Synthesis of Foam-like Freestanding Co_3O_4 Nanosheets with Enhanced Electrochemical Activities

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Electronic Supplementary Information

Synthesis of Co_3O_4 nanosheets: The cobalt metal was obtained by electrodeposition method. The electrolyte was composed of cobalt sulfate ($CoSO_4 \cdot 7H_2O$, 73 g L^{-1}) and triethanolamine (TEA, 70 ml L^{-1}). All reagents are of analytical grade. The pH value was adjusted to 3 by dilute hydrochloric acid. Nickel foil (0.1 mm) was used as cathode and commercial cobalt plate (99.9%) was used as anode. The cobalt metal was obtained by electrodeposition under a constant current density of 10 mA cm^{-2} and constant temperature of 30 ^oC. The obtained cobalt metal was then washed thoroughly by de-ionized water.

For preparation Co_3O_4 nanosheets, the obtained cobalt metal was firstly immersed into alkaline solution (KOH, 1 M), and then the substrate coated with a thin electrolyte film was exposed to atmosphere for a few minutes. Consequently, the substrate was covered by a dark purple-like film. The obtained precursor was washed by 95% ethanol for several times, dried in atmosphere for 2 hours, then slowly heated to 250 ^oC at a rate of 1 ^oC min^{-1}, and maintained at 250 ^oC for 2 hours in a furnace. Finally, the product of a black film was obtained (Scheme S1).

This facile method for synthesis of freestanding porous Co_3O_4 nanosheets is composed a growth step and a thermal treatment step. In the first growth step according to our research, the cobalt metal is oxidized to cobalt hydroxide in alkaline electrolyte, the reaction can be described as follows:

$2Co + O_2 + 2H_2O \rightarrow 2Co(OH)_2$

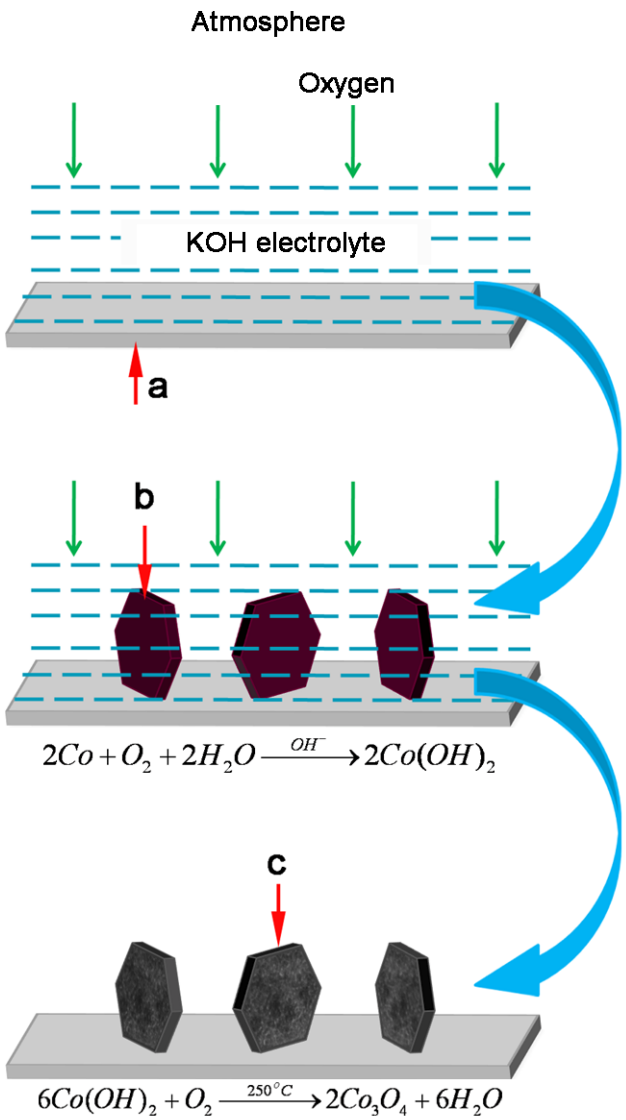
In the thermal treatment process, the precursor transformed to Co_3O_4 crystalline, the reaction can be illustrated as:

$6Co(OH)_2 + O_2 \rightarrow 2Co_3O_4 + 6H_2O$

The porous inside structure may be formed due to the dehydration and transformation of crystalline during thermal treatment.Besides, in the first step the operational temperature, the concentration of alkaline solution and the operating time may influence the particle size of the product. While in the second step, the thermal treatment temperature may have effect on the pore size. Consequently, the growth mechanism and its affecting factors are required for further research.

