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


# Maximizing utilization of carbon fibers by bimetallic-catalytic etching and electrochemical modification for difunctional aqueous supercapacitors

*Jie Zhang[1,2], Hao Zhang[1,2], Wenli Li[1,2], Guangwen Xu[1], Yanbin Cui[1,2,]**

[1]State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China

[2] Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China

*E-mail: ybcui@ipe.ac.cn

*Corresponding author: Prof. Yanbin Cui

# Supporting information

## Experimental Section

## Preparation of Lg-CC

The Co-Fe LDH nanosheets were synthesized by a cathodic electrodeposition method in a standard three-electrode cell in which a piece of carbon cloth (2×1 $cm^2$, 0.33 mm in thickness), Pt foil, and Saturated calomel electrode (SCE) were used as the working electrode, the counter electrode, and the reference electrode, respectively. Specifically, a precursor solution of $Co(NO_3)_2 \cdot 6H_2O$ (15 mmol) and $Fe(NO_3)_3 \cdot 9H_2O$ (5 mmol) was performed at a constant potential of -1.3 V for 80 s (Temperature: ~25 °C). The obtained Co-Fe LDH/CC catalyst was then annealed at 900 °C for 80 min under the $CO_2$ atmosphere, followed by immersing in 3 M HCl overnight. Finally, the product was washed several times with DI water to remove the residual acid and dried at 60 °C. Afterwards, the O-CC sample was prepared as the similar process with that of Lg-CC except for the loading Co-Fe LDH.

## Preparation of Ralg-CC

The Lg-CC as a working electrode was activated electrochemically for 2 h at a constant potential of 2.2 V in 1 M $Na_2SO_4$ aqueous solution followed by electrochemical reduction in same system at 50 mV/s in the potential window of -1.5~0.8 V and conducted for 50 cycles to obtain Ralg-CC.

## Fabrication of flexible asymmetric supercapacitor

To balance the charge of negative electrode, onion-like $MnO_2$/CC (O-$MnO_2$/CC) positive electrode was fabricated using a step-wise electroplating method in a $Mn(CH_3COO)_2 \cdot 4H_2O$ (0.4 M) and $Na_2SO_4$ (0.6 M) solution at two different operation voltages 3 V (250 s) and 1 V (100 s) among three-electrode system containing Lg-CC as working electrode, a Pt foil as counter electrode, and a saturated calomel electrode (SCE) as reference electrode. The mass loading of the positive electrodes was controlled based on the charge balance equation ($C_+V_+=C_-V_-$). Besides, after immersing a piece of cellulose paper (NKK-MPF30AC-100, Japan) in a 1 M $Na_2SO_4$ aqueous solution for 10 min, a separator was obtained and then carefully entangled with the O-$MnO_2$/ACC and Ralg/CC. Eventually, the assembled device was wrapped with a thin parafilm to prevent the volatilization of water.

## Materials characterization

The X-ray diffraction (XRD) patterns were collected by a Rigaku Smartlab X-ray diffractometer using Cu Kα radiation. The morphology and microstructure images were observed by a JEM-7001F scanning electronic microscope (SEM) and a JEOL-2100 transmission electron microscope (TEM). Raman spectra were recorded by a confocal laser inVia Raman microscope (Renishaw, $\lambda_e$ = 514nm). The pore size distribution curve was produced from the isotherm by Density Functional Theory (NLDFT) methods. X-ray photoelectron spectroscopy (XPS) measurements of the samples were fulfilled by utilizing a Thermal-Fisher ESCALAB 250Xi X-ray spectrophotometer. The water contact angle was measured by the optical contact angle measurement system (DSA100S, KRUSS GmbH, Germany). Cyclic

voltammetry (CV), galvanostatic charge/discharge (GCD), as well as electrochemical impedance spectroscopy (EIS) of the individual electrode were carried out in a three-electrode electrochemical work station having Platinum and Saturated calomel electrode as counter and reference electrode, respectively. The aqueous electrolyte for Zn ion supercapacitor was 1M $ZnSO_4$/1 M $Na_2SO_4$.

