# Highly Ordered Mesoporous Cr<sub>2</sub>O<sub>3</sub> Materials with Enhanced

## **Performance for Gas Sensors and Lithium Ion Batteries**

Hao Liu,<sup>a</sup> Xiwen Du,<sup>b</sup> Xianran Xing,<sup>c</sup> Guoxiu Wang<sup>\*d</sup> and Shi Zhang Qiao<sup>\*a</sup>

<sup>a</sup> ARC Centre of Excellence for Functional Nanomaterials, Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, QLD 4072 Brisbane, Australia

<sup>b</sup> Tianjin Key Laboratory of Composite and Functional Materials, School of Materials Science and Engineering, Tianjin University, Tianjin 300072, China

<sup>c</sup>Department of Physical Chemistry, University of Science & Technology Beijing, Beijing 100083, China

<sup>d</sup> Centre for Clean Energy Technology, School of Chemistry and Forensic Science, University of Technology Sydney, Broadway Sydney, NSW 2007, Australia.

Correspondence and requests for materials should be addressed to <u>s.qiao@uq.edu.au</u> (S.Z. Qiao); <u>Guoxiu.Wang@uts.edu.au</u> (G.X. Wang).

### Experimental

#### Synthesis of materials

The SiO<sub>2</sub> templates of 2-dimensional (2D) hexagonal SAB-15 and 3-dimensional (3D) bi-continuous cubic KIT-6 mesoporous silica templates were synthesized according to the previous reports [1, 2]. The Cr<sub>2</sub>O<sub>3</sub> replicas from the 2D hexagonal SBA-15 and 3D cubic KIT-6 were obtained from a vacuum assisted solvent evaporation method. Typically, 1.0 mmol Cr(NO<sub>3</sub>)<sub>2</sub>·9H<sub>2</sub>O was dissolved in 15 ml ethanol to form a transparent solution. Then, 0.15 g dry SBA-15 or KIT-6 was added to the solution. After stirring for 12 h, the solvent was removed by evaporation at room temperature in vacuum oven (<10<sup>-3</sup> bar). The dry powder was ground and sintered at 400° C for 2 h to decompose the nitrate. The impregnation step was repeated once to obtain chromium oxide precursor/SiO<sub>2</sub> composites. After the final

calcination at 600 °C for 6 h, the silica templates were removed at the heating temperature of 80 - 90 °C in 2M NaOH solution for 12 hours twice, and then the final mesoporous  $Cr_2O_3$  were obtained after washing and drying at 50°C.

The bulk  $Cr_2O_3$  was bought from Aldrich Company. The particle size is 1 micron with CAS number: 1308-38-9 and product number 202169. The surface area of commercial  $Cr_2O_3$  is calculated to be 6.0 m<sup>2</sup>/g. The performance of bulk  $Cr_2O_3$  for gas sensors and lithium ion battery were also investigated for comparison.

#### Characterizations

The small angle X-ray diffraction (SAXRD) patterns were collected by a Bruker D8 Advacned X-ray diffractometer by using the Cu K $\alpha$  radiation ( $\lambda$ =0.15406 nm), within the scanning range from 0.5 to 5°. Wide angle X-ray diffraction patterns were collected from 20° to 80°. N<sub>2</sub> adsorption–desorption isotherms were obtained by using a Quadrasorb SI analyzer at 77 K. All the samples were degassed before nitrogen sorption measurement by a FloVac Degasser from Quantachrome Instruments Company, at the temperature of 200°C for 24h, under a vacuum pressure below than 50 mTorr. Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BJH) analyses were used to determine the surface area, pore volume, and pore size distribution. The BET surface area was calculated using experimental points at a relative pressure of  $P/P^0$ =0.05-0.25. The pore size distribution was derived from the adsorption branch using Barret-Joyner-Halenda (BJH) method. The total pore volume was estimated by the nitrogen amount adsorbed at a relative pressure ( $P/P^0$ ) of 0.99. The ordered mesoporous and crystalline structures of  $Cr_2O_3$  samples were analyzed by transmission electron microscopy (TEM) and high resolution TEM analysis (JEOL 2100, accelerating voltage 200kV).

#### Gas sensing measurement

The gas sensing properties of the as-prepared  $Cr_2O_3$  samples were measured using a WS-30A gas sensor measurement system.  $Cr_2O_3$  powders were mixed with anhydrous terpineol binder to form slurry, and then pasted on to ceramic tubes between Au electrodes, which were connected with four platinum wires. The assembled sensors were fitted into the gas-sensing measurement apparatus. Given amounts of volatile solutions, e.g. ethanol, acetone, isopropanol, formaldelhyde, ammonia solution and 92# gasoline, were injected on a hot plate in the testing chamber by a micro-syringe injector. The gas sensing sensitivity was defined as the ratio  $R_{gas}/R_{air}$ , where  $R_{air}$  and  $R_{gas}$  are the electrical resistance of the sensors in air and in testing gas, respectively. The working temperature for sensors is 150 °C by heating a resistor at a constant voltage. Before testing, the sensor elements were preheated at the working voltage for several hours to achieve stable working conditions. The response signals were recorded at a stable gas concentration after the gas was introduced or released.