Characterization: X-ray diffraction patterns of both the precursor and product were characterized on an X-ray diffractometer D/Max 2250 using Cu Kα radiation with λ=1.54059 Å. The morphologies were observed on a scanning electron microscopy (SEM, Carl Zeiss Ultra55 operated at 5 kV). Further observation of insight architecture was taken on transmission electron microscopy Philips CM200 operated at 160 kV.

Electrochemical Test:[1] The as prepared Co_3O_4 nanosheets were used as working electrode and a lithium plate as counter electrode. The electrolyte was 1 M LiPF6 in a 1:1 v/v mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). The Co_3O_4/Li half cell was assembled in a glove-box filled with pure argon (99.999%). The cell was tested under a constant charge/discharge current density of 150 mA g^{-1} in voltage windows between 2.5 V and 0.01 V (vs. Li) and operated on an Arbin® BT2000 battery testing system at ambient temperature (25 ^oC).



Scheme S1 Synthesis of freestanding 2D Co_3O_4 nanosheets. (a) Cobalt metal electrodeposited on conductive substrate; (b) Hexagonal brucite-like β-$Co(OH)_2$ precursor and (c) Freestanding Co_3O_4 nanosheets.

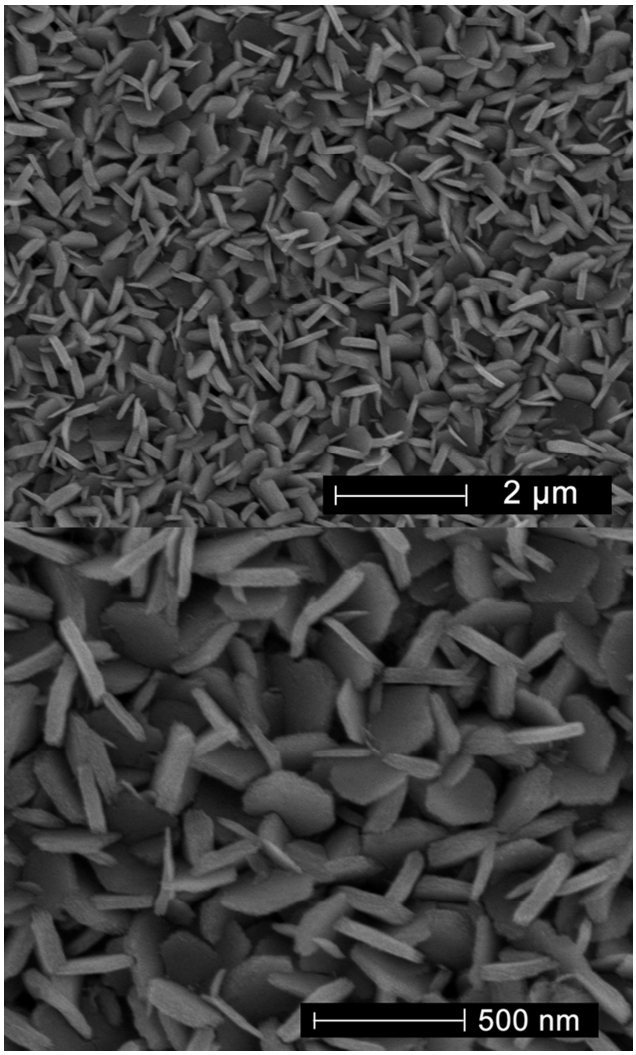


Fig. S1 (a) SEM and (b) close view SEM images of Co_3O_4 nanosheets coating with a conductive platinum layer.

