Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supplementary Information

Corn protein-derived nitrogen-doped carbon materials with oxygen-rich functional groups: A highly efficient electrocatalyst for the all-vanadium redox flow batteries

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Table S1. Summary of electrochemical properties of various electrocatalysts in VRFB system

System	Cell type	Catalyst type	Cycle number	100% SOC [V] [a]	Current density [mA cm^{-2}]	EE[b]	CE[c]	Ref.
Carbon based	Flow cell	N-CB	100	0.8-1.65	50 (150)	87.0 (68.8)	97.5 (98.8)	**This work**
	Flow cell	CNT/CNF	30	0.8-1.65	40 (100)	84.9 (65.1)	96.7 (97.2)	21
	Flow cell	MWCNT	50	0.75-1.65	50	82.0	93.9	11
	Flow cell	MWCNT	100	0.8-1.7	10 (40)	73.6 (62.5)	80.3 (87.6)	12
	Flow cell	N-CNT	50	0.8-1.7	10	77.0	81.3	13
Metal based	Flow cell	Bismuth decorating	50	0.8-1.6	50 (150)	90 (78)	97 (98)	6
	Flow cell	Niobium Oxide	50	0.8-1.6	50 (150)	88 (78.7)	97 (98.5)	19
	Flow cell	Tungsten trioxide	50	0.8-1.65	30 (60)	83.1 (78.1)	91.1 (95.1)	14
	Flow cell	Manganese oxide	20	0.8-1.7	40	78	86	15
	Flow cell	Iridium	50	0.8-1.75	20 (60)	69.7 (58.5)	79.7 (61.7)	16

[a] (State of Charge) [b] (Energy efficiency) [c] (Coulombic efficiency)

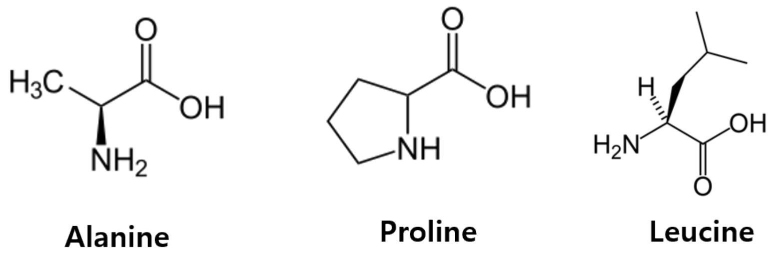

Figure S1. The molecular structure of the major amino acids in the zein protein.