#### **Electrochemical testing for lithium storage**

The  $Cr_2O_3$  anode electrodes were fabricated by mixing the active materials with acetylene black (AB) and a binder, poly(vinylidene fluoride) (PVdF), at weight ratios of 40:40:20. The mixture was dispersed in NMP solvent to form a slurry and uniformly pasted on Cu foil with a blade. These prepared electrode sheets were dried at 120 °C in a vacuum oven for 12 h and pressed under a pressure of 200 kg/cm<sup>2</sup>. CR2032-type coin cells were assembled in a glove box for electrochemical characterization. A non-aqueous solution of 1 M LiPF<sub>6</sub> in a 1:1 of ethylene carbonate (EC) and dimethyl carbonate (DMC) was used as electrolyte. Li metal disk was used as the counter electrode for electrochemical testing. The cells were galvanostatically charged and discharged in a current density range of 0.1C (~100 mA/g) within the voltage range of 0.01–3 V. For the high rate testing, the charge/discharge current gradually increased from 0.1C to 0.2, 0.5, 1, 2, 5 and 10C, then decrease to 1C and 0.1C, step by step. Cyclic voltammetry (CV) curves were collected by an electrochemistry workstation (CHI660C) at 0.5 mV/s within a range of 0.01–3.0 V.

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|                                  | Space group | Pore size<br>distribution<br>(nm) | Surface area<br>(m²/g) | Pore volume<br>(cc/g) |
|----------------------------------|-------------|-----------------------------------|------------------------|-----------------------|
| SBA-15                           | P6mm        | 9.9                               | 472                    | 0.98                  |
| KIT-6                            | Ia3d        | 8.8                               | 854                    | 1.26                  |
| H-Cr <sub>2</sub> O <sub>3</sub> | P6mm        | 3.3                               | 88                     | 0.23                  |
| C-Cr <sub>2</sub> O <sub>3</sub> | Ia3d        | 2.8                               | 93                     | 0.25                  |

Table S1 Physical Properties of different templates and their Cr<sub>2</sub>O<sub>3</sub> replicas.



**Fig. S1** Characterizations of SBA-15 and KIT-6 and silica templates. (a) The SAXRD pattern of SBA-15 (inset is the TEM image of 2-dimensional hexagonal SBA-15). (b) The SAXRD pattern of KIT-6 (inset is the TEM image of 3-dimensional cubic KIT-6).



Fig. S2 Nitrogen sorption isotherms and corresponding pore size distributions of (a) SBA-15 and (b) KIT-6 silica templates.



**Fig. S3** Low magnification TEM images of (a) and (b):  $H-Cr_2O_{3;}$  (c) and (d):  $C-Cr_2O_3$  in large scale, which demonstrate highly ordered mesoporous structure in all domains.



**Fig. S4** SAXRD comparation of mesoporous H-Cr<sub>2</sub>O<sub>3</sub> and C-Cr<sub>2</sub>O<sub>3</sub> materials obtained with/without vacuum assistant.



Fig. S5 Wide angle XRD patterns of mesoporous H-Cr<sub>2</sub>O<sub>3</sub> and C-Cr<sub>2</sub>O<sub>3</sub> materials.



**Fig. S6** The first 5 cycles of cyclic voltammetry curves of B-Cr<sub>2</sub>O<sub>3</sub>, H-Cr<sub>2</sub>O<sub>3</sub> and C-Cr<sub>2</sub>O<sub>3</sub>. Scanning rate 0.5mV s<sup>-1</sup> within the testing range 0.01-3V.



**Fig. S7** The Nyquist plots of B- $Cr_2O_3$ , mesoporous H- $Cr_2O_3$  and C- $Cr_2O_3$  after 5 cycles CV testing. Frequency range between 100k and 10m Hz at room temperature



**Fig. S8** The coulombic efficiencies of B-Cr<sub>2</sub>O<sub>3</sub>, mesoporous H-Cr<sub>2</sub>O<sub>3</sub> and C-Cr<sub>2</sub>O<sub>3</sub> at the charge/discharge current of 0.1C for 100 cycles.



**Fig. S9** The electrochemical performance of B-Cr<sub>2</sub>O<sub>3</sub>, mesoporous H-Cr<sub>2</sub>O<sub>3</sub> and C-Cr<sub>2</sub>O<sub>3</sub> by multiple step galvanostatic testing (at rates of 0.1, 0.2, 0.5, 1, 2, 5, 10C, and then return to the 1 and 0.1C step by step).