### **Electronic Supplementary Information**

# Co<sub>3</sub>O<sub>4</sub> microcubes with exceptionally high conductivity using CoAl layered double hydroxide precursor via soft chemically synthesized cobalt carbonate

*Churchil A. Antonyraj,<sup>a</sup> Divesh N. Srivastava,<sup>b</sup> Gurudas P. Mane,<sup>c</sup> Sivashunmugam Sankaranarayanan,<sup>a</sup> Ajayan Vinu,<sup>c,d</sup> and Kannan Srinivasan<sup>a\*</sup>* 

<sup>a</sup>Discipline of Inorganic Materials & Catalysis, Central Salt and Marine Chemicals Research Institute, Council of Scientific and Industrial Research (CSIR), GB Marg, Bhavnagar 364002, India

<sup>b</sup>Analytical Discipline and Centralized Instrument Facility, Central Salt and Marine Chemicals Research Institute, Council of Scientific and Industrial Research (CSIR), GB Marg, Bhavnagar 364002, India

<sup>c</sup>International Center for Materials Nanoarchitectonics, World Premier International Research Center, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

<sup>d</sup> Multifunctional Nanoporous Materials Group, Australian Institute for Bioengineering and Nanotechnology (AIBN), The University of Queensland, Corner College and Cooper Roads, Brisbane Qld 4072, Australia

### **Corresponding Author Information**

\* Tel: +91-278-2567760 ext. 7030. Fax: +91-278-2567562. E-mail: <u>skannan@csmcri.org</u>; <u>kanhem1@yahoo.com</u>;

### Experimental

Synthesis of LDH and its decomposition to cobalt carbonate: CoAl-LDH was synthesized using urea hydrolysis method by taking 0.27 M of  $Co(NO_3)_2$ , 0.135 M of  $Al(NO_3)_3$  and 1.584 M of urea in 200 ml of water and N<sub>2</sub> gas was purged for 30 min to remove dissolved O<sub>2</sub> and CO<sub>2</sub>. This mixture was kept in a round-bottomed flask (500 ml) attached to a reflux condenser at 90 °C for 30 h with stirring under N<sub>2</sub> atmosphere. One portion (150 ml) of this was filtered, washed with distilled water till neutral pH and dried in vacuum at room temperature and the sample was named here as CoAl-LDH.

Decomposition of CoAl-LDH was done by taking another portion (50 ml) of LDH synthesized with mother liquor into a Teflon-lined autoclave (70 ml) and heated at different temperatures ranging from 120 to 200 °C for 12 h. After cooling to room temperature, the solid precipitate was collected by filtration, washed with deionized water and dried in vacuum at room temperature and the sample treated at 150 °C is named as CoCO<sub>3</sub>-decomp. 750 mg of this sample is treated with 300 ml of 3.3 mM HCl for 6 h, washed till pH neutral and treated subsequently with 300 ml of 5 mM of NaOH for 6 h to remove AlOOH and amorphous alumina phases to obtain highly pure and crystalline CoCO<sub>3</sub>-L.

*Urea hydrolysis:* 0.135 M of  $Co(NO_3)_2$  and 1.584 M of urea in 50 ml of water were taken in a Teflon-lined autoclave and heated at 150 °C for 12 h. The solid precipitate is collected by filtration, washed with deionized water and dried in vacuum at room temperature. The sample was named as  $CoCO_3$ -U.

*Co-precipitation:* 1M solution of  $Co(NO_3)_2$  was slowly (1 ml min<sup>-1</sup>) and simultaneously mixed with 2 M  $(NH_4)_2CO_3$  in a Schott autotitrator at a constant pH of 7.5 ± 0.1 under stirring at room temperature. The sample was aged in the mother liquor at 90 °C for 30 h, filtered off, washed with deionized water and dried in vacuum at room temperature. The sample was named as CoCO<sub>3</sub>-P.

Commercial cobalt carbonate is purchased from sd-fine chem. pvt. Ltd., India and named here as CoCO<sub>3</sub>-C.

