Electronic Supplementary Material (ESI) for ChemComm.

Cobalt Carbonate Hydroxide/C: An Efficient Dual Electrocatalyst for Oxygen Reduction/Evolution Reactions

Yao Wang, Wei Ding, Siguo Chen, Yao Nie, Kun Xiong, Zidong Wei*

The State Key Laboratory of Power Transmission Equipment & System Security and New Technology, College of Chemistry and Chemical Engineering, Chongqing University, Chongqing,400044 (China)

*Corresponding Author: Zidong Wei

Fax: +86 23 65102531;

E-mail: zdwei@cqu.edu.cn (Wei);

Supporting information

1. Experimental section

1.1. Synthesis of free CCH, CCH+C, CoO/C, CCH/C catalyst.

In a typical synthesis, ethylene glycol (15-20 mL), concentrated $NH_3 \cdot H_2O$ (10-15mL, 28 wt.%), 1 M Na_2CO_3 aqueous solution (1-2 mL), 1 M $Co(NO_3)_2$ aqueous solution (4-6 mL) and 0.354g Vulcan XC-72 carbon black were mixed step by step under vigorous stirring. After 2h vigorous stirring, the precursor was transferred into a Teflon-lined stainless steel autoclave, a thermal treatment was performed for the Teflon-liner in an electric oven at 170°C for 2h and 16 h, noted as CCH-2/C, CCH-16/C, respectively. After the autoclave was cooled down naturally to room temperature, samples deposited at the bottom were collected and washed by centrifugation for at least three cycles using deionized water (D.I. water) and one cycle using pure ethanol. The as-synthesized samples were then dried in a vacuum oven at 40°C overnight to remove the absorbed water for the subsequent characterizations. The CoO/C nanocomposite was prepared by calcination of the as-synthesized CCH-2/C precursors in Ar at 350 °C for 2 h, and then cooled to ambient temperature. The free CCH was synthesized at an identical procedure without carbon black for 16h as described in ref [1]. Hereafter, the hybrid material is designated as CCH-2/C, CCH-16/C whereas the physical mixture of CCH with carbon black is designated as CCH+C.

1.2. Characterization of catalysts

The morphology and structure of CCH/C hybrid catalysts were observed under field emission scanning electron microscopy (FE-SEM, Hitachi S-4700). Low-resolution transmission electron microscopy (TEM) was carried out on a Zeiss LIBRA 200 FETEM instrument operating at 200 kV. The crystal structures of CCH/C were confirmed using the automated X-ray diffraction equipment (XRD, Rigaku D/MaXIIIA, Japan). Polarized zeeman atomic absorption spectrophotometer (PZAAS, Hitachi Z-2700) was carried out to investigate Co content. The surface area of CCH/C is calculated from N_2adsorption isotherms using Brunauer-Emmett-Teller BET

(Shimadzu, Micromeritics ASAP 2010 Instrument).

1.3. Electrochemical activity tests

Electrochemical measurements: All electrochemical experiments were performed in a standard three-electrode cell at room temperature on a Parstat 2273 potentiostat/galvanostat workstation assembled with a model 636 rotational system (AMETEK) at room temperature. The cell is consisting of a glassy carbon working electrode (GC electrode, 3 mm in diameter, PINE: AFE3T050GC), an Ag/AgCl (saturated KCl) reference electrode, and a platinum foil counter electrode. All potentials in this study, however, are given relative to the reversible hydrogen electrode (RHE). The working electrodes were prepared by applying catalyst ink onto glassy carbon (GC) disk electrodes. In brief, the electrocatalyst was dispersed in ethanol and ultrasonicated for 15 minutes to form a uniform catalyst ink. Well-dispersed catalyst ink (0.18 mg Co cm^{-2}) was applied onto a pre-polished GC disk. After drying at room temperature, a drop of 0.05 wt. % Nafion solution was applied onto the surface of the catalyst layer to form a thin protective film.

The catalysts were characterized by a cyclic voltammetry (CV) test at room temperature in 0.1 M aqueous KOH. The linear sweep voltammetry(LSV) was obtained in an O_2-saturated 0.1 M KOH electrolyte at a scan rate of 10 mV s^{-1} in the potential range 0 to 1.2 V (ORR) or 1.1–2.1 V (OER) in 0.1 M aqueous KOH. In the ORR experiment, the electrolyte was bubbled with high-purity O_2 for 30 min before each test and maintained under atmospheric conditions with constant O_2 gas flow during the measurements.

