Trace Metals Dramatically Boost Oxygen Electrocatalysis of N-doped Coal-derived Carbon for Zinc-air Battery

Huimin Liu[a], Xinning Huang[b], Zhenjie Lu[a], Tao Wang[c], Yaming Zhu[a], Junxia Cheng[a], Yue Wang[a], Dongling Wu[c,*], Zhenyu Sun[d,*] , Alex W. Robertson[e], and Xingxing Chen[a,*]

[a] *Research Group of Functional Materials for Electrochemical Energy Conversion, School of Chemical Engineering, University of Science and Technology Liaoning, Qianshan Middle Road 185, 114051 Anshan, P. R. China*

[b] *Engineering Training Center, University of Science and Technology Liaoning, Qianshan Road 185, 114051 Anshan, P. R. China*

[c] *Key Laboratory of Energy Materials Chemistry, Institute of Applied Chemistry, Xinjiang University, Shengli Road 14, 830046 Urumqi, P. R. China*

[d] *State Key Laboratory of Organic–Inorganic Composites, College of Chemical Engineering, Beijing University of Chemical Technology, Beijing 100029, P. R. China*

[e] *Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, U.K.*

* *Corresponding authors. E-mail: xingchenstar79@163.com (X. X. Chen), wudl@xju.edu.cn (D. L. Wu), sunzy@mail.buct.edu.cn (Z.Y. Sun)*

Experimental

Chemicals and solutions

Brown coal was obtained from Hailar Coal Mine, Inner Mongolia, China. Its proximate analysis and EDX analysis can be found in Table S1 and Figure S1 [11]. NaOH (≥96%), HF (≥40.0%), HCl (35%), $ZnCl_2$ (98%), ethanol (≥99.8%), and KNO_3 (analytical reagent, AR) were purchased from Tianjin Rgent® Chemicals Co. Ltd. (China). Nafion (5%) and Pt/C (20 wt%) were bought from Sigma-Aldrich (China). $FeCl_3{\cdot}6H_2O$ (AR) was bought from Sinopharm Chemical Reagent Co. Ltd. (China). $SiCl_4$ (98%), $C_4H_6CuO_4{\cdot}H_2O$ (99.0%), $AlCl_3$ (99%), ethanol (99.5%) were purchased from Shanghai Macklin Biochemical Co. Ltd. (China), KOH (≥95%), $Co(NO_3)_2{\cdot}6H_2O$ (ACS), $NiN_2O_6{\cdot}6H_2O$ (98%), $MgCl_2$ (99.9%), and $CaCl_2$ (>96%) were obtained from Aladdin Reagent Co. Ltd. (China). $C_4H_6MnO_4{\cdot}4H_2O$ (99.0%） was supplied from Tianjin Damao Chemical Reagent Factory. All aqueous solutions were prepared using triple-distilled deionized water.

Sample preparation

The original brown coal (OC) was first crushed by ball milling followed by drying in an oven at 378 K for 4 h to obtain air-dried coal. 7.0 g of the crushed coal was then added to 140 mL of triple-distilled deionized water and left at room temperature for 12 h with continuous stirring of the solution. The suspension was filtered and washed with water. To 6 g of the washed coal was added to 36 mL of 5.4 M HCl. The suspension was continuously stirred for 24 h at room temperature, afterwards, the sample was filtered and washed with water until no Cl^- was measurable in the waste solution detected by adding a drop of $AgNO_3$ to observe the formation of AgCl precipitation. To 5 g of the HCl-washed coal was added 40 mL of HF solution (40 wt%) and stirred at room temperature for 24 h. The purified coal (PC) was finally obtained after filtration and further washed with water until the solution reached a pH of 7. PC was then added to different trace element precursors ($FeCl_3.6H_2O$, $AlCl_3$, $CaCl_2$, KNO_3, $Co(NO_3)_2{\cdot}6H_2O$, $SiCl_4$, $MgCl_2$, $C_4H_6CuO_4{\cdot}H_2O$, $NiN_2O_6{\cdot}6H_2O$, or $C_4H_6MnO_4{\cdot}4H_2O$) in an ethanol solution. The trace element (Fe, Al, Ca, K, Co, Si, Mg, Cu, Ni, or Mn) to PC weight ratio was 1 wt%, respectively. After thorough mixing of the suspension, it was dried at room temperature overnight. The samples were individually put in a quartz boat and inserted into a chemical vapor deposition (CVD) reactor. The reactor was first flushed with Ar at room temperature for 15 min to remove air, and then heated in a stream of NH_3 and Ar (1:9 volume ratio) at a flow rate of 100 mL min^{-1} to 1050 °C at a heating rate of 10 °C min^{-1}. The reactor was then held at this temperature for 2 h and cooled down in the same NH_3/Ar atmosphere at a flow rate of 100 mL min^{-1} to room temperature. The prepared catalysts are denoted as NPCC (N-doped purified coal-derived carbon), without the addition of trace elements, as the reference sample, Fe-NPCC, Al-NPCC, Ca-NPCC, K-NPCC, Co-NPCC, Si-NPCC, Mg-NPCC, Cu-NPCC, Ni-NPCC, and Mn-NPCC.

For investigation of the removal of Al-removal from the Al-NPCC sample, the sample was immersed in 0.1 M KOH for 48 h at room temperature, followed by washing with water until a pH of 7 was reached. The sample was dried at 80 °C in vacuum for 24 h before N_2 adsorption-desorption measurements at 77 K.