### Calcination of cobalt carbonate to cobalt oxide spinel:

Thus obtained CoCO<sub>3</sub> samples were heated in a muffle furnace at a heating rate of 5 °C/min till 500 °C in static air and kept at that temperature for 3 h for complete decomposition to Co<sub>3</sub>O<sub>4</sub>. The corresponding samples are named as: Co<sub>3</sub>O<sub>4</sub>-L, Co<sub>3</sub>O<sub>4</sub>-U, Co<sub>3</sub>O<sub>4</sub>-P and Co<sub>3</sub>O<sub>4</sub>-C.

Elemental analysis for cobalt and aluminium in cobalt oxides was determined using inductivity coupled plasma optical emission spectrometry (ICP-OES: Perkin Elmer, OES, Optical 2000 DV) by dissolving the sample in adequate quantity of mineral acid.

The reaction chemistry and schematic presentation of experiments performed are given below:

#### **Schematic Presentation of Experiments**



*Conductance measurement:*  $Co_3O_4$  pellets were made by taking 75% of  $Co_3O_4$ , 20% graphite and 5% PTFE and pelletized at an applied pressure of 5 tones. The electrical measurements (Source Meter Unit - Keithley – 2635A) were done in a custom made pellet holder of Teflon with stainless steel contacts. The whole system was placed in an airtight controlled heating apparatus. I-V characteristics were recorded at different temperatures after stabilizing at each temperature for 10 minutes. The current-voltage (I-V) characteristics were recorded in ±10 voltage window. The readings were recorded at the end of one second with applied voltage and the whole scan was completed in 21 seconds. The measurements were done in duplicate and the error in the current measured was ± 3%.





**Fig. S1** PXRD patterns of (a) CoAl-as-synthesized (90 °C), (b) hydrothermal of "a" at 120 °C, (c) hydrothermal of "a" at 150 °C, (d) hydrothermal of "a" at 200 °C (\*Cobalt carbonate (Spherocobaltite), # Aluminium oxyhydroxide (AlOOH), + Hydrotalcite)





**Fig. S2** PXRD patterns of (a) CoCO<sub>3</sub>-L, (b) CoCO<sub>3</sub>-L after acid treatment, (c) CoCO<sub>3</sub>-L after acid and base treatment (\* Cobalt carbonate (Spherocobaltite), # Aluminium oxyhydroxide (AlOOH))

## Figure S3

•	Element	Weight	Atomic
		%	%
	C K	26.16	46.02
	O K	28.59	37.76
	Co K	45.25	16.23
	Total	100.00	
	Element	Weight	Atomic
		%	%
	O K	67.09	78.30
	Al K	30.04	20.79
EHT = 20.00 KV V/D = 1 Mag = 259 X 0 CSMCR Chamber = 5.430-001 Pa Pilot: 10, = 6025 31jum : Signal A SEL Spil Size = 280 0 CSMCR Date 22 Feb 2010	Co K	2.88	0.91
	Total	100.00	

Fig. S3 SEM-EDAX images of CoCO<sub>3</sub>-L after acid treatment

## Figure S4



Fig. S4 HRSEM images displaying the morphological changes occurred during the soft chemical decomposition (a) CoAl-LDH to (b)  $CoCO_3$ -L



Figure S5 Formation mechanism of CoCO<sub>3</sub> through soft-chemical decomposition of CoAl-LDH

PXRD and FT-IR spectra of the as-synthesized CoAl-LDH sample (marked as 0 h) and after its hydrothermal treatment in mother liquor at indicated time