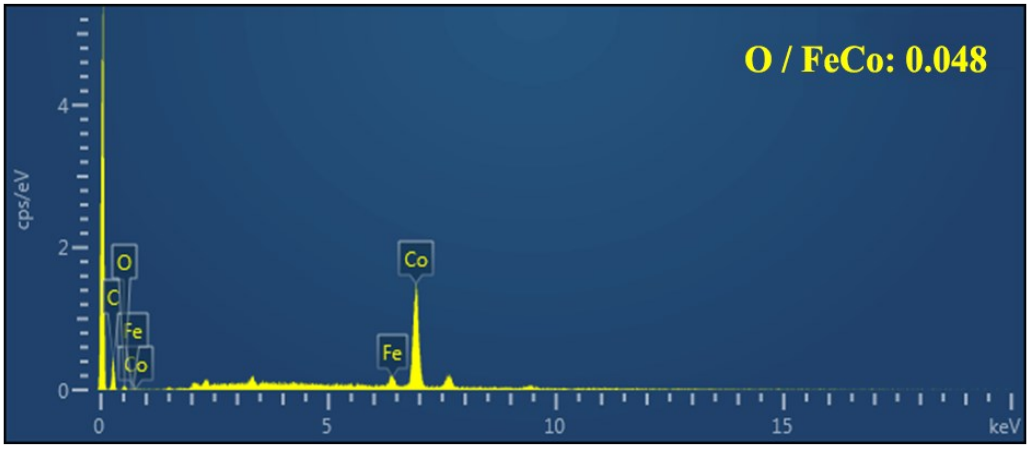


Fig. S1 EDS image of carbon cloth loaded with LDH precursors thermally treated at at 800 °C.

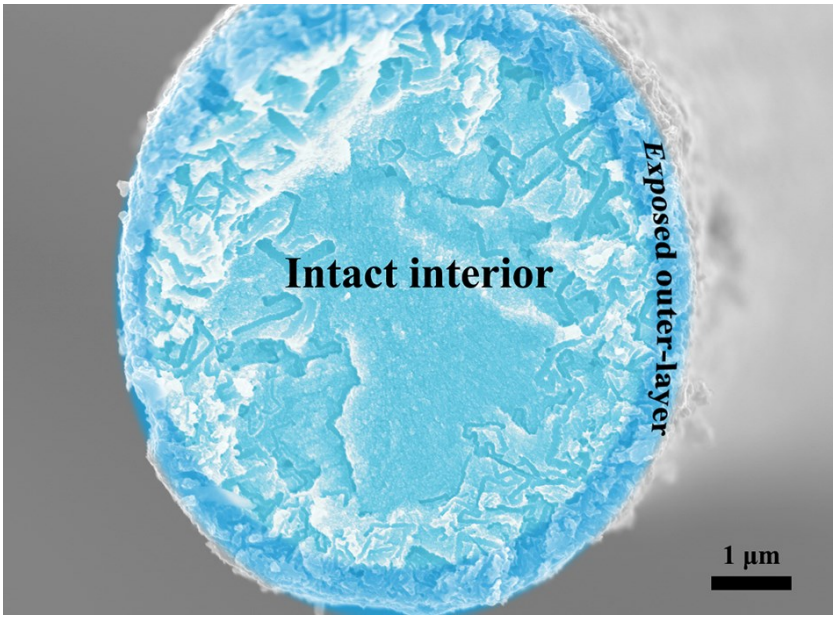


Fig. S2 Cross-sectional SEM image of Ralg-CC.

