Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting information

Flexible and rechargeable Zn–air batteries based on green feedstocks with a 75% round-trip efficiency

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Experimental

All chemicals, including 10 wt.% Pt/C catalyst, PVA (M_W 30000–70000), urea, $Co(NO_3)_2 \cdot 6H_2O$, glucose, and methylcellulose, were purchased from Sigma-Aldrich and used without further purification. The 20 wt.% Pt/C catalyst was received from Sunrise Power Co., Ltd., China.

Material characterization

The compositions and phases of the Co/3D-NC, Co@Co_3O_4/3D-NC, and Co_3O_4/3D-NC samples were identified by powder wide-angle XRD using Rigaku Ultima IV diffractometer with Cu Kα radiation (λ= 0.154178 nm). SEM (JEOL-6700F) and TEM (JEOL JEM-2010) were used to characterize the surface textual properties. XPS measurements were performed on a VG Scienta R3000 XPS using monochromatic Al Kα X-ray source. All binding energies were calibrated by setting C 1s at 284.8 eV. Raman measurements were carried out on a RM 1000 (Ranishaw, UK) spectrometer.

Synthesis of Co/3D-NC, Co/Co_3O_4/3D-NC and Co_3O_4/3D-NC

Co nanocomposites embedded on 3D nitrogen-doped carbon were synthesized by a simple pyrolysis approach. In a typical synthesis, 5.6 mmol $Co(NO_3)_2 \cdot 6H_2O$, 0.2 mol urea, and 55.6 mmol glucose were dissolved in 15 mL of deionized water. The clarified solution was dried at 80 °C overnight and then carbonized at 700 °C under a N_2 atmosphere for 5 h. The pyrolytic products were denoted Co/3D-NC. Finally, the obtained Co/3D-NC was oxidized at a different pyrolysis temperature (250 and

300 °C) in the air for 0.5 h to obtain Co/Co_3O_4/3D-NC and Co_3O_4/3D-NC, respectively.

Preparation of the gel polymer electrolyte

The gel was prepared from 5 g of commercial PVA and 0.5 g methylcellulose, which were fully dissolved in 95 mL of distilled water at 90 °C by magnetic stirring for about 2 h. After cooling to room temperature, the homogeneous solution was used for solution casting to form the polymer membranes. Finally, the methylcellulose modified solid-state electrolyte was obtained by immersing the membrane in a 6 M KOH solution, followed by equilibration for 24 h.

Electrochemical measurements

For the preparation of the working electrode, 5 mg of the catalyst powder was dispersed in 1 mL of a 3:1 v/v water/isopropanol solution. Subsequently, 45 μL of a 5 wt.% Nafion solution was added. The mixed solution was sonicated for at least 1 h to obtain a homogeneous ink. The working electrode was prepared by uniformly drop-casting 8 μL of the catalyst ink onto the glass carbon (GC) electrode and then dried at room temperature overnight. A freshly prepared 0.1 M KOH aqueous solution was used as the electrolyte, which was continuously purged with pure O_2 during the tests. Linear sweep voltammetry (LSV) and Tafel plot measurements were carried out using a conventional three-electrode system with a flowing gas system, a Pt wire as the counter electrode, and an Ag/AgCl (3M KCl) electrode as the reference electrode. The ORR performance of the catalyst was obtained by sweeping the potential from 0.1 to -0.8 V (vs. Ag/AgCl) at different disk rotation speeds at a scan rate of 10 mV s^{-1}. The OER performance was determined at 1600 rpm using same scan rate. The potentials reported in our study were referenced to the reversible hydrogen electrode (RHE) through RHE calibration, $E(\text{RHE}) = E(\text{Ag/AgCl}) + 0.951$ V.

Fabrication of aqueous ZABs

The measurements on the Zn–air batteries were performed using an IVIUMSTAT electrochemical Interface & Impedance Analyzer at room temperature. Briefly, a zinc foil was used as the anode and the catalyst was loaded onto the gas diffusion layer with a loading of 2.0 mg cm^{-2}. The electrolyte was 6.0 M KOH.

Fabrication of flexible SZABs

A zinc foil with a thickness of 0.2 mm was used as the anode. The bifunctional electrocatalysts were coated on a carbon cloth and used as the gas diffusion layer, with a catalyst loading of 1 mg cm^{-2}. The SZABs were obtained by placing the electrodes face-to-face with the solid-state methylcellulose-modified polymer electrolytes. The discharge polarization curves and galvanostatic charge-discharge profiles were measured using a battery tester (LANHE CT2001A).