Electrochemical measurements

The electrochemical performance of the prepared catalysts was evaluated using a bipotentiostat (CHI 760E, CH Instruments, China) in combination with a speed-control unit (PINE Research Instrumentation, USA). 1 mL of the sample suspension containing 5 mg of the catalyst powder, 20 μL Nafion (5%), 490 μL ethanol, and 490 μL water was prepared with the aid of ultrasonication for 30 min. A rotating ring disk electrode (RRDE) with glassy carbon (A = 0.2472 cm^2) as the disk and Pt (A = 0.1866 cm^2) as the ring, and a glassy carbon rotating disk electrode (RDE) (A = 0.196 cm^2) served as the working electrode on which the catalyst ink (10.4 μL for the RRDE or 8.3 μL for the RDE) were drop coated to get a final catalyst loading of 0.21 mg cm^{-2}. A Ag/AgCl/3M KCl electrode and a glassy carbon plate were used as reference electrode and counter electrode, respectively. Before each measurement, the electrodes were polished on a polishing cloth using Al_2O_3 paste of 0.3 μm grain size followed by rinsing with triple-distilled deionized water. The electrode was first electrochemically preconditioned in Ar-saturated 0.1 M NaOH by running cyclic voltammetry (CV) in the potential range of 0 to -1 V vs. Ag/AgCl/3M KCl at a scan rate of 100 mV s^{-1} until reproducible voltammograms were obtained (typically 20 cycles). Linear sweep voltammetry (LSV) measurements were carried out in the same electrolyte saturated, first with Ar to record the background current, then with O_2 within the same potential window at a rotation speed of 1600 rpm to record the performance of the catalysts for ORR. During the ORR activity measurements, the Pt-ring of RRDE was meanwhile held at a fixed potential of 0.4 V to study H_2O_2 production during ORR. To evaluate the OER performance of the catalysts, LSV was carried out between 0 to 1.2 V vs. Ag/AgCl/3M KCl at a scan rate of 5 mV s^{-1} in O_2-saturated 0.1 M NaOH with a rotationg speed of 1600 rpm. Kinetic analysis of the ORR was performed by Koutecky Levich (K-L) analysis using the equation given below [11]:

$$1 / j = 1 / j_L + 1 / j_K = 1 / B\omega^{1/2} + 1 / j_K$$

$$B = 0.62n\mathrm{F}C_0D^{2/3}V^{-1/6}$$

$$j_K = nFkC_0$$

where j is the measured current density at the glassy carbon, j_K and j_L are the kinetic and diffusion-limiting current densities, respectively, ω is the angular velocity of the electrode, B is the Levich slope, n is the number of electrons transferred in the ORR process, F is the Faraday constant (96485 C mol^{-1}), D is the diffusion coefficient of dissolved oxygen in the electrolyte, which for a 0.1 M NaOH solution is 1.90×10^{-5} cm^2 s^{-1}, and C_0 is the concentration of oxygen in the electrolyte (1.2×10^{-6} mol cm^{-3}), v is the kinematic viscosity of the electrolyte (0.01 cm^2 s^{-1}), and k is the rate constant for the ORR (m s^{-1}).

The yield of the intermediate product (% HO_2^-) and the number of transferred electrons (n) during the ORR were calculated from the RRDE data using the following two equations [11]:

HO_2^- (%) = 200 * $\{(I_R / N_0) / [(I_R/N_0) + I_D]\}$

$n = 4 * I_D / [(I_R/N_0) + I_D]$

where I_D is the disk current, I_R is the ring current, and N_0 is the collection efficiency of the ring electrode (0.37) (Pine Research Instrumentation, USA). The long-term stability of the catalysts for the ORR was tested by applying a constant current density at -1 mA cm^{-2} for 280 h in O_2-saturated 0.1 M NaOH. Methanol poisoning experiments were carried out to check the effect of methanol crossover by addition of 3 M methanol (1% v/v) into the electrolyte under magnetic stirring while the electrode was poised at a constant potential of -0.2 V. For the OER, the stability of the catalysts was evaluated by running cyclic voltammograms in the potential range of 0 to 1.2 V at a scan rate of 100 mV s^{-1} for 1000 cycles and recording the linear sweep voltammograms at a scan rate of 5 mV s^{-1} before and after the 1000 CV cycles.

The potentials reported in the experimental description are with respect to the Ag/AgCl/3 M KCl reference electrode, while all the potentials reported in the following results were corrected for the resistance of the solution (iR_s) and converted to the reversible hydrogen electrode (RHE) by the equation [11]:

$E = E_{Ag/AgCl} + E^0_{Ag/AgCl} + 0.059*pH-iR_s$

where E is potential versus RHE, $E_{Ag/AgCl}$ is the measured potential vs. Ag/AgCl/3M KCl, $E^0_{Ag/AgCl}$ is the standard potential of the Ag/AgCl/3M KCl at zero pH (0.207 V) on the standard hydrogen electrode (SHE) scale, R_s is the resistance of the electrolyte. Rechargeable Zn–air batteries were assembled by using a zinc-foil as the anode, and the catalyst supported on carbon paper as the air cathode, and 6 M KOH containing 0.2 M $ZnCl_2$ as the electrolyte. The catalyst ink was sprayed onto the carbon paper to an average loading of 1.0 mg cm^{-2} and dried at room temperature. The charge/discharge performance and cycling stability were measured at an alternating current density of 5 mA cm^{-2} with each cycle lasting 600 s for 500 cycles in total.

Characterization of samples

Scanning electron microscopy (SEM, HITACHI SU8010) and high-resolution transmission electron microscopy (TEM, HITACHI H-600) were used to characterize the morphology and structure of the as-produced samples. Raman spectra were recorded using a Bruker Vertex 70 system (532 nm laser). X-ray diffraction (XRD) measurements were carried out on a Bruker D8 X-ray diffractometer in the 2θ range from 10 to 80°, with a Cu K_α radiation ($\lambda = 1.5418$ Å) source. X-ray photoelectron spectroscopy (XPS) measurements were carried out using an ESCALab 250Xi electron spectrometer equipped with a 300 W Al K_α X-ray source. Elemental analysis of C, N, H, S, and O was performed on an elemental analyzer Vario EL.

