Supporting Information for:

Freestanding Mesoporous Quasi-Single-Crystalline Co₃O₄ Nanowire Arrays

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1: Co₃O₄ nanowire array synthesis.

In a typical synthesis, 10mmol Co(NO₃)₂·6H₂O was firstly dissolved in 10ml nanopure water (18M Ω) under magnetic stirring. Then 40ml 28-30% concentrated ammonia was slowly added. The solution was continuously stirred for half an hour before it was transferred to a covered petri dish. Various substrates, such as silicon wafer, microslide, conducting glass, were fixed using a Teflon clamp with the interested side facing downwards, which is approximately 1-2mm away from the bottom of the petri dish. It was kept in an oven at 90°C for around 14h.

The heating procedure for converting the as-made nanowires into pure spinel Co_3O_4 phase is as following: after the overnight growth in solution, the nanowires were taken out, completely washed with deionized water, and dried in the air. They were then heated up to 250 °C at 1 °C/min in a furnace and maintained at that temperature for 4 hours.



2: Diameter distribution of the as-made nanowires growing on Si wafer.

3: FT-IR spectra of the as-made nanowires and the nanowires after thermal treatment at 250°C.



Figure S2. F1-IR spectra of as-made nanowires (bottom) and nanowires after thermal treatment at 250°C (top). In the spectrum of the as-made nanowires, the two very strong peaks centered at 667 and 585 cm⁻¹ are characteristic of spinel Co₃O₄; The peak around 3629 cm⁻¹ is characteristic of O-H stretching vibrations of β -Co(OH)₂; the sharp peak around 1384 cm⁻¹ comes from v3 vibration of NO₃⁻, which possibly are intercalated in the layered hydrotalcite-like intermediate structure during the transition from β -Co(OH)₂ to Co₃O₄; The broad peak around 3450 cm⁻¹ can be attributed to O-H group of intercalated water or hydrogen-bound O-H groups of hydroxide. All these peaks are well documented in literatures^[1]. After calcination, the 3629 and 1384 cm⁻¹ peaks disappear completely, indicating thorough conversion of minor β -Co(OH)₂ to Co₃O₄.





S3. Figure BET measurements of samples treated at (top) 250 °C, (middle) 350 °C, and (bottom) 500 °C. The surface area is 73.5, 16.3, and 8.4 m^2/g , respectively. The right panels are pore size distributions. After 250 °C treatment, there is a sharp peak at 3.3 nm in the pore size distribution. After 350 °C treatment, this peak decrease and a large broad peak at 5.3 nm appears. After 500 °C treatment, there is no apparent peak.

5: Morphological and structural evolution of the reaction products on Si substrate at different reaction time.



Figure S4. SEM images (left, top view) and the corresponding XRD patterns (middle panel) of the products on Si wafer with different reaction time: (A) 2h; (B) 4h; (C) 6h and (D) 8h. For clarity, the XRD spectra between 35-40 degrees are magnified in the right panel. β -Co(OH)₂ nanoplates are the dominant morphology on substrate at 2h, which later changes to a film coating on the substrate. Nanowires then grow out of the film. XRD characterization shows that the products are made of brucite β -Co(OH)₂ during the initial 6 hours' reaction. The spinel Co₃O₄ phase appears after reaction for 6 hours. Selected area electron diffraction and the color change from red to black also confirm the evolution from hydroxide to Co₃O₄.

There are three questions associated with the growth process: (1) what's the heterogenerous nucleation mechanism on the substrate? (2) What's the mechanism of the platelets growth? (3) What's the reason for the crystals to change growing habit from plates (2-D growth) to nanowires (1-D) growth?

We think the heterogenerous nucleation on the substrate comes from the preferential adsorption of Co(II) cations on the substrate, which increases the local cation concentration and results in the formation of nuclei. Brucite has a layer structure and comprises sheets of hexagonally close-packed OH ions with Co(II) bonded to six OH. The sheets are parallel to (0001) plane. These Co(OH)₂ sheets are bonded to one-another by weak OH-OH dipole interactions. Therefore, brucite crystals have the tendency to grow into thin nanoplatelets. This has also been reported by other groups^[2].

Therefore, we can answer questions (1) and (2). However, we can not give a definite answer to question (3) at this time. It is hard to rationalize that pure brucite can favor 1-D growth along the c-axis, considering the weak interactions between $Co(OH)_2$ sheets along this direction. We think that the counterions should play an important role in the nanowire growth. When we changed the reactant from cobalt nitrate to cobalt acetate, micro-disks rather than nanowires grew on the substrate. Therefore, considering nitrate ions appear in the FI-IR spectrum of the asmade nanowires shown in the Figure S2 of the *Supporting Information*, we suggest that the nanowires could be cobalt(II) hydroxide nitrate at the beginning, in which nitrate partially replaces hydroxide in the brucite structure. In fact, single-crystalline cobalt-hydroxide-carbonate nanorods with diameter of 100-200 nm have been previously reported^[3]. Moreover, in a serious of our recent experiments on other transition metal hydroxide and oxide under similar conditions, we observed that Ni(OH)₂ forms nanoplatelets, Cd(OH)₂ forms nanowires. It is interesting that these hydroxides with the same crystalline structure (hexagonal, P-3m1) choose very different growth behaviors.

6. TEM characterization of intermediate brucite β -Co(OH)₂ nanowires



image of the nanowires. Compared to the final Co_3O_4 nanowires, these β -Co(OH)₂ nanowires have relatively smooth surface. The inset is the SAED pattern of a single nanowire. The nanowire grows along [001] direction. (B) HRTEM of the β -Co(OH)₂ nanowires. Scale bars are (A) 400 nm and (B) 5 nm.

7: Co₃O₄ nanowire arrays for electrochemical H₂O₂ sensor.



Figure S6. (Left) Current response to hydrogen peroxide concentration in aqueous solution. (\odot) represent data from Co₃O₄ nanowire array grown on a conducting glass and (\Box) represent data from the bare conducting glass as the control. (Right) Effect of thermal treatment at different temperature on the sensitivity of nanowire arrays. These measurements were done on the same sample to avoid difference between samples. To our surprise, despite lower surface area, the sensing current of 350 °C sample is slightly higher than 250 °C sample. This can be related to the larger pore size of the 350 °C sample, which facilitates the diffusion of the reactants. Higher temperature treatment at 500 °C results in lower current, due to the loss of mesopores and the decay of the electric conductivity of the conducting glass substrate after thermal treatment.

Fluorine doped tin oxide (FTO) conducting glass was used as substrate to grow Co_3O_4 nanowire arrays. For electrical measurement, three-electrode system connected to potentialstat CV-50W was employed, with Co_3O_4 -loaded FTO as working electrode, Ag/AgCl (saturated with 4M KCl) as reference electrode and a platinum wire as counter electrode. The electrolyte was 0.05M tris(hydroxylmethyl)aminomethane buffer solution with 0.1M NaCl to increase conductivity. In the chronoamperometry mode, the potential between working electrode and reference electrode was set to be -150mV, and the sensitivity was 1mA/V. At this potential and electrolyte pH, interference from oxygen is prevented. Certain volume of 30 wt% H_2O_2 solution was added to the electrolyte under constant stirring speed of 650rpm, and its concentration was calculated based on added solution volume and its density.

Reference List

- [1] Z. P. Xu, H. C. Zeng, *Chemistry of Materials* **1999**, *11*, 67.
- [2] Y. Hou, H. Kondoh, M. Shimojo, T. Kogure, T. Ohta, *Journal of Physical Chemistry B* 2005, *109*, 19094.
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