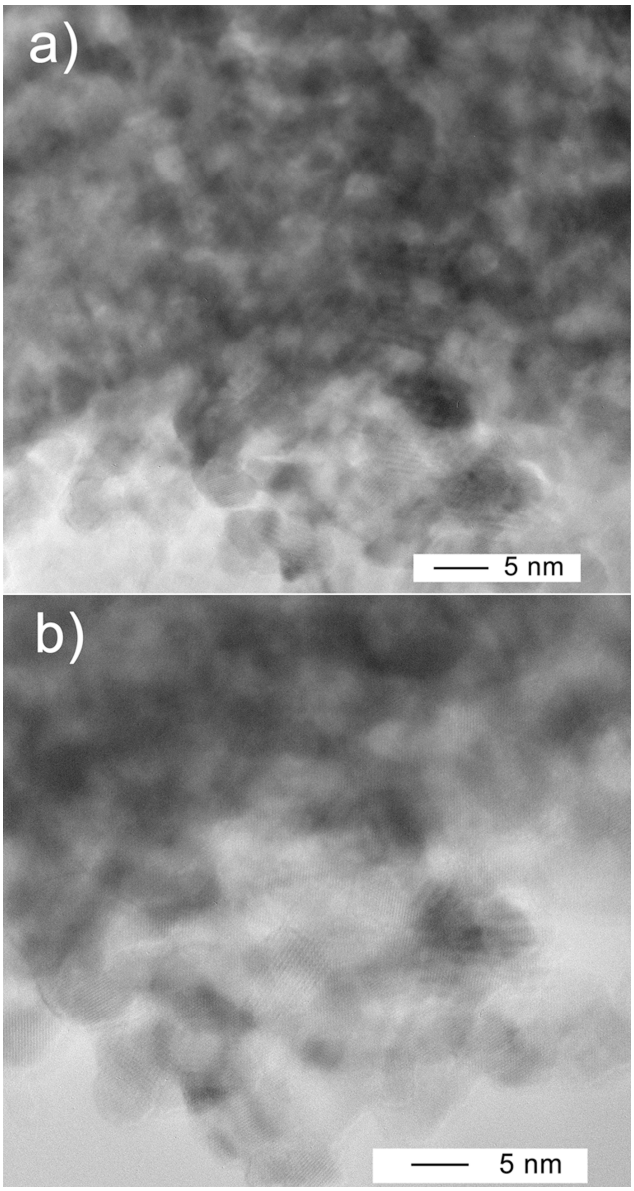


Fig. S2 Close view TEM images of Co_3O_4 nanosheets. The observed pore size was mainly less than 5 nm. The average Co_3O_4 particle size was calculated by XRD pattern (figure 1) according to Scherrer equation: $d=0.89*\lambda/[FWHM*\pi/180)*\cos\theta]$. Where $\lambda=0.15406$ nm, FWHM (calculated by Jade5.0) =0.78-1.061 (^{o}), $2\theta=36.856$-$36.881(^o)$. Consequently, the average particle size was calculated to be 8-11 nm.

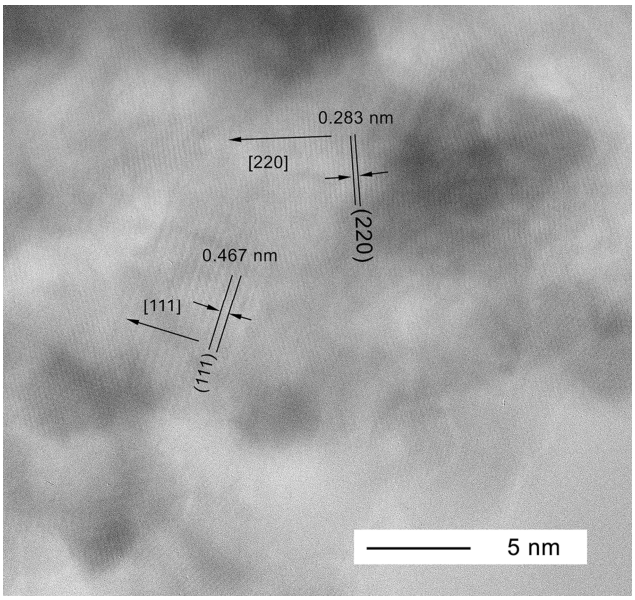


Fig. S3 High resolution figure of HRTEM of Co_3O_4 nanosheets. The high resolution transmission electron microscopy (HRTEM) image (Figure 3c) shows a well-defined crystalline structure with lattice spacing of 0.467 Å and 0.283 Å, corresponding to the value of the (111) and (220) plane of the Co_3O_4 phase.