Table S1. Proximate analysis of coal sample from Hailar coal mine.

Sample	**M_{ad}[a]/%**	**A_{ad}[b]/%**	**V_{ad}[d]/%**	**V_{daf}[d]/%**	**FC_{ad}[e]/%**
Original Coal	30.87	10.30	26.46	---	32.37

[a] M_{ad}: moisture, [b] A_{ad}: ash, [c] V_{ad}: volatile matter, [d] V_{daf}: volatile matter, [e] FC_{ad}: fixed carbon (All the quantities are on a dry weight basis).

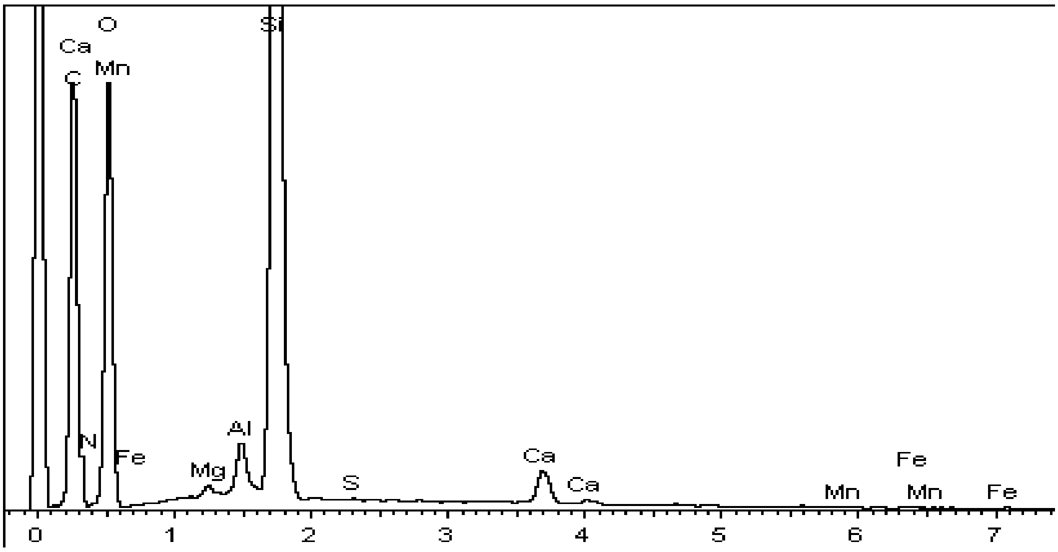
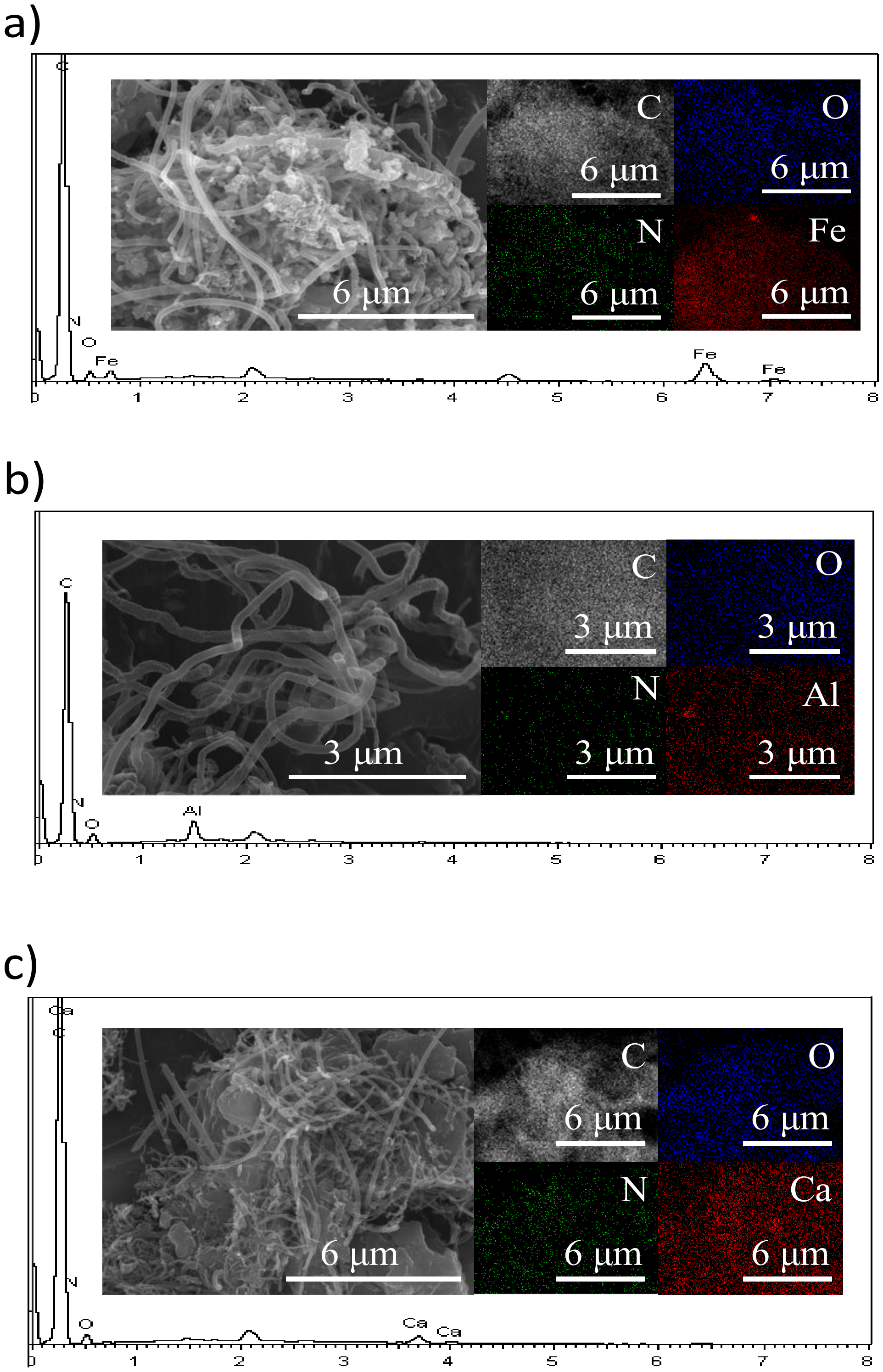


