Electronic Supplementary Information (ESI)

Heteroatom-Doped Electrodes for All-Vanadium Redox Flow Batteries with Ultralong Lifespan

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Experiment

Preparation and characterizations of the PF-GF electrode

Firstly, the pristine GF (Hunan Yinfeng) was immersed in the KPF6 aqueous solution (20 mg ml^{-1}) with ultrasonic treatment for 30 min. Then, after drying at 80 ℃ for 12 hours, the sample was annealed under the argon atmosphere at 850 ℃ for 40 min. Finally, the sample was washed with 1 mol L^{-1} HCl and ultrapure water in sequence until the pH attains to neutral. The PF-GF electrode was obtained after dried at 80 ℃ for 12 hours. For comparison, the pristine GF was treated under the same conditions except using KPF6 aqueous solution.

The morphology and structure of PF-GF electrode were characterized by scanning electron microscope (SEM) (Hitachi S4800) operating at 8 kV and transmission electron microscopy (TEM) (JEOL JEM-2011).The Raman (Thermal fisher LabRAM HR800) spectra were achieved with a 532 nm laser excitation. The X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Scientific ESCALab 250Xi with 200 W Al Kα radiation.

Electrochemical tests

The cyclic voltammetry (CV) measurements were accomplished by a typical three-electrode system with PF-GF electrode (0.5×0.5 cm^{-2}) as the working electrode, Ag/AgCl as the reference electrode and Pt as the counter electrode in the 0.05 M $VOSO_4$ + 3 M H_2SO_4 electrolyte on the electrochemical workstation (PARSTATVMC). The impedance experiments (EIS) are conducted with the same device over a frequency ranging from 0.1Hz to 100 kHz at an amplitude of 5 mV. The galvanostatic charging and discharging tests were performed with a single cell on the battery testing system (Land CT2001A, China). The PF-GF (2×2 cm^2) was used as the working electrode, the Nafion 115 (DuPont, USA) was employed as the separator. The electrolyte for positive and negative electrodes was 0.75 M $VOSO_4$ + 0.375 M $V_2(SO_4)_3$ + 3 M H_2SO_4 (15 mL) (Hunan Yinfeng Co. Ltd.). The operation voltage was from 0.8 V to 1.6 V. All the measurements were carried out at room temperature.

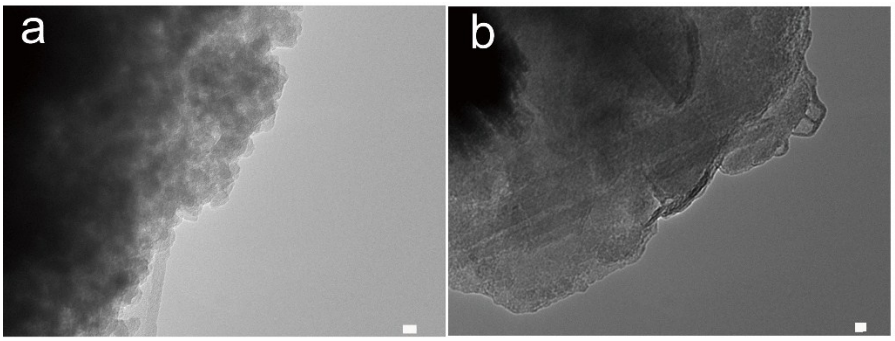

Fig. S1 TEM images for GF (a) and PF-GF (b), all the scale bars in figures are 10 nm.

