Supplementary Material

Enhanced energy efficiency in aqueous organic redox flow batteries: Carbon-based heterostructure electrodes guided by interface engineering strategy

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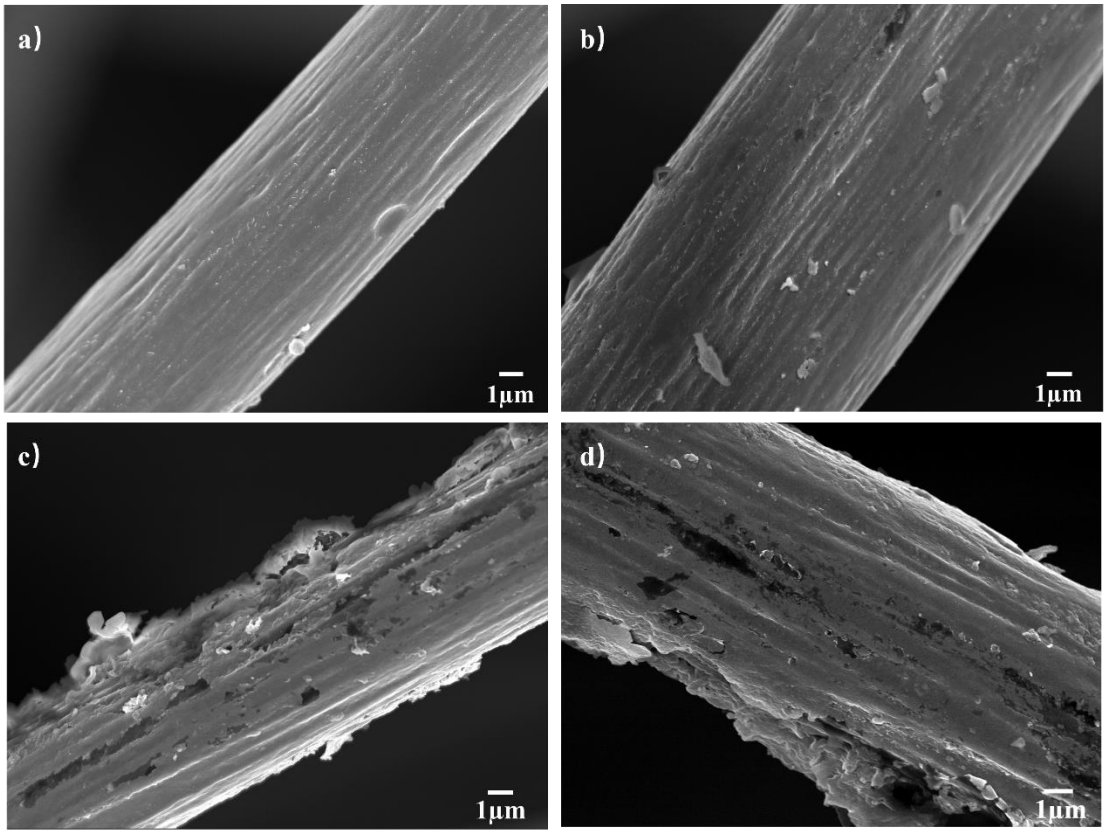

Fig. S1 SEM images of rGOCF-1(a, b) and rGOCF-5 (c, d).

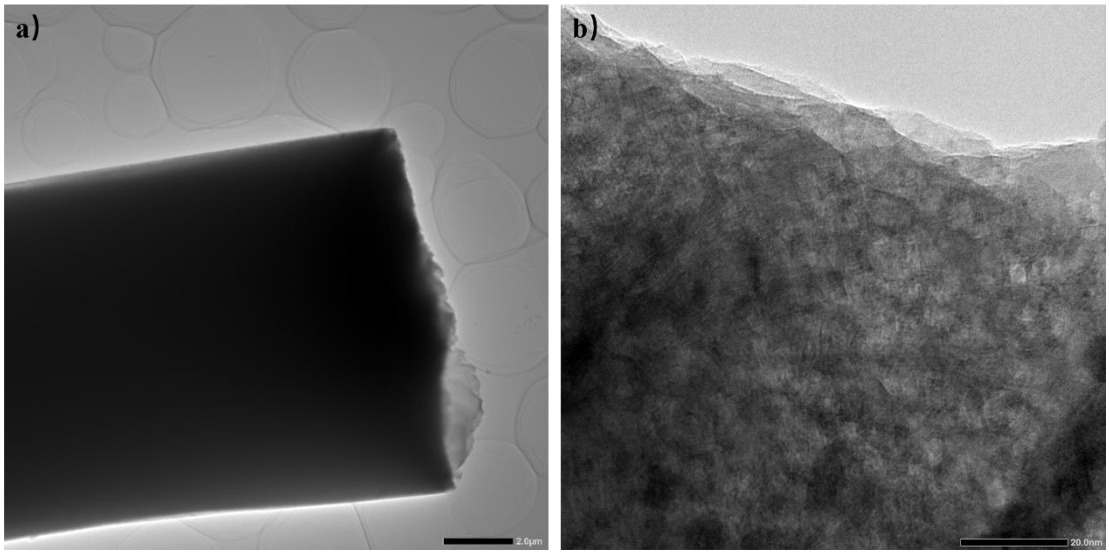

Fig. S2(a,b) The HRTEM images of CF.