Figure S1. EDS spectrum of original coal revealing the presence of trace elements, such as Si, Ca, Mn, Fe, Al and Mg.


a)
C
N
O
Fe
Fe
Fe
0
1
2
3
4
5
6
7
8
6 µm
C
6 µm
O
6 µm
N
6 µm
Fe
6 µm
b)
C
N
O
Al
0
1
2
3
4
5
6
7
8
3 µm
C
3 µm
O
3 µm
N
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Al
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c)
Ca
C
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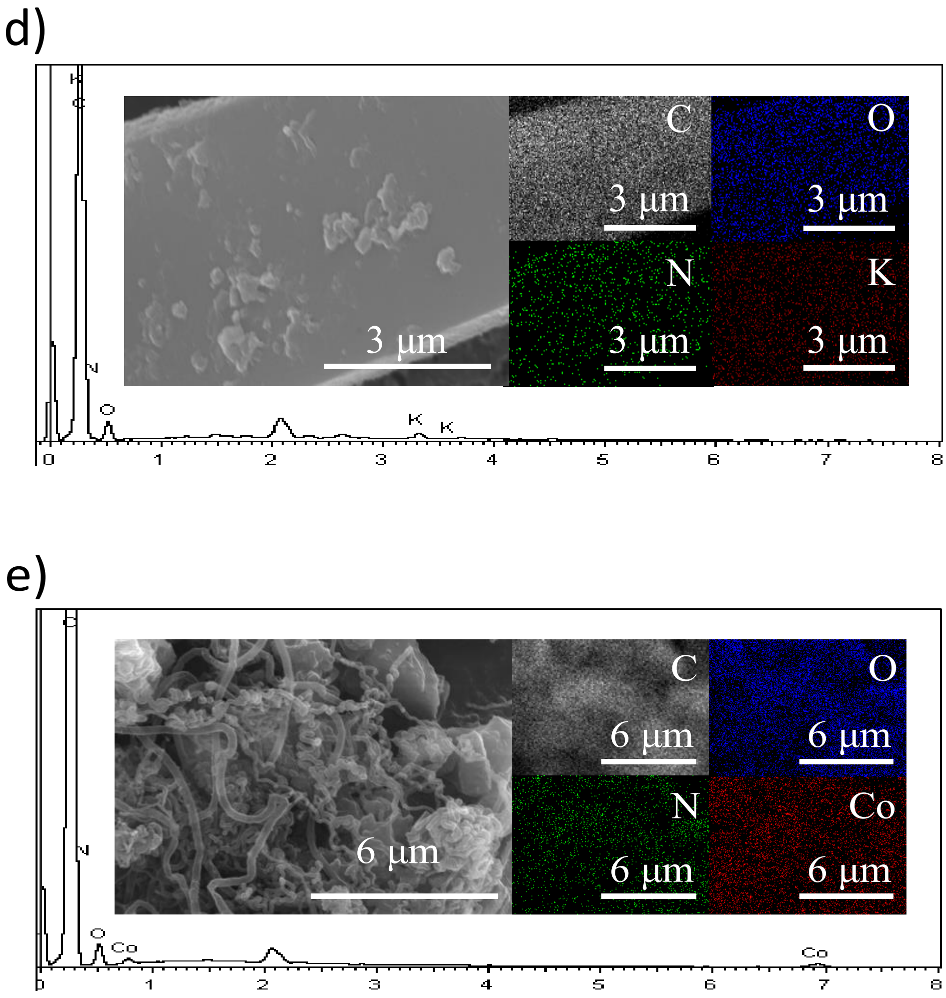

Figure S2. SEM images and the corresponding elemental mapping and EDS spectra of a) Fe-NPCC, b) Al-NPCC, c) Ca-NPCC, d) K-NPCC, e) Co-NPCC samples revealing the presence of the respective trace elements.