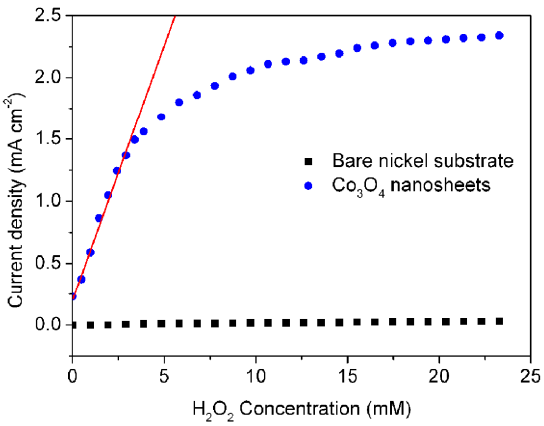


Fig. S4 Co_3O_4 nanosheets for hydrogen peroxide sensing in aqueous solution. Three-electrode system was assembled by using the as-synthesized Co_3O_4 nanosheets, Ag/AgCl (saturated with 4 M KCl) and a platinum plate as working electrode, reference electrode and counter electrode, respectively. Besides, a bare nickel substrate was also used as a working electrode for comparison. The electrolyte was composed of 0.05 M tris(hydroxylmethyl)aminomethane buffer solution with 0.1M NaCl to increase conductivity.[2] The electrochemical measurement was taken on an CHI 920C potentiostat with the potential between working electrode and reference electrode as -150mV. It can be seen that the as prepared electrode record a high sensitivity in the linear range, indicating promising application value for sensors.

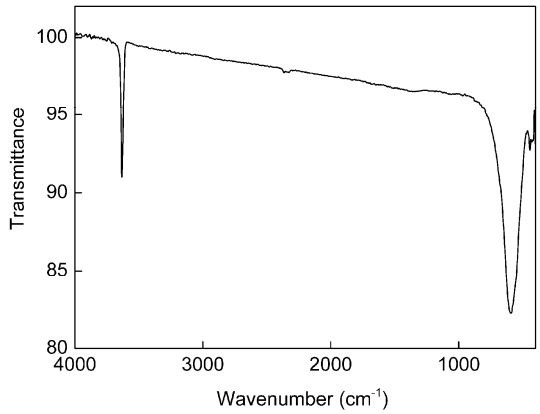


Fig. S5 FT-IR spectra of the β-$Co(OH)_2$ precursor. The sharp peak observed at 3630 cm^{-1} is assigned to overlapping stretching modes of hydroxyl group in the brucite-like structure.[3] The peak at 590 cm^{-1} is associated with Co-O stretching and Co-OH bending vibrations. The FT-IR spectra was determined on an Nicolet Nexus 470 FT-IR analyzer. A polished Cobalt plate was used as the background.

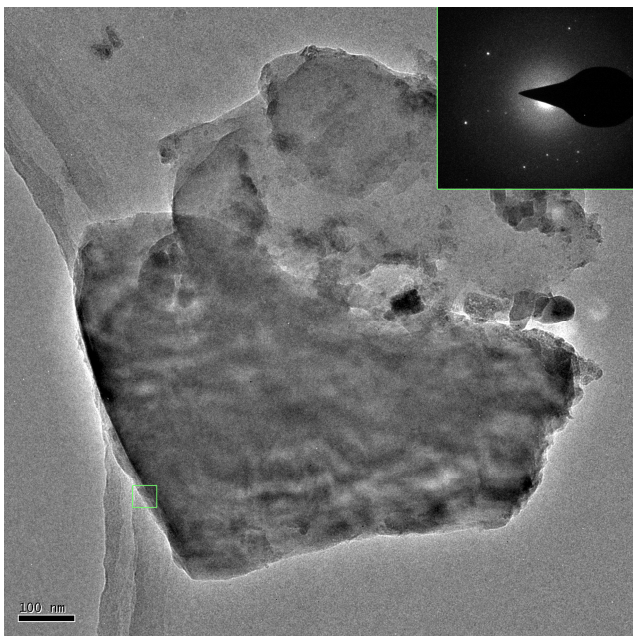


Fig. S6 TEM image and selected-area electron diffraction (SAED) of cobalt hydroxide precursor.

Notes and references

1 H.-J. Wang, J.-M. Wang, W.-B. Fang, H. Wan, L. Liu, H.-Q. Lian, H.-B. Shao, W.-X. Chen, J.-Q. Zhang and C.-N. Cao, *Electrochem. Commun.* 2010, **12**, 194.
2 Y. Li, B. Tan, and Y. Wu, *J. Am. Chem. Soc.* 2006, **128**, 14258.
3 H. El-Batlouni, H. El-Rassy and M. Al-Ghoul, *J. Phys. Chem. A* 2008, **112**, 7755.