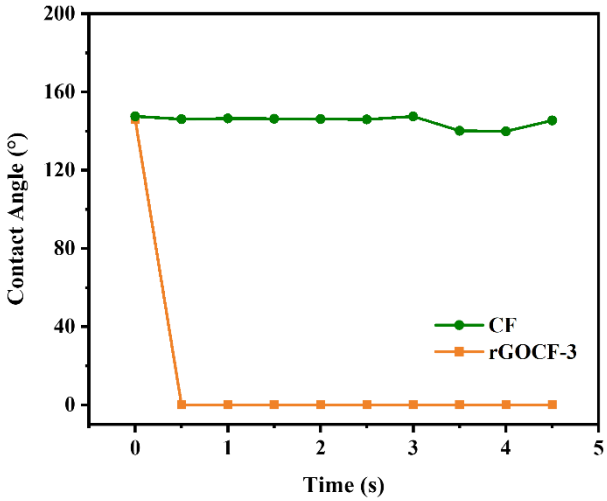

Fig. S3 Contact angles of CF and rGOCF-3.

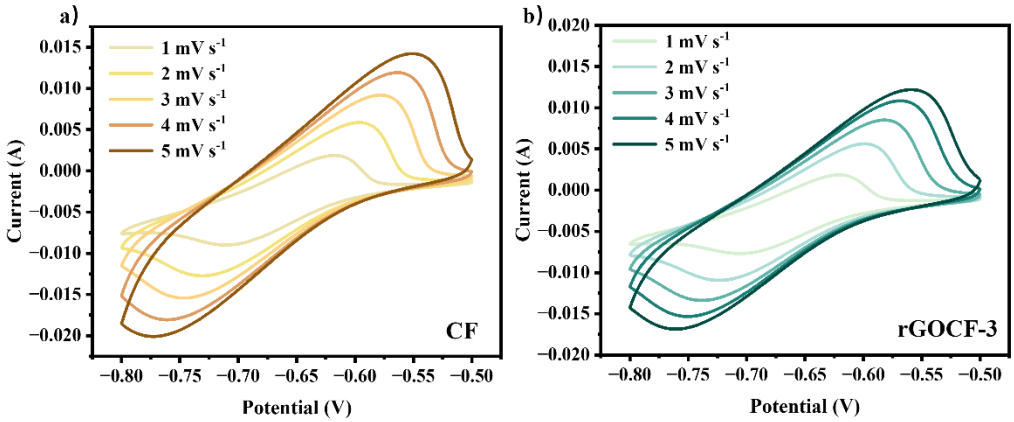

Fig. S4 CV curves of the CF (a) and rGOCF-3 (b) electrodes at various scan rates in negative reactions.

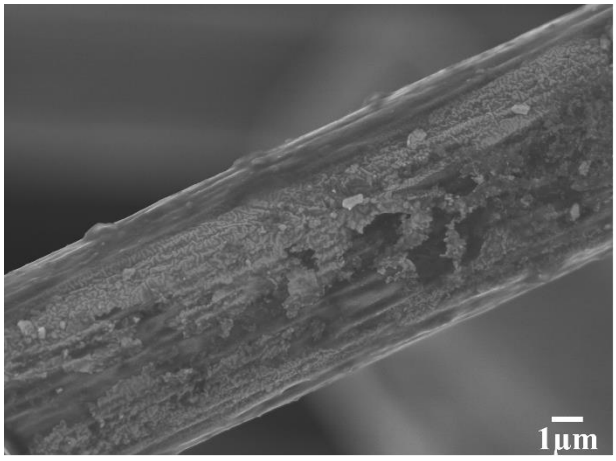

Fig. S5 The SEM images of rGOCF-3 after the cell test.

Electrode	Positive						Negative					
	I_{pa}(mA)	E_{pa}(V)	I_{pc}(mA)	E_{pc}(V)	I_{pa}/I_{pc}	ΔE(V)	I_{pa}(mA)	E_{pa}(V)	I_{pc}(mA)	E_{pc}(V)	I_{pa}/I_{pc}	ΔE(V)
CF	11.19	0.829	-8.86	0.651	1.26	0.178	1.87	-0.619	-7.74	-0.706	0.24	0.087
rGOCF-1	12.88	0.842	-10.55	0.639	1.22	0.203	1.75	-0.618	-8.55	-0.703	0.20	0.085
rGOCF-3	15.86	0.835	-13.57	0.644	1.16	0.191	2.21	-0.617	-8.79	-0.699	0.25	0.082
rGOCF-5	12.93	0.828	-10.94	0.647	1.18	0.181	2.36	-0.615	-8.32	-0.705	0.28	0.090

Table S1. Electrochemical properties obtained from CV curves of the positive and negative reactions on various electrodes.