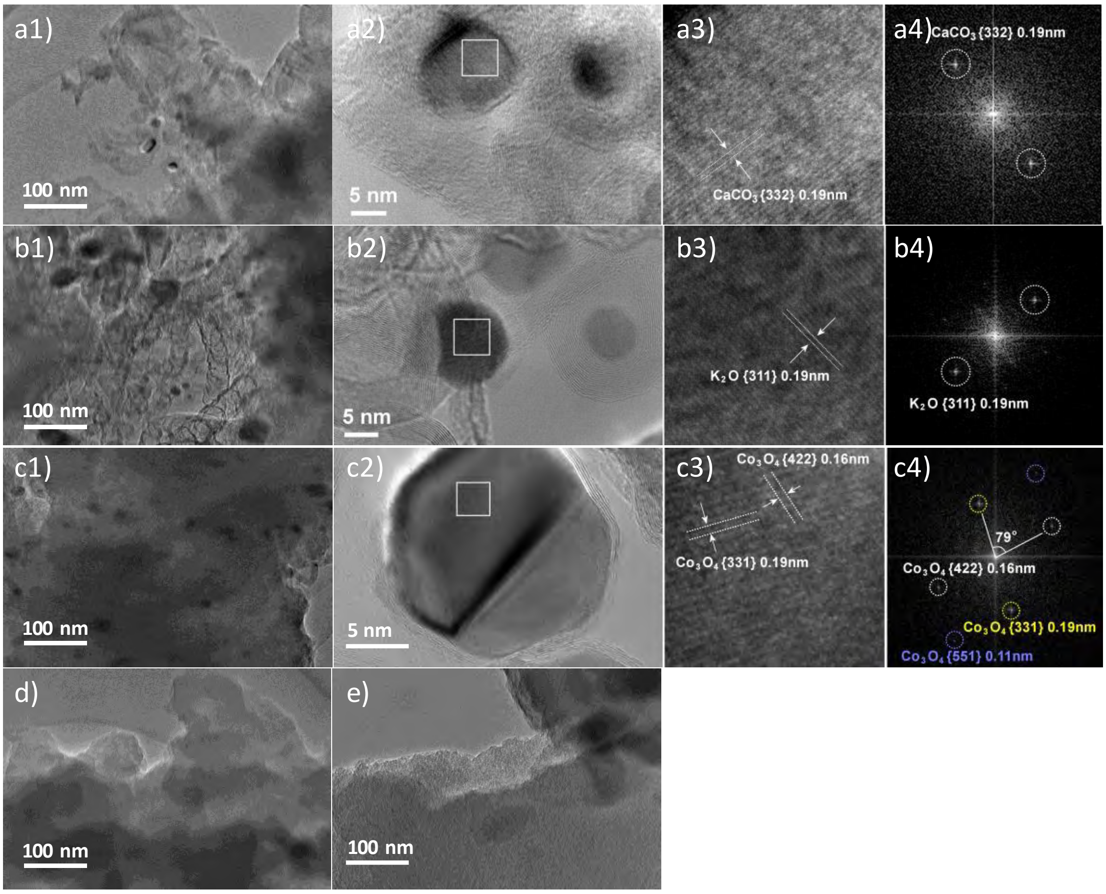

Figure S3. TEM images at different magnification scales and the representative fast Fourier transform (FFT) of a) Ca-NPCC, b) K-NPCC and c) Co-NPCC; and TEM images of d) PC and e) NPCC.

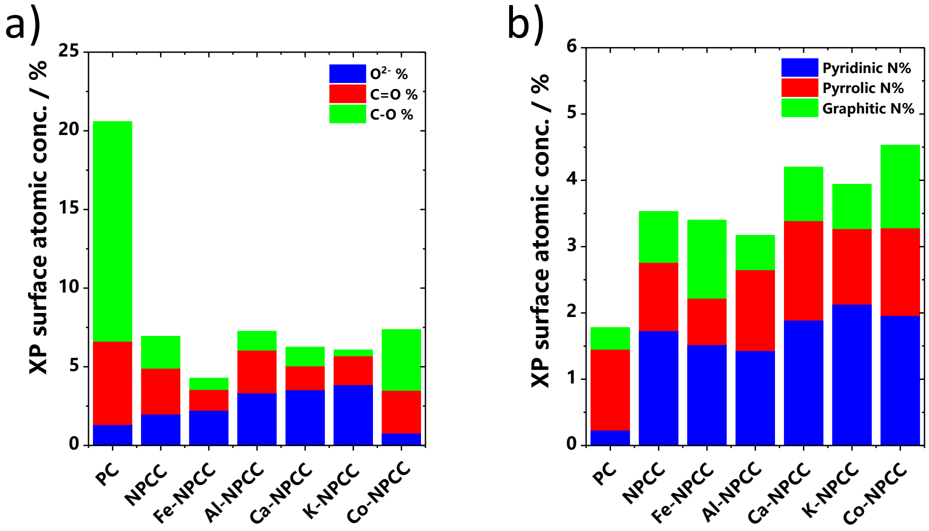

Figure S4. XPS-derived surface atomic concentrations of different a) oxygen groups and b) nitrogen groups for PC, NPCC, Fe-NPCC, Al-NPCC, Ca-NPCC, K-NPCC, and Co-NPCC.

