Electronic Supplementary Information

Co/CoO/CoFe$_2$O$_4$/G nanocomposite derived from layered double hydroxide towards mass production of efficient Pt-free electrocatalyst for oxygen reduction reaction

Rui-Jie Huo,$^{a}$ Wen-Jie Jiang,$^{b}$ Sai-Long Xu,$^{a}$ Fa-Zhi Zhang,$^{a}$ and Jin-Song Hu$^{*b}$

$^a$ State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China; E-mail: xusl@mail.buct.edu.cn.

$^b$ Institute of Chemistry, Chinese Academy of Sciences, Beijing 100090, China; E-mail: hujs@iccas.ac.cn.

‡ These authors contributed equally to this work.
**Experimental**

**Preparation**

CoFe-LDH/GO precursor was prepared according to a scalable method including as separate nucleation step and an aging step.\(^1\) Briefly, a salt solution were obtained by dissolving Co(NO\(_3\))\(_2\)•6H\(_2\)O and Fe(NO\(_3\))\(_3\)•9H\(_2\)O in a Co/Fe molar ratio of 2:1 in freshly deionized water to give rise to a solution with a total cationic concentration of 1.2 M. Graphene oxide was dispersed in deionized water and stirred for 12 h to form a homogeneous dispersion. An aqueous base solution was obtained by adding NaOH (1.92 M) and Na\(_2\)CO\(_3\) (0.8 M) into the GO dispersion. Equal volumes of salt and base solutions were then simultaneously added into a modified colloid mill at a rotor speed set at 3000 rpm. The resulting slurry was mixed for 3 minute and then aged at 100 °C for 48 h. The product was washed thoroughly with deionized water by centrifugation, and finally dried at 60 °C for 24 h to obtain CoFe-LDH/GO.

Co/CoO/CoFe\(_2\)O\(_4\)/G nanocomposite was prepared by calcining LDH/GO precursors in a programmable tube furnace at 650°C for 2h with a temperature ramping rate of 2°C/min.

**Characterization**

Powder X-ray diffraction was carried out on Rigaku XRD-6000 powder dffractometer with CuK\(\alpha\) radiation (40 kV, 30 mA, \(\lambda=1.542\) Å). The data were collected at a scanning speed of 10° min\(^{-1}\). Scanning electron microscope (SEM) images were obtained using a Zeiss Supra 55 scanning electron microscope. Samples were dispersed in ethanol and then deposited onto silicon wafer for SEM observation. Transmission electron microscopy (TEM) characterization was performed through a JEOL JEM-2100 electron microscope equipped with STEM and EDX at an accelerating voltage of 200 kV. The X-ray photoelectron spectroscopy (XPS) analyses were conducted through a Kratos Axis ULTRA X-ray Photoelectron Spectrometer incorporating a 165 mm hemispherical electron energy analyzer.

**Electrochemical test**

The glass carbon rotating disk electrode (3 mm in diameter, INF-EL-EDI101, France Radiometer Analytical S.A.) was polished mechanically with 0.5~0.7 μm down to 0.03~0.05 μm alumina slurry to obtain a mirror-like surface and then washed with Mill-Q water and ethanol prior to use. In the typical procedure for ink preparation, 2 mg catalysts was dispersed in 400 μL ethanol and sonicated for 30 minutes to form a homogeneous ink. 5 μL ink was loaded on polished glassy carbon electrode to achieve a catalyst loading of 354 μg/cm\(^2\). A drop of 0.5 wt.% nafion (Sigma-Aldrich) solution was then applied onto electrode surface. After dried in the air, the electrode was ready for test. Commercial
Johnson-Matthey Pt/C with a Pt loading of 20 wt.% was used for comparison and the catalyst loading on electrode was 15μg/cm²Pt.

Electrochemical experiments were conducted in a standard three-electrode cell at room temperature on PARSTAT 2273 advanced electrochemical system, consisted of a working electrode, Ag/AgCl reference electrode and a platinum foil counter electrode, as reported previously in our previous studies.⁴ All the CV measurements were carried out at a scanning rate of 50 mV/s. The LSV curves were recorded at a scanning rate of 10 mV/s. Before each ORR test, the electrolyte was purged with O₂ at least for 30 min to achieve O₂-saturated electrolyte. RDE measurements were conducted at varying rotating speeds from 400 to 3600 rpm by using CTV101 Speed Control Unit (France Radiometer Analytical S.A.).

The electron transfer number (n) per oxygen molecule involved in ORR process can be calculated from the slopes of Koutecky-Levich plots using the following equation⁴:

\[
\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B\omega^{1/2}}
\]

Where \( j_k \) is the kinetic current and \( \omega \) is the electrode rotating rate. \( B \) could be determined from the slope of the K-L plots based on the Levich equation as follows:

\[
B = 0.62nF(D_0)^{2/3} \theta^{-1/6}C_0
\]

Where \( n \) represents the electron transfer number, \( F \) is the Faraday constant \((F = 96485 \text{ C mol}^{-1})\), \( D_0 \) is the diffusion coefficient of O₂ in 0.1 M KOH \((1.9 \times 10^{-5} \text{ cm}^2\text{s}^{-1})\), \( \theta \) is the kinetic viscosity \((0.01 \text{ cm}^2\text{s}^{-1})\), and \( C_0 \) is the bulk concentration of O₂ \((1.2 \times 10^{-6} \text{ mol cm}^{-3})\). The constant 0.62 is adopted when the rotating speed is expressed in rad s⁻¹.

Reference

Figure S1

**Fig. S1** Co 2p XPS spectra of Co/CoO/CoFe$_2$O$_4$/G nanocomposite.
Figure S2

**Fig. S2** LSV curves of pure graphene and Co/CoO/CoFe$_2$O$_4$/G for ORR recorded at a scan rate of 10 mV s$^{-1}$ and rotation speed of 1600 rpm
Fig. S3 The electron transfer numbers ($n$) at various potentials for Co/CoO/CoFe$_2$O$_4$/G.