Electrode	Positive			Negative		
	D_1 ($cm^2 s^{-1}$)	D_2 ($cm^2 s^{-1}$)	k ($cm\ s^{-1}$)	D_1 ($cm^2 s^{-1}$)	D_2 ($cm^2 s^{-1}$)	k ($cm\ s^{-1}$)
CF	2.9×10^{-4}	1.94×10^{-4}	2.37×10^{-2}	8.38×10^{-6}	1.44×10^{-4}	2.98×10^{-2}
rGOCF-3	6.13×10^{-4}	4.7×10^{-4}	2.77×10^{-2}	1.17×10^{-5}	1.85×10^{-4}	5.3×10^{-2}

(Note: D1 is the peak oxidation current, D2 is the peak reduction current)

Table S2. Electrochemical properties obtained from Equation S1-S3 of the positive and negative reactions on CF and rGOCF-3.

The Randles-Sevcik equation(Equation S1) and the Nicholson's method (Equation S2-3) are as follows:

When the measured solution temperature is 25℃ :

$$i_p = 2.69 \times 10^5 n^{\frac{3}{2}} A D^{\frac{1}{2}} C v^{\frac{1}{2}} \qquad \text{(Equation S1)}$$

$$\psi = \frac{-0.6288+0.0021\triangle E_p}{1-0.0017\triangle E_p} \qquad \text{(Equation S2)}$$

$$\psi = k\left(\frac{\pi DnF}{RT}\right)^{-\frac{1}{2}} v^{-\frac{1}{2}} \qquad \text{(Equation S3)}$$

In the formula, i_p represents the peak current in the cyclic voltammetry curve, with the unit is ampere; n is the number of electrons transferred in redox reaction; A is the area of the working electrode, in cm^{-2}; D is the diffusion coefficient of the active substance, in $cm^2\ s^{-1}$; C is the concentration of the active substance in the solution, in mol cm^{-3}; v is the scanning rate set at that time, in Vs^{-1}; ΔE_p is the peak potential difference, in mV; F is Faraday's constant, in C mol^{-1}; R is the gas constant, in J K^{-1} mol^{-1}; T is the thermodynamic temperature, in K; k is the electron transfer rate constant, in cm s^{-1}.

Energy efficiency (η) is the ratio of discharge energy to charge energy, expressed as a percentage. The calculation formula is as follows:

$$\eta = \left(\frac{E_{discharge}}{E_{charge}}\right) \times 100\% \qquad \text{(Equation S4)}$$

Carbon electrode	Electrolyte type	Current density (mA cm^{-2})	CE (%)	VE (%)	EE (%)	Ref
high temperature etching and carbon nanoparticles modified/GF	MV/4-HO-TEMPO	80	-	-	54.4	[1]
N/S heteroatoms and Ti doped WO_3 modified/GF	DHAQ/ $K_4Fe(CN)_6$	40	70.64	-	-	[2]
rGO/GF	MV/4-HO-TEMPO	60	94.2	56.7	50.4	[3]
N/B codoped/GF	1,8-DHAQ/ $K_4Fe(CN)_6$	60	67.9	-	-	[4]
3D rGO/CP	MV/4-HO-TEMPO	50	82.17	57.29	46.15	[5]
Spherical mesoporous carbon modified/CC	AQS/BQDS	30	95.3	-	58.90	[6]
N_2 Plasma treated/CF	Tiron/AQDS	60	-	62.4	62.1	[7]
PEG-rGO/CF	2,7-AQDS/ FerrocyanideFB	50	98.8	-	49.6	[8]
3D heterostructure rGo/CF	**MV/ TEMPTMA**	**50**	**99.5**	**80.1**	**80.1**	**This work**
		70	**99.4**	**73.4**	**73.3**	

Table S3. The comparison in the performances of AORFBs using carbon electrode.

References

1. C. T. Nie, H. J. Han, Y. H. Li, S. H. Zheng and Y. Wang, *ACS Appl. Nano. Mater.*, 2024, **7**, 9950-9959.
2. X. Cai and C. Huang, *Electrochim. Acta*, 2024, **493**, 144382.
3. X. Li and C. Huang, *RSC Adv.*, 2020, **10**, 6333-6341.
4. J. Deng, X. Cai and C. Huang, *Energy Storage*, 2022, **5**, e435.
5. X. Li, J. Li, C. Huang and W. Zhang, *Electrochim. Acta*, 2019, **301**, 240-250.
6. W. Kakaen, L. Intakhuen, A. Siyasukh and K. Punyawudho, *Int. J. Hydrogen Energy*, 2021, **46**, 6448-6460.
7. A. Permatasari, J. W. Shin, W. Lee, J. An and Y. Kwon, *Int. J. Energy Res.*, 2021, **45**, 17878-17887.
8. A. J. Molina-Serrano, J. M. Luque-Centeno, D. Sebastian, L. F. Arenas, T. Turek, I. Vela, F. Carrasco-Marin, M. J. Lazaro and C. Alegre, *ACS Appl Energy Mater*, 2024, **7**, 2779-2790.