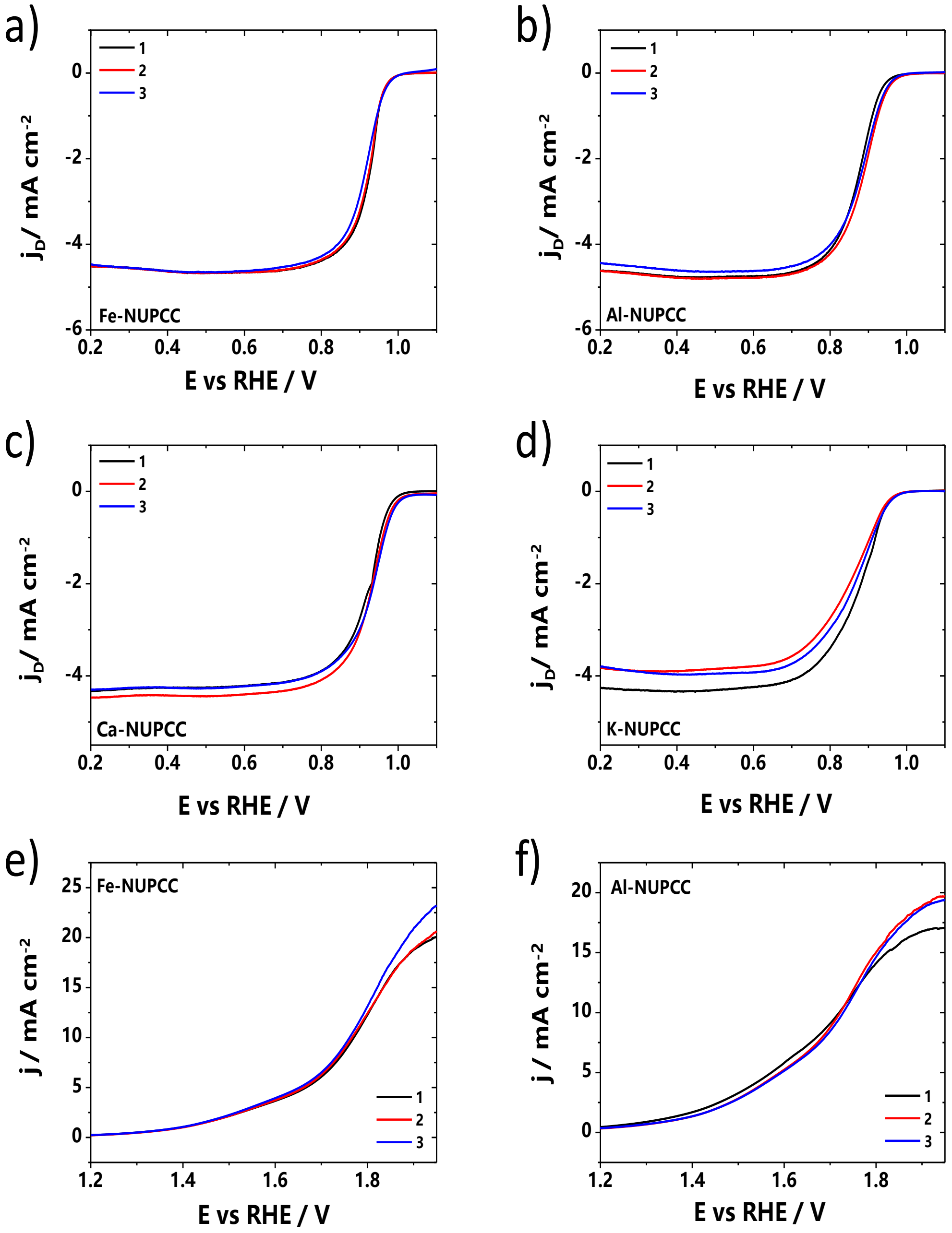

Figure S5. Linear sweep voltammograms showing the ORR performance of N-doped coal derived carbon modified with 1% wt. of the respective metals indicated a) Fe-NPCC, b) Al-NPCC, c) Ca-NPCC, d) K-NPCC, and the OER on e) Fe-NPCC and f) Al-NPCC.

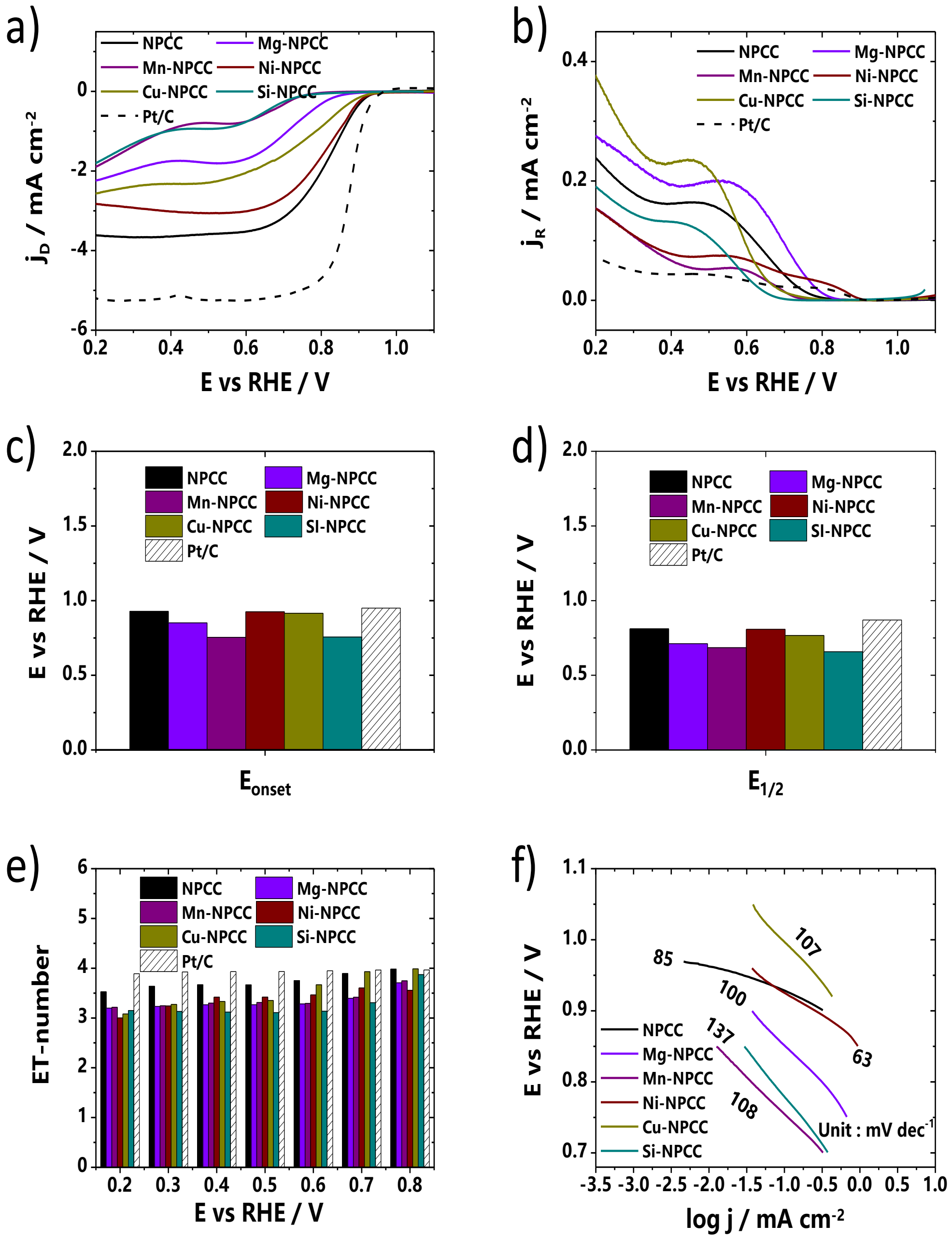

Figure S6. a) Linear sweep voltammetry (LSV) curves of NPCC and metal (Mg, Mn, Ni, Cu and Si)-doped NPCC samples showing a) the ORR and b) H_2O_2 production at 1600 rpm recorded with RRDE electrode in O_2-saturated 0.1 M NaOH solution with a scan rate of 5 mV s^{-1}, c) onset potential, d) half-wave potential, e) average electron transfer number at different potentials, f) Tafel plots derived from the ORR curves in a).