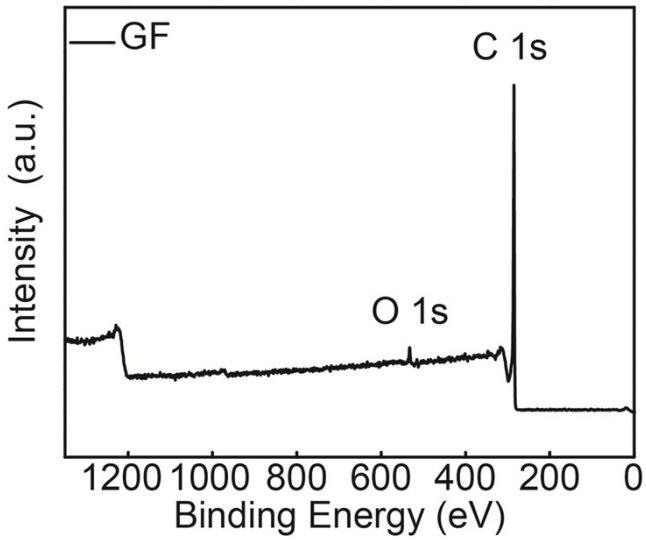

Fig. S2 XPS spectrum of the GF.

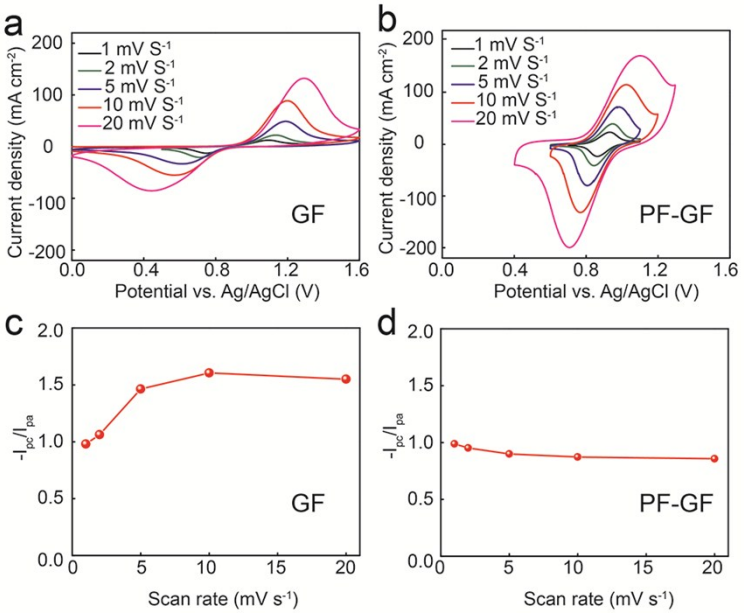

Fig. S3 CV profiles of the (a) GF and (b) PF-GF electrodes at various scanning rates. The plot of I_{pc}/I_{pa} versus scan rate for the (c) GF and (d) PF-GF electrodes.

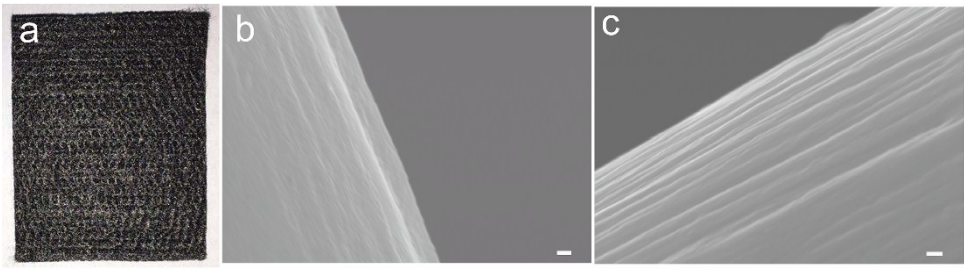

Fig. S4 Photograph of PF-GF (a), and SEM images for PF-GF (b) and GF (c) after charging and discharging for 1000 cycles. The scale bars in figures (b) and (c) are 100 nm.