The kinetic parameters can be analyzed on the basis of the Koutecky-Levich (K-T) equations:

$$1/J = 1/J_k + 1/B\omega^2; \quad \text{where} \quad B = 0.62nFAv^{-1/6}C_o(D_o)^{2/3}$$

where J is the measured current density, J_k is the kinetic current density, ω is the angular velocity, n is the number of electrons transferred, F is the Faraday constant, v is the kinematic viscosity, C_o is the bulk concentration of O_2, and D_o is the diffusion

coefficient of O_2 in 0.1 M KOH solution.

Figure S1

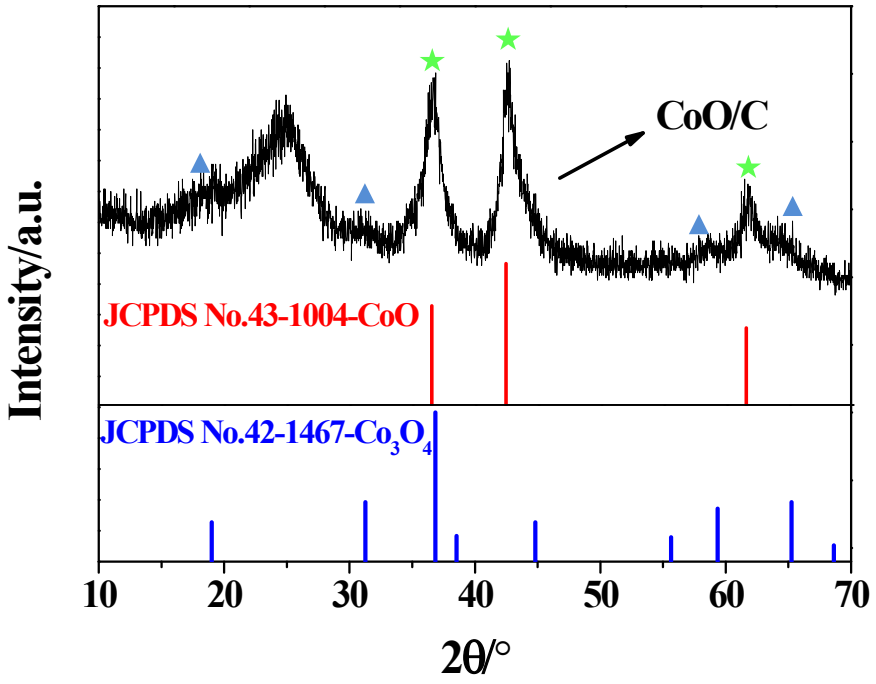

Fig.S1 XRD patterns of CoO/C. Triangles and Pentastars represent Co_3O_4 and CoO, respectively.

The increasing intensity of the broad peak in Fig. S1 at around 24° was derived by the existence of carbon black. And the existence of Co_3O_4 was derived by the oxidation of CoO when XRD tested.

Figure S2

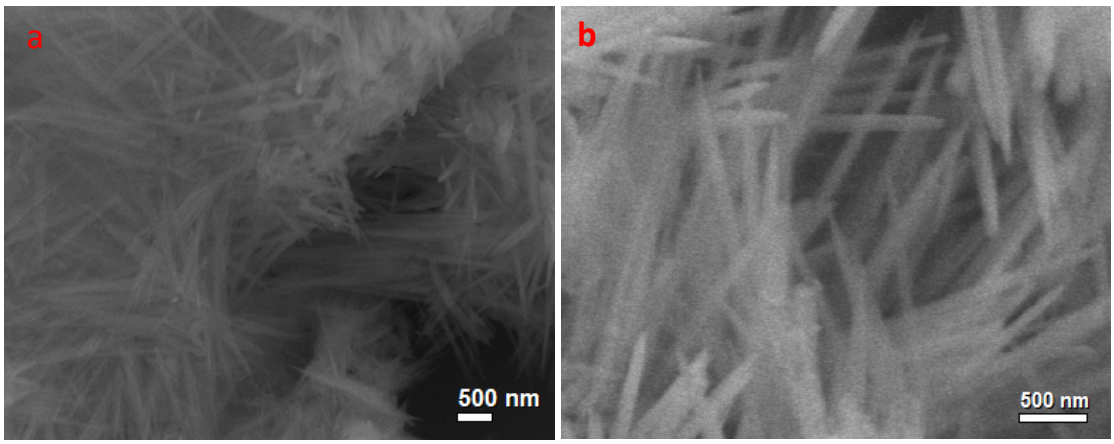

Fig. S2 (a, b) SEM images of CCH.