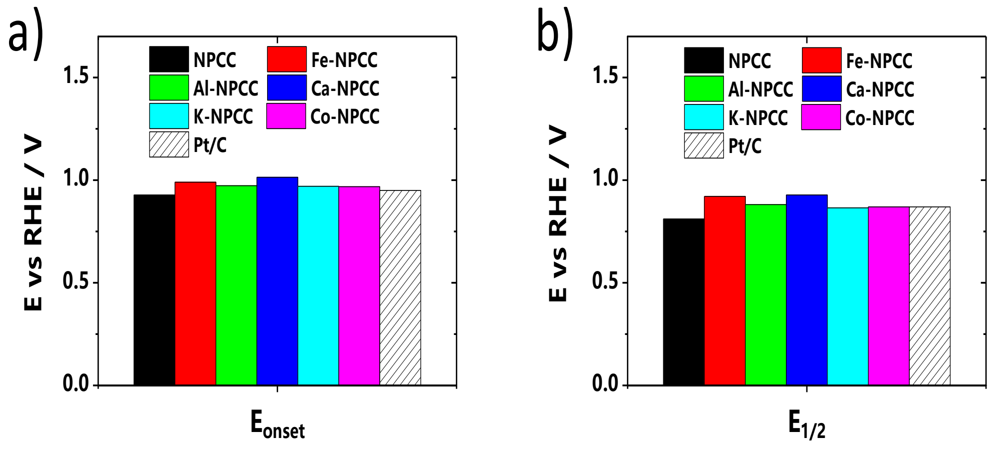

Figure S7. a) Onset potential, b) half-wave potential of the NPCC and metal (Fe, Al, Ca, K and Co)-doped NPCC samples during ORR.

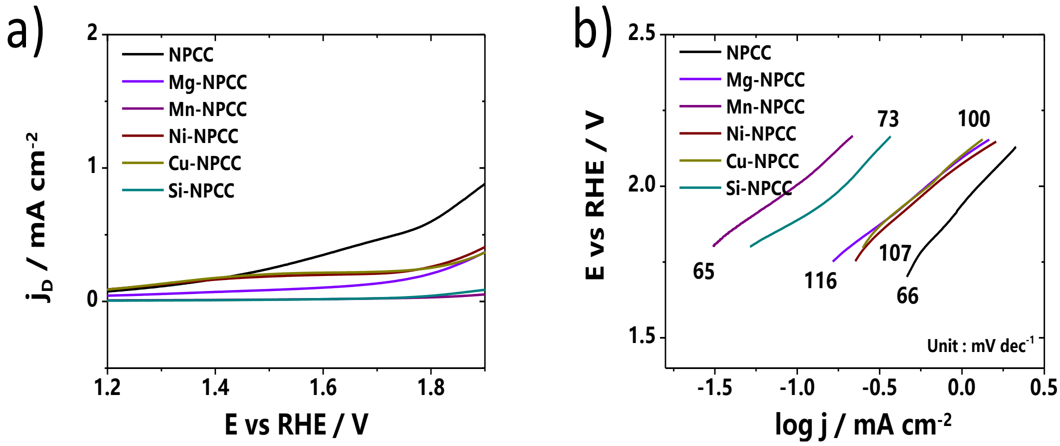

Figure S8. a) LSV curves of NPCC and metal (Mg, Mn, Ni, Cu and Si)-doped NPCC sample electrodes showing the OER of the catalysts in 0.1 M NaOH, (b) corresponding Tafel plots.

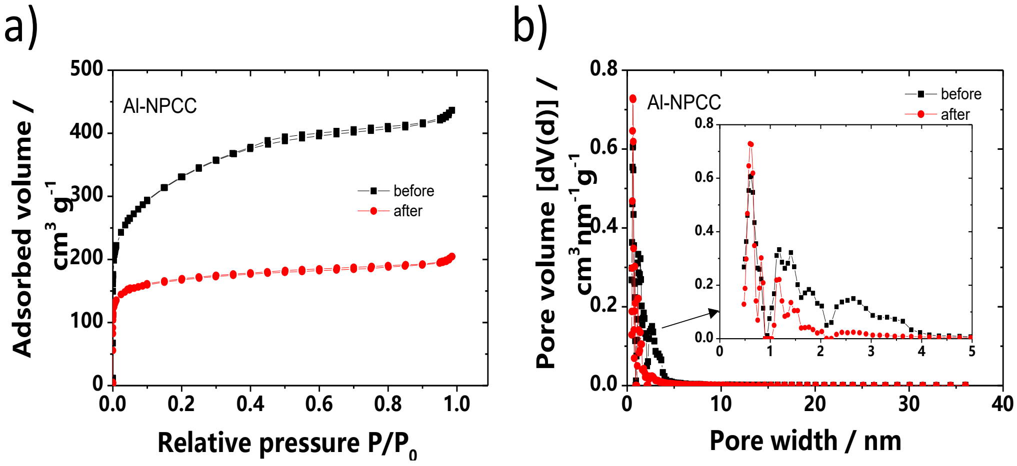

Figure S9. a) N_2 adsorption–desorption isotherms, and b) DFT pore size distribution curves of Al-NPCC before and after alkaline treatment.