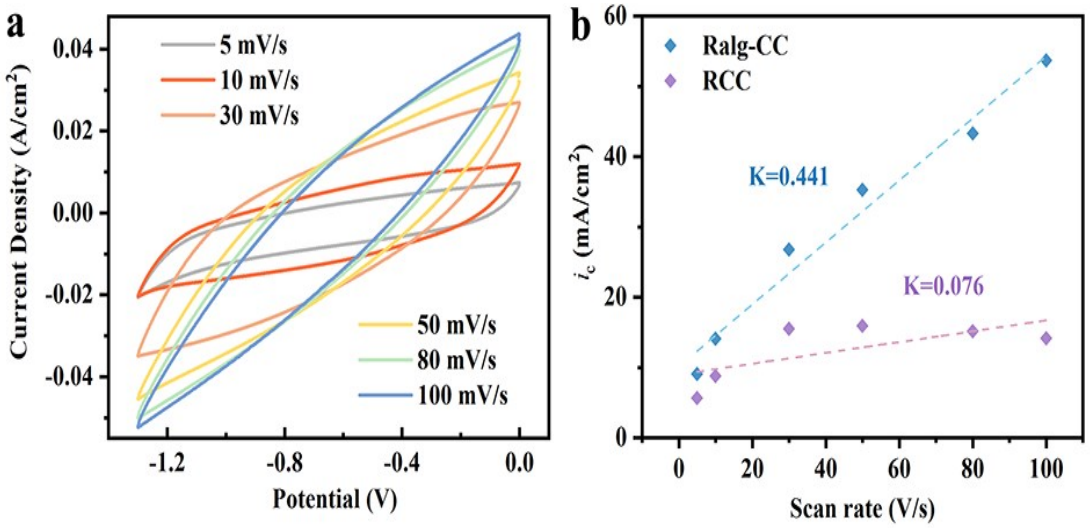


Fig. S3 (a) CV curves of RCC at various scan rates. (b) The halves of the anodic and cathodic current measured at -0.6 V vs SCE plotted as a function of scan rate.

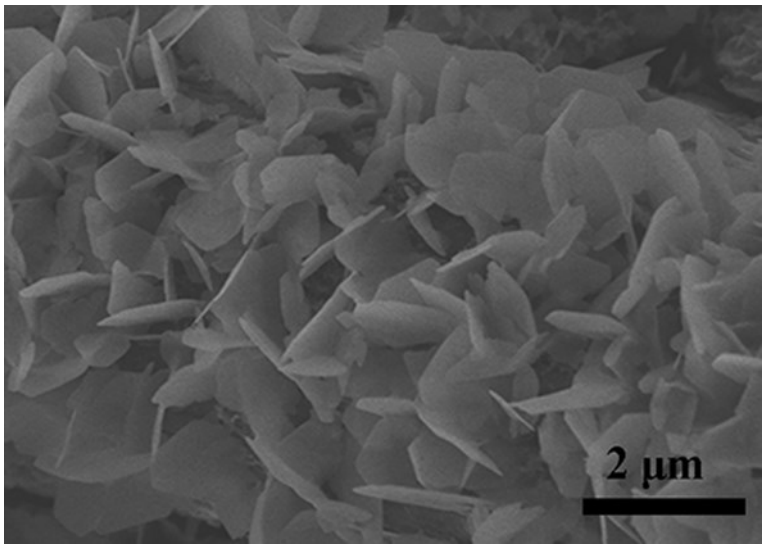


Fig. S4 SEM image of Ralg-CC after the cycling test in $ZnSO_4/Na_2SO_4$ electrolyte.

**Table S1** Comparison study on the electrochemical performance of Ralg-CC in this work with previously reported results.

| Active materials | Electrolyte | Potential（V） | Capacitance ($mF/cm^2$) | Ref. |
|---|---|---|---|---|
| **Activated Carbon Felt** | 1M $Na_2SO_4$ | -1~0 | 907.83 | [1] |

| | | | | |
|---|---|---|---|---|
| **MOF-derived N-doped carbon bubbles/carbon tube arrays** | 1M $H_2SO_4$ | 0~1 | ~370 | [2] |
| **CC@CoO@S-$Co_3O_4$** | 2M KOH | 0~0.45 | 873 | [3] |
| **PANI/ZnO/ZIF-8/Graphene/ polyester** | 3M Kcl | -0.2~1 | ~750 | [4] |
| **Co−Mn MOF** | 2M KOH | 0~0.35 | ~600 | [5] |
| **CoP/Carbon Cloth** | 1M LiCl | -0.8~0 | 571.3 | [6] |
| **Electrochemically pretreated carbon nanotube film/PPY** | 5M LiCl | -1~0.1 | 965.3 | [7] |
| **$MoS_2$@CTNT** | 0.5M $Na_2SO_4$ | -0.8~0 | 557.83 | [8] |
| **H-$VO_x$/CC** | 5M LiCl | -1~0 | 554 | [9] |
| **Ralg-CC** | **1M $Na_2SO_4$** | **-1.3~0** | **1089** | **This work** |

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