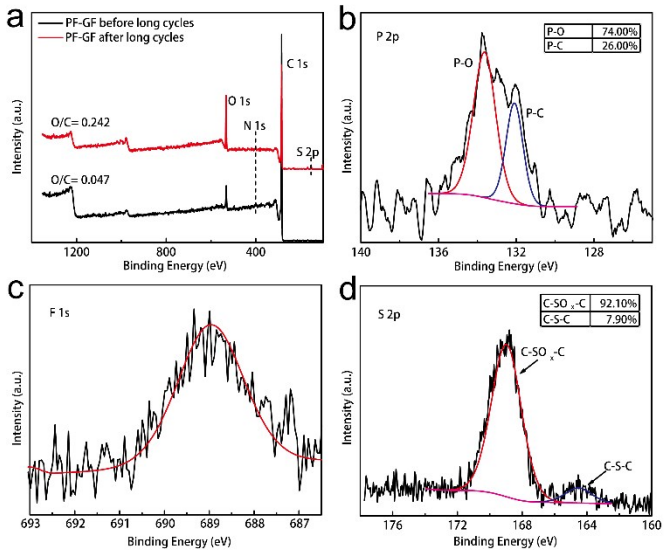

Fig. S5 (a) XPS spectrum of the PF-GF after (red) and before (black) 1000 cycles, (b) P 2p spectrum of the PF-GF before long-time cycling test, (c) F 1s and (d) S 2p spectra of the PF-GF after long-time cycling test.

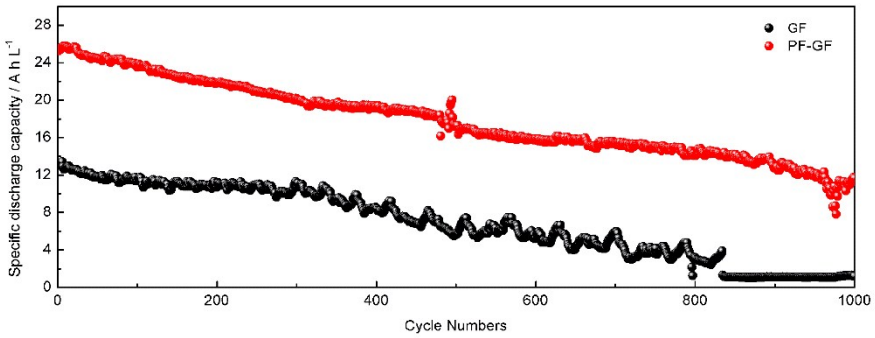

Fig. S6 Specific discharge capacity for VRFBs based on the pristine GF (black) and PF-GF (red) electrodes.

Table S1 Comparison of the CE, VE, EE and lifespan of the P and F co-doped graphite felt electrode with previous work on graphite felt electrodes.

Reference	Electrode	Current density (mA cm^{-2})	CE (%)	VE (%)	EE (%)	Lifespan (cycle)
1	Nitrogen-Doped Carbon Nanotube/Graphite Felts	10	81.3	94.7	77.0	50
2	Bismuth Nanoparticle/Graphite Felt	150	97.0	80.4	77.0	
3	Carbon Nanofiber/Nanotube/Graphite Felt	100	97.7	67.5	66.0	
4	Niobium Oxide/Graphite Felt	150	97.0	77.6	75.7	50
5	Corn protein-derived nitrogen-doped	50	97.0	89.4	86.7	100
6	PbO_2/Graphite Felt	70	99.5	82.4	82.0	30
7	Porous carbon/Graphite Felt	60	96.8	82.7	80.1	
8	Nb-doped hexagonal WO_3 nanowire/Graphite Felt	80	93.2	83.8	78.1	30
9	Graphene-Nanowall/Graphite Felt	25			90.0	100
10	ZrO_2-Nanoparticle/Graphite Felt	100	92.0	83.3	76.6	200
11	CO_2-activated/graphite felt	50	94.5	88.9	84.2	
12	Water-activated/graphite felt	50	95.1	87.4	81.3	
This works	***P and F co-doping graphite felt***	***120***	***96.6***	***82.0***	***79.2***	***1000***

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