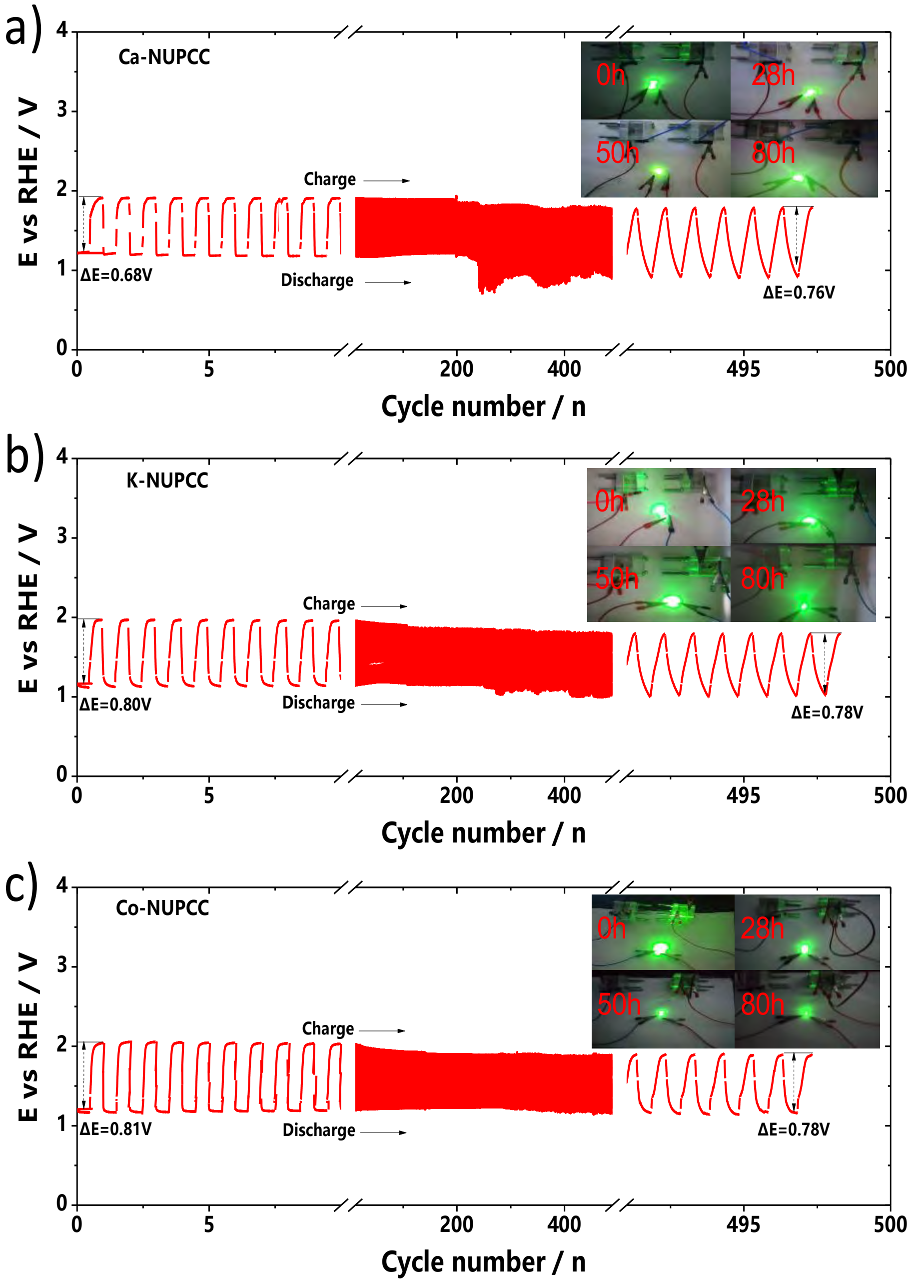

Figure S10. Photos of green LED bulbs powered by the assembled Zn–air batteries, and the performance of rechargeable Zn-air batteries based on a) Ca-NUPCC b) K-NUPCC and c) Co-NUPCC as the cathode and Zinc-foil as anode at a current density of 5 mA cm^{-2} in galvanostatic charging/discharging cycles.

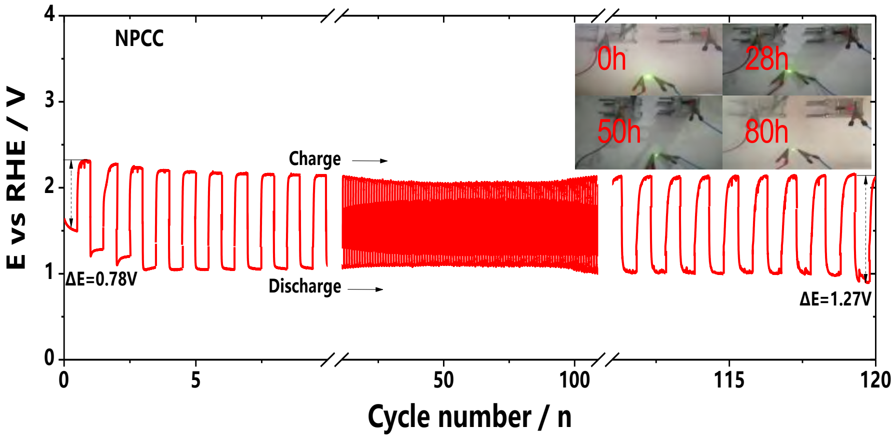

Figure S11. Photos of green LED bulbs powered by the assembled Zn–air batteries, and the performance of rechargeable Zn-air batteries based on a) Ca-NPCC b) K-NPCC and c) Co-NPCC as the cathode and Zinc-foil as anode at a current density of 5 mA cm^{-2} in galvanostatic charging/discharging cycles.