

Electronic Supplementary Information

Co/CoO/CoFe₂O₄/G nanocomposite derived from layered double hydroxide towards mass production of efficient Pt-free electrocatalyst for oxygen reduction reaction

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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 $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 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_2CO_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/CoFe₂O₄/G nanocomposite was prepared by calcinating 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 diffractometer with $\text{CuK}\alpha$ radiation (40 kV, 30 mA, $\lambda=1.542 \text{ \AA}$). The data were collected at a scanning speed of $10^\circ \text{ min}^{-1}$. 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 $\mu\text{g}/\text{cm}^2$. 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 $15\mu\text{g}/\text{cm}^2_{\text{Pt}}$.

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.^{2,3} 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 ω is the electrode rotating rate. *B* could be determined from the slope of the K-L plots based on the Levich equation as follows:

$$B = 0.62nF(D_0)^{2/3}\vartheta^{-1/6}C_0$$

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 ($1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), ϑ 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

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Figure S1

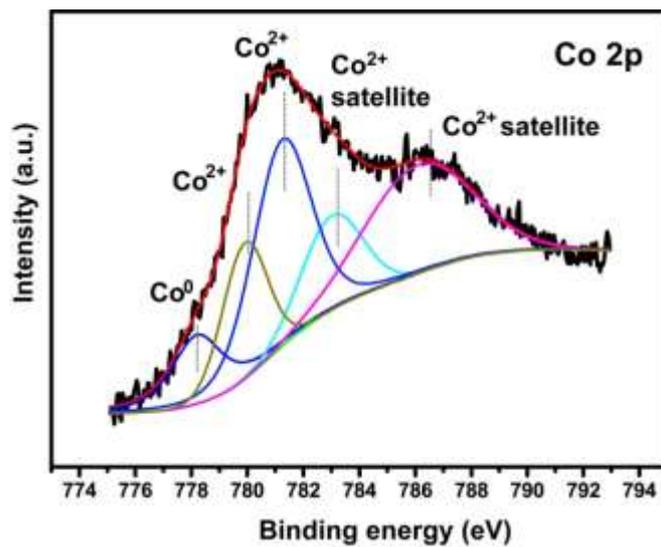


Fig. S1 Co 2p XPS spectra of Co/CoO/CoFe₂O₄/G nanocomposite.

Figure S2

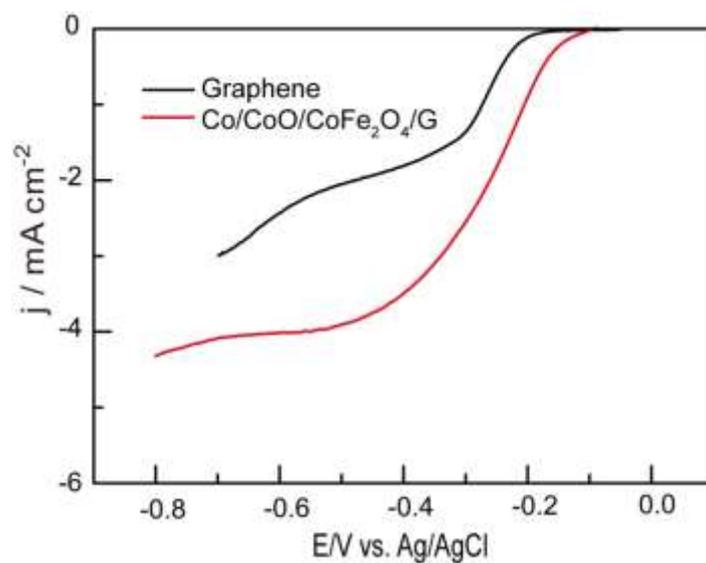


Fig. S2 LSV curves of pure graphene and Co/CoO/CoFe₂O₄/G for ORR recorded at a scan rate of 10 mV s^{-1} and rotation speed of 1600 rpm

Figure S3

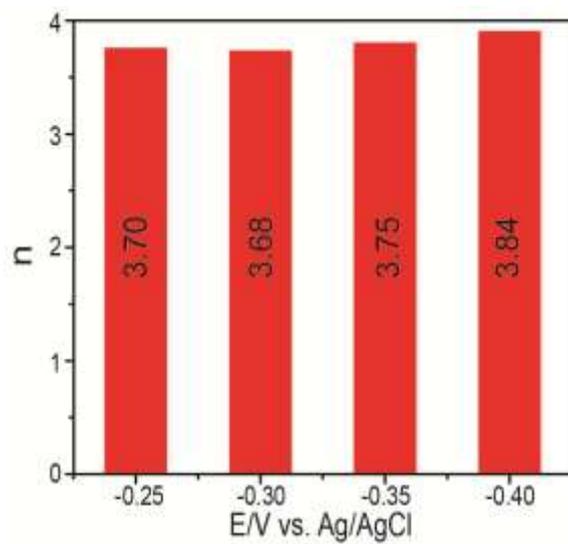


Fig. S3 The electron transfer numbers (n) at various potentials for Co/CoO/CoFe₂O₄/G.