculated to be 3.6 nm, which is in good agreement with the width of the nanowires forming the helical arrays. This means that the quantum size effects are preserved when nanowires (3.6 nm) form self-supported bundles having a diameter of 120 nm, which is critical to micro-device fabrication.

As an n-type semiconductor, the cubic  $In_2O_3$  has an oxygendeficient fluorite structure with twice the unit-cell edge of the corresponding fluorite cell and 1/4 of the anions missing in an ordered way.<sup>1d,h</sup> The photoluminescence (PL) properties (Fig. 5B) of self-supported arrays of nanowires are identical to nanodots and scattered nanowires, with two main emission signals centered at 370 and 470 nm. It is recognized that bulk  $In_2O_3$  exhibits no PL emission.<sup>10a</sup> The blue PL emissions, welldocumented for cubic  $In_2O_3^{1d}$  nanocrystals, are presumed to stem from the systematic oxygen vacancy. In our case, one blue emission additionally shifts from 439 to 443 nm when In<sub>2</sub>O<sub>3</sub> transforms from nanodots to a self-supported helical array of nanowires. The PL emission in the UV region at room temperature is quite rare for  $In_2O_3$ . The UV region emission observed here is thus closely related to the quantum confinement effect. The same phenomenon has been documented, although only for highly crystalline cubic In<sub>2</sub>O<sub>3</sub> nanoparticles.<sup>1c,d,10b</sup> The different emission peaks in both regions arise from the different energy levels produced by the oxygen vacancies caused during the annealing process,<sup>10c</sup> especially

in the hard-templating method. As shown in Fig. 5B, the measured PL intensity increases progressively from nanodots to nanowires and helical arrays, apparently implying the fact that the better ordered  $In_2O_3$  nanostructure presents a higher PL emission intensity.

In conclusion, it is found in this work that the dimension of chiral pores of mesoporous silica as a template plays an important role in controlling the morphologies and then the optical properties of nanocasted metal oxides. Using pore-swollen chiral mesoporous silica as a hard template, self-supported helical arrays of  $In_2O_3$  and  $Co_3O_4$  nanowires could be fabricated. The whole synthetic procedure might be extended to the synthesis of other self-supported helical metal oxides and metal sulfides, *etc.* The novel helical self-supported metal oxides are expected to have fascinating application in micro-devices, such as optics, magnetics, and beyond.

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