PXRD and FT-IR results showed partial conversion of carbonate containing CoAl-LDH to nitrate containing LDH upon hydrothermal treatment of as-synthesized sample after 2 h. This was supported by the appearance of  $d_{003}$  basal reflection around 8.7 Å in PXRD and a band observed at 1385 cm<sup>-1</sup> (indicated as red arrow) in FT-IR, characteristic of nitrate containing LDH materials.<sup>1</sup> No significant change in the pH was noted during (see figure below) this time however with subtle increase in the Co/Al atomic composition as determined through ICP-OES analysis. Formation of nitrate containing CoAl-LDH through urea hydrolysis at high temperature is known earlier.<sup>2</sup> On increasing time to 4 h, a sharp increase in the pH was noted (to 9.0) that did not change with its further increase. This could be due to the formation of ammonium carbonate which probably then reacted with nitrate containing LDH, possibly through dissolution-reprecipitation resulting in cobalt carbonate and aluminium oxyhydroxide (see PXRD and FT-IR of 4 h sample). Since solubility of nitrate containing LDH is higher than its corresponding carbonate from<sup>3</sup>, feasibility of this reaction would be better. On further increase in time (up to 12 h), crystallization of cobalt carbonate takes place (as evidenced from the increase in the intensity of reflections in PXRD) where assembling of rectangular to hexagonal nano flakes to micro sheets occurs which then overlay one over the other forming microcubes (morphology changes and schematic mechanism are given below).

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Treatment	Co/Al atomic	Co in supernatant	Al in supernatant	
time (h)	ratio in solid*	(mg/L)	(mg/L)	
0	2.3	80.9	0.0	
2	3.1	91.7	0.1	
4	3.3	1.7	0.0	
6	4.0	1.0	0.1	
8	11.4	1.0	0.0	
10	14.3	1.0	0.0	
12	8.2	0.9	0.1	

ICP-OES analysis of solids and supernatant solutions obtained after hydrothermal treatment of freshly synthesized CoAl-LDH in mother liquor at various time

\*The variation in Co/Al atomic ratio for solids after 4 h could be due to heterogeneity of the samples having multiple phases



Supernatant solution at different time interval and values indicated are pH of the solution



Morphological (SEM) changes during the formation of  $CoCO_3$  through soft-chemical decomposition of CoAl-LDH and schematic mechanism

### **Reaction Chemistry**

$$CO(NH_{2})_{2} + 3H_{2}O \xrightarrow{90 \text{ °C}} 2NH_{4}^{+} + CO_{2} + 2OH^{-}$$

$$2NH_{4}^{+} + CO_{2} + 2OH^{-} \xrightarrow{90 \text{ °C}} 2NH_{4}^{+} + CO_{3}^{2-} + H_{2}O$$

$$4Co(NO_{3})_{2} + 2Al(NO_{3})_{3} + CO_{3}^{2-} + 14NH_{4}^{+} \xrightarrow{90 \text{ °C}} Co_{4}Al_{2}(OH)_{12}.CO_{3.x} H_{2}O + 14NH_{4}NO_{3}$$

$$Co_{4}Al_{2}(OH)_{12}.CO_{3.x} H_{2}O + NH_{4}NO_{3} \xrightarrow{150 \text{ °C}} Co_{6}Al_{2}(OH)_{12}.NO_{3.x} H_{2}O + NH_{4}CO_{3}$$

$$Co_{6}Al_{2}(OH)_{12}.NO_{3.x} H_{2}O + 12CO_{3}^{2-} \xrightarrow{150 \text{ °C}} 12CoCO_{3} + 2AlOOH + Al_{2}O_{3}$$

$$Co_{6}Al_{2}(OH)_{12}.NO_{3.x} H_{2}O + 12CO_{3}^{2-} \xrightarrow{150 \text{ °C}} 12CoCO_{3} + 2AlOOH + Al_{2}O_{3}$$

$$Co_{6}OCO_{3} + O_{2} \xrightarrow{500 \text{ °C}} 2Co_{3}O_{4} + 6CO_{2}$$

(1) S. Huang, H. Peng, W.W. Tjiu, Z. Yang, H.Zhu, T. Tang, T. Liu, J. Phys Chem. B, 2010, 114, 16766.

(2) J.B. Han, J. Lu, M. Wei, Z.L. Wang, X. Duan, Chem. Commun., 2008, 5188.

(3) R.K. Allada, A. Navrotsky, H.T. Berbeco, W.H. Casey, Science, 2002, 296, 721.