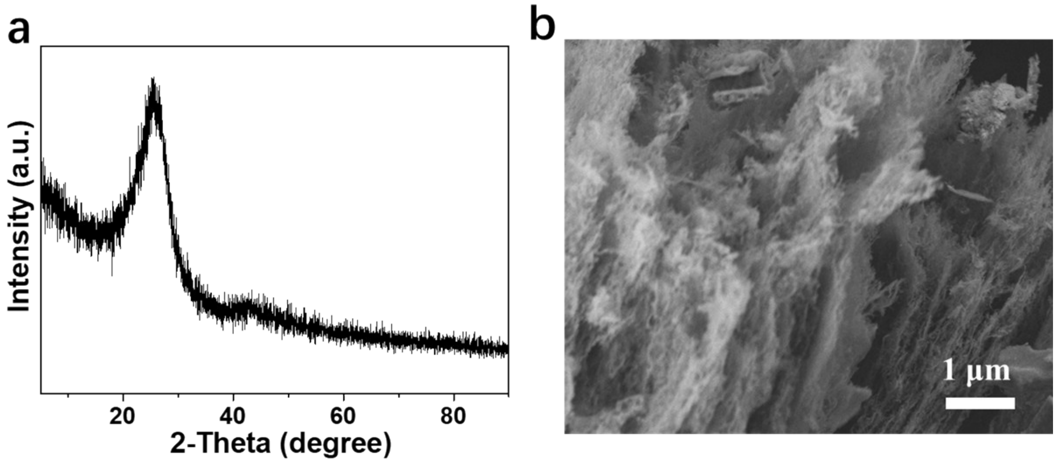

Fig. S1. (a) XRD spectrum and (b) SEM image of 3D-NC. The XRD pattern displays a diffraction peak at 26.1°, which matches well with the graphitic carbon phase (JCPDS No. 41-1487).

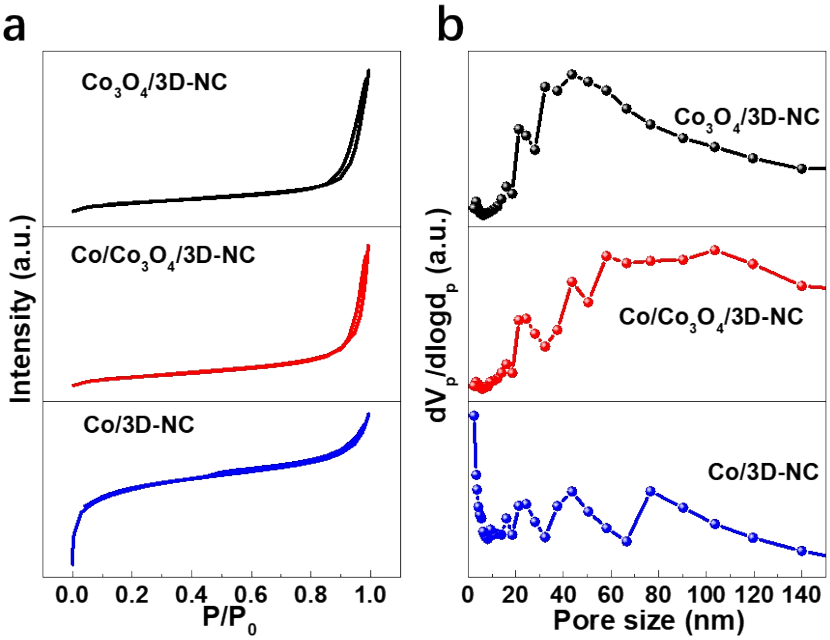

Fig. S2. (a) N_2 adsorption-desorption isotherms and (b) Pore size distribution curves of Co/3D-NC, Co/Co_3O_4/3D-NC and Co_3O_4/3D-NC.