Figure S3

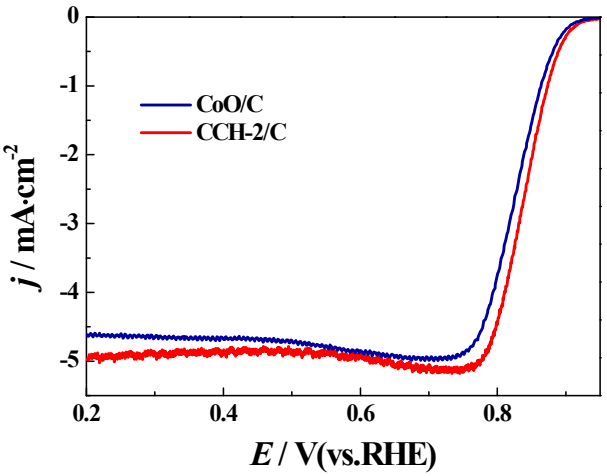

Fig.S3 LSV curves of CCH-2/C and CoO/C (loading 0.18 mg Co cm^{-2}) catalysts in O2-saturated 0.1 M KOH with a sweep rate of 10 mV s^{-1} at 1600 rpm.

Figure S4

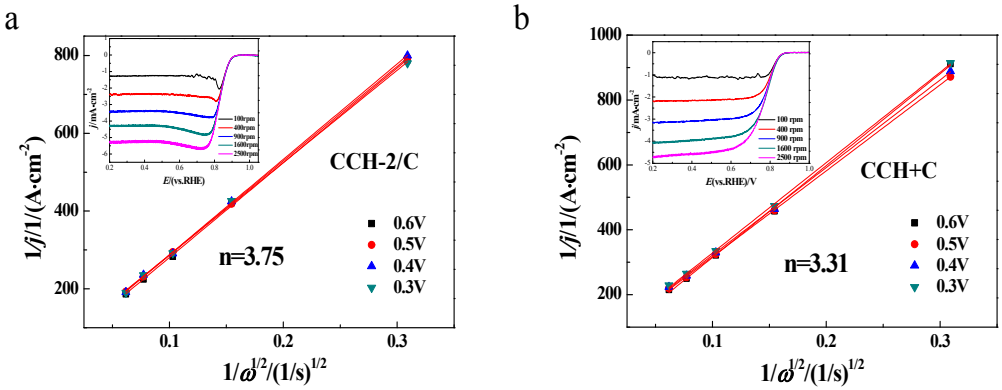

Fig.S4(a, b) Koutecky–Levich plots for (a) CCH-2/C, (b) CCH+C at different potentials (0.30, 0.4, 0.5, 0.6 vs. RHE) at a scan rate of 5 mV s^{-1}. Inset: reduction polarization curves at 0.1 M KOH at various rotation rates.

Fig. S4a and Fig. S4b show the constructed K-L curves, which exhibit good linearity and the slopes basically remain constant over a wide potential range (0.3–0.6 V), thus suggesting consistent electron transfer for oxygen reduction reaction. The average electron transfer number (n) was calculated to be 3.75 from the slopes of K-L plots, compared to ORR catalyzed by a CCH+C catalyst measured in the same 0.1M KOH electrolyte (n~3.31), suggesting the strong integration between CCH and C existing and an apparent quasi-four-electron process on CCH-2/C catalyst, which is desirable for achieving high-efficiency electrocatalytic ORR.