Fig. S6 DTGA profiles of (a) CoCO<sub>3</sub>-C, (b) CoCO<sub>3</sub>-P, (c) CoCO<sub>3</sub>-U, (d) CoCO<sub>3</sub>-L





Fig. S7 TPR profiles of (a)  $Co_3O_4$ -C, (b)  $Co_3O_4$ -P, (c)  $Co_3O_4$ -U, (d)  $Co_3O_4$ -L

### Estimation of Co<sup>4+</sup> by oxygen content analysis through iodometric titration

Oxygen content analysis was carried out as reported.<sup>4</sup> 50 mg of material was dissolved in 10 ml of HCl (35.4 %) containing KI (10 g/L) in a tightly packed container for 4-6 h (complete dissolution). The Co ions (Co<sup>3+</sup> and Co<sup>4+</sup>) in higher oxidation states are reduced to Co<sup>2+</sup> and forms stoichiometric amount of iodine in the solution. The liberated iodine was titrated against standard sodium thiosulpate solution (0.025 M) using freshly prepared starch as indicator. Excess oxygen present in the sample is due to the presence of Co<sup>4+</sup> that results in high electrical conductivity. Titrations were done in triplicate and the average values are reported and the variation in the titre values is  $\pm 0.1$  ml.

$$2\mathrm{Co}^{3+} + 3\mathrm{I}^{-} \rightarrow 2\mathrm{Co}^{2+} + \mathrm{I}_{3}^{-}$$

 $\mathrm{Co}^{4+} + 3\mathrm{I}^{-} \rightarrow \mathrm{Co}^{2+} + \mathrm{I}_{3}^{-}$ 

 $\mathrm{I_3}^- + 2\mathrm{S}_2\mathrm{O}_3^{2\text{-}} \rightarrow 3\mathrm{I}^- + \mathrm{S}_4\mathrm{O}_6^{2\text{-}}$ 

Table 1S Oxygen content and calculated formula of different Co<sub>3</sub>O<sub>4</sub> materials by iodometry

Material	Oxygen content	Calculated Formula <sup>#</sup>
Co <sub>3</sub> O <sub>4</sub> -C	4.03	$Co^{2+}Co^{3+}_{1.95}Co^{4+}_{0.05}O_{4.03}$
Co <sub>3</sub> O <sub>4</sub> -P	4.00	$Co^{2+}Co^{3+}{}_{2.00}Co^{4+}{}_{0.00}O_{4.00}$
Co <sub>3</sub> O <sub>4</sub> -U	4.03	$Co^{2+}Co^{3+}_{1.94}Co^{4+}_{0.06}O_{4.03}$
Co <sub>3</sub> O <sub>4</sub> -L	4.08	$Co^{2+}Co^{3+}_{1.84}Co^{4+}_{0.16}O_{4.08}$

<sup>#</sup>values rounded to two significant figures

(4) K. Conder, E. Pomjakushina, A. Soldatov, E. Mitberg, Mater. Res. Bull., 2005, 40, 257.

### Effect of calcination temperature on the conductivity of Co<sub>3</sub>O<sub>4</sub>

In order to study the effect of calcination temperature which is known to influence the electrical conductivity of the oxide samples,  $CoCO_3$ -L was thermally treated at three different temperatures (based on thermogravimetric analysis) namely 400, 500 and 650 °C in air for 3 h and the obtained oxide samples were assessed for electrical conductivity measurements. The results showed an increase in the conductivity with an increase in calcination temperature (Table 2S) probably due to an increase in the concentration of Co<sup>4+</sup> as reported earelier.<sup>5</sup>

Table 2S Specific conductivity of  $Co_3O_4$  obtained by calcining  $CoCO_3$ -L at different temperatures

Calcination Temp (°C)	Specific conductivity (S/cm)
400	7.67×10-4
500	8.27×10 <sup>-4</sup>
650	13.44×10 <sup>-4</sup>

(5) M. Douin, L. Guerlou-Demourgues, M. Menetrier, E. Bekaert, L. Goubault, P. Bernard and C. Delmas, *Chem. Mater.*, 2008, **20**, 6880.





Fig. S8 The electrical conductivity of  $Co_3O_4$  materials at different temperatures – Smallpolaron model