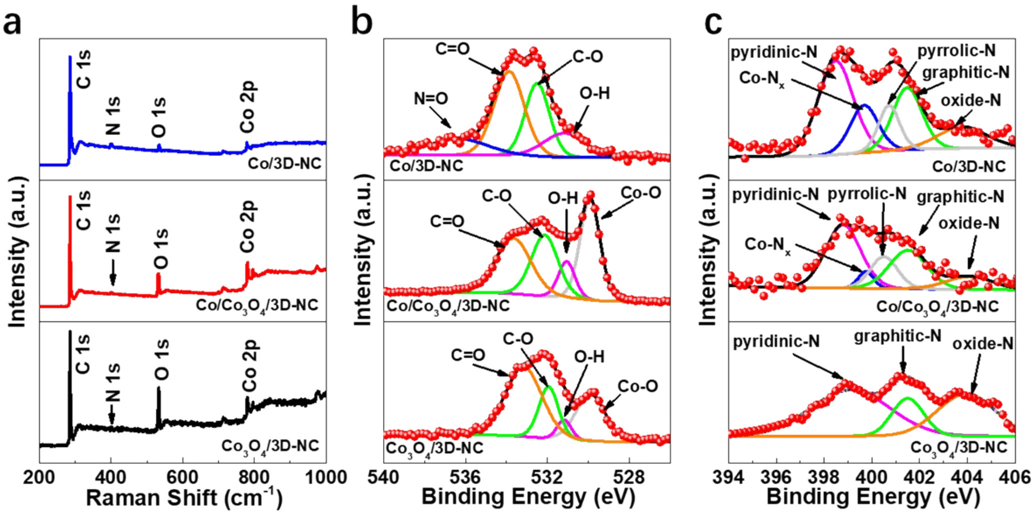

Fig. S3. (a) XPS survey spectra, high-resolution (b) O 1s and (c) N 1s XPS spectra of of Co/3D-NC, Co/Co_3O_4/3D-NC and Co_3O_4/3D-NC.

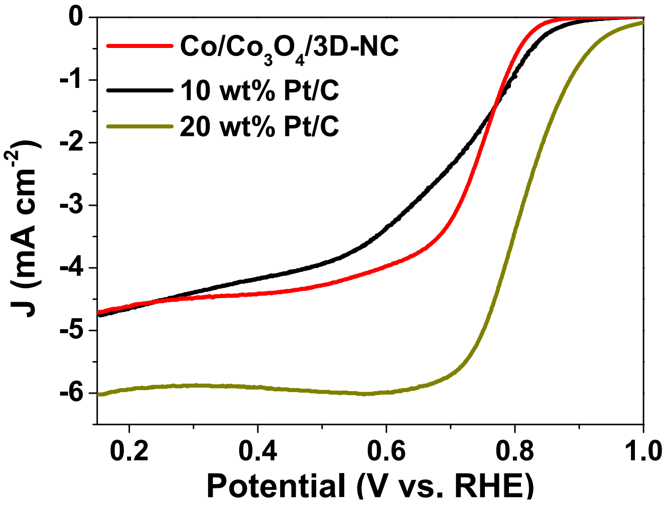

Fig. S4. Comparison of ORR polarization curves of Co/Co_3O_4/3D-NC with commercial 10 wt.% and 20 wt.% Pt/C.

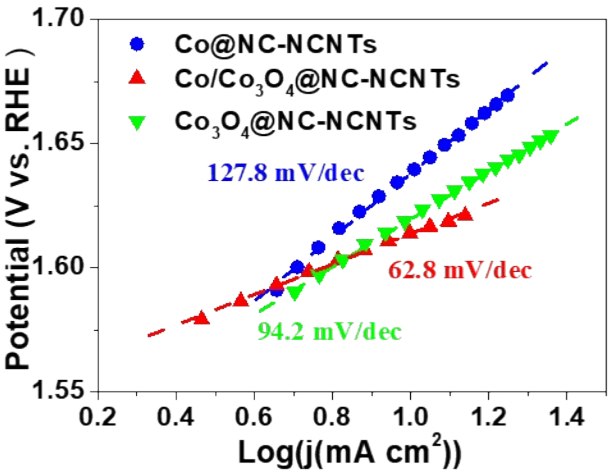

Fig. S5. The Tafel slop of Co/3D-NC, Co/Co_3O_4/3D-NC and Co_3O_4/3D-NC for OER process.

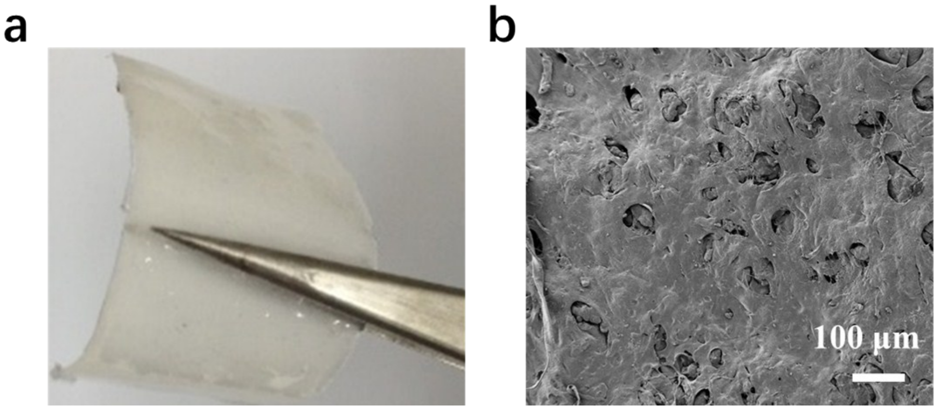

Fig. S6. Photo image (a) and SEM image (b) of methylcellulose modified PVA membrane.