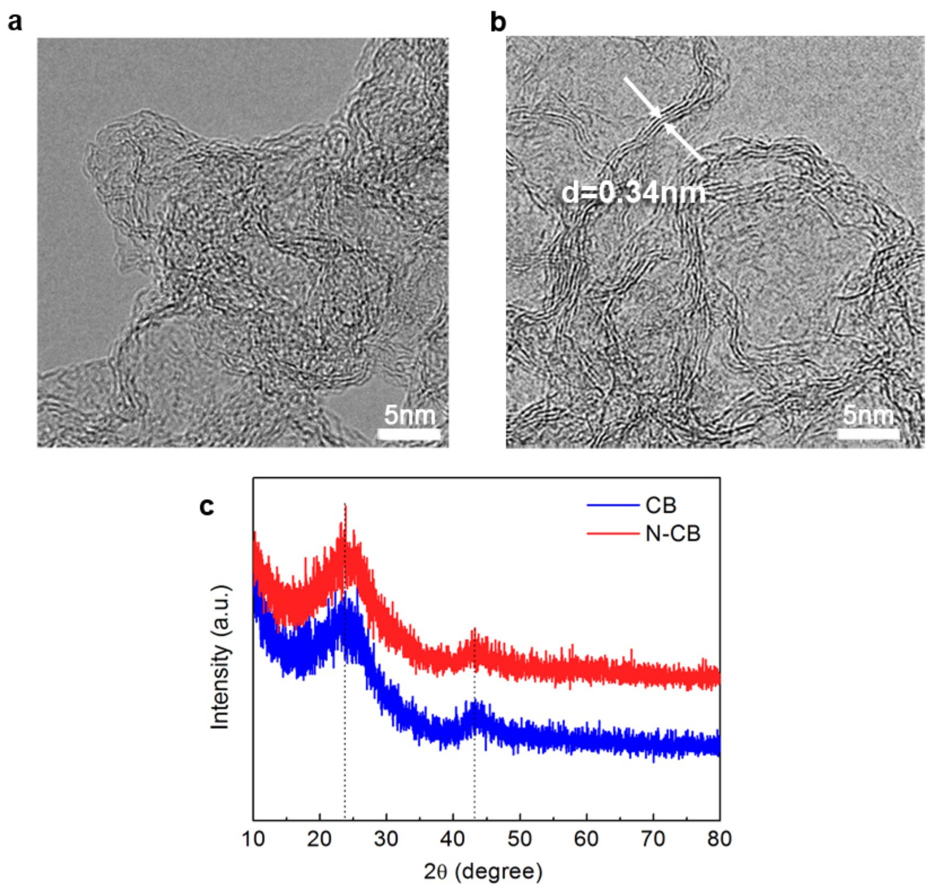

Figure S2. HR-TEM image of the a) CB and c) N-CB catalyst, showing the graphite interlayer with a distance of 0.34 nm, corresponding to (002) plane. c) XRD patterns of the CB and N-CB catalyst.

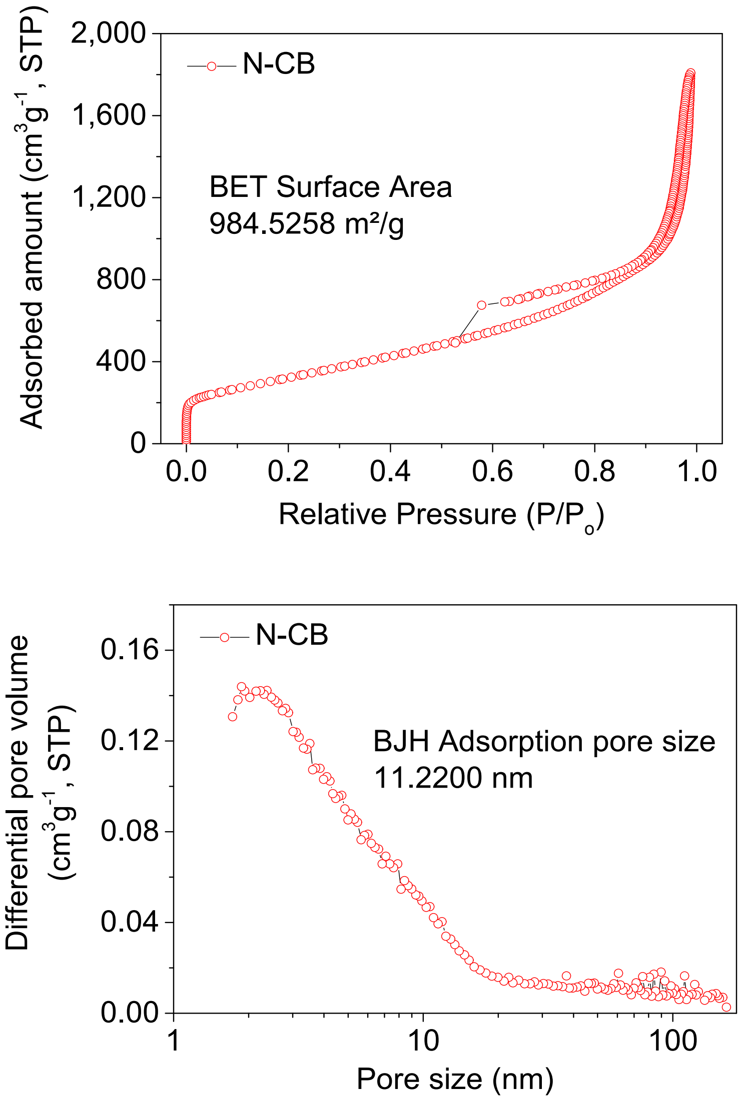

Figure S3. Nitrogen adsorption–desorption isotherm and BJH pore-size distribution plot of N-CB sample.