Figure S5

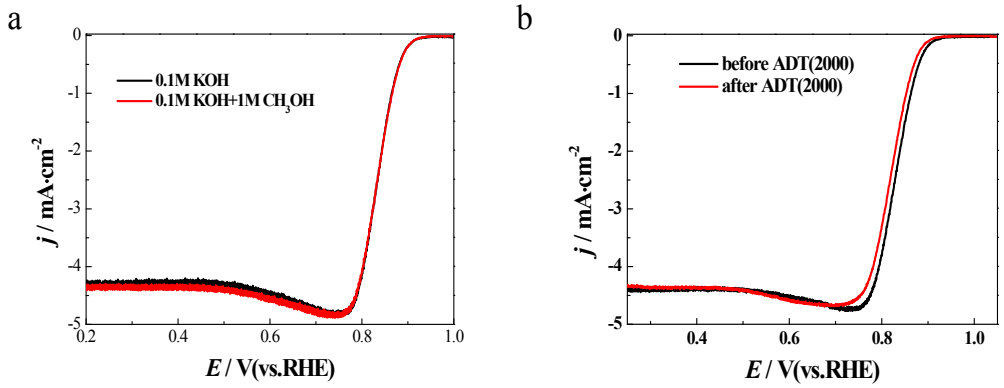

Fig. S5 Polarization curves illustrating (a) methanol tolerance and (b) durability of the CCH-2/C hybrid catalyst. Methanol tolerance was examined in the oxygen saturated solution containing methanol (1M).

The CCH/C catalyst has excellent tolerance towards methanol; polarization curves were recorded for ORR in the presence of high concentration of methanol (1 M) and the voltammetric response is essentially the same as in the absence of methanol, confirming that the new hybrid material has excellent tolerance towards methanol (Fig.S5a). The polarization curve (Fig.S5b) obtained before and after 2000 cycles shows no decrease in the limiting current. Interestingly, no significant change in the onset potential was noticed; only 10 mV negative shifting in the half-wave potential was noticed after extensive 2000 cycles, implying the high durability of the hybrid catalyst.

Figure S6

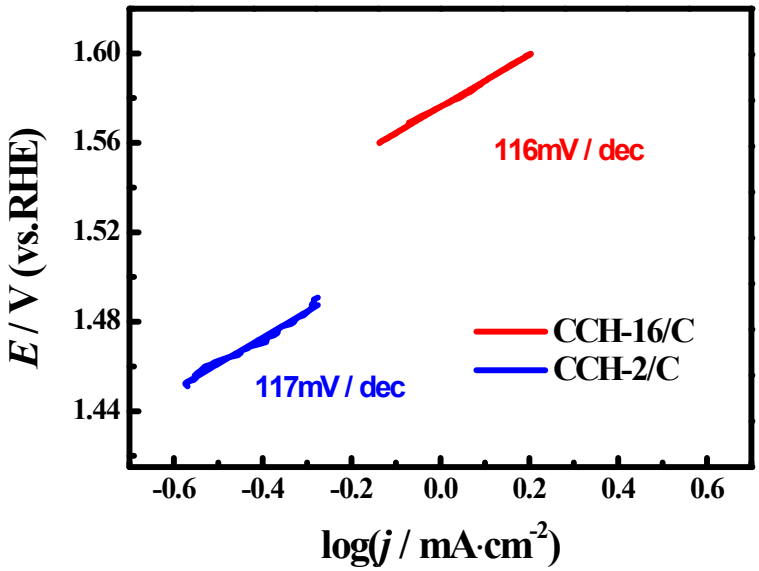

Fig.S6 Tafel plots of OER catalyzed by CCH-2/C catalyst and CCH-16/C catalyst.

Figure S7

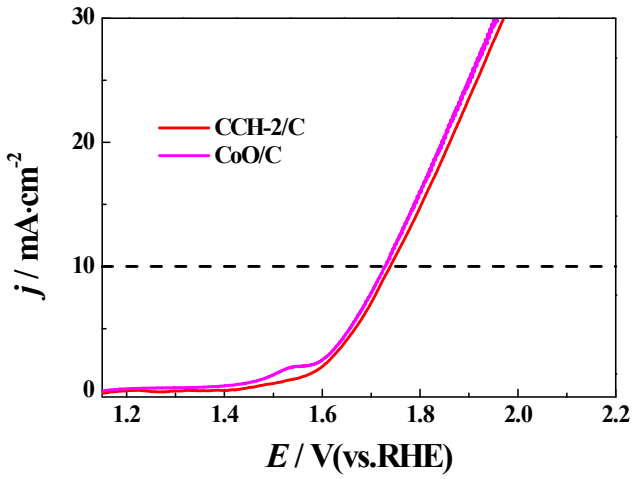

Fig.S7 LSV curves of CCH-2/C and CoO/C (loading 0.18 mg Co cm^{-2}) catalysts in O_2-saturated 0.1 M KOH with a sweep rate of 10 mV s^{-1} at 1600 rpm.

Reference

1 Y. Wang, H. J. Zhang, L. Lu, L. P. Stubbs, C. C. Wong and J. Y. Lin, *Acs Nano*, 2010, **4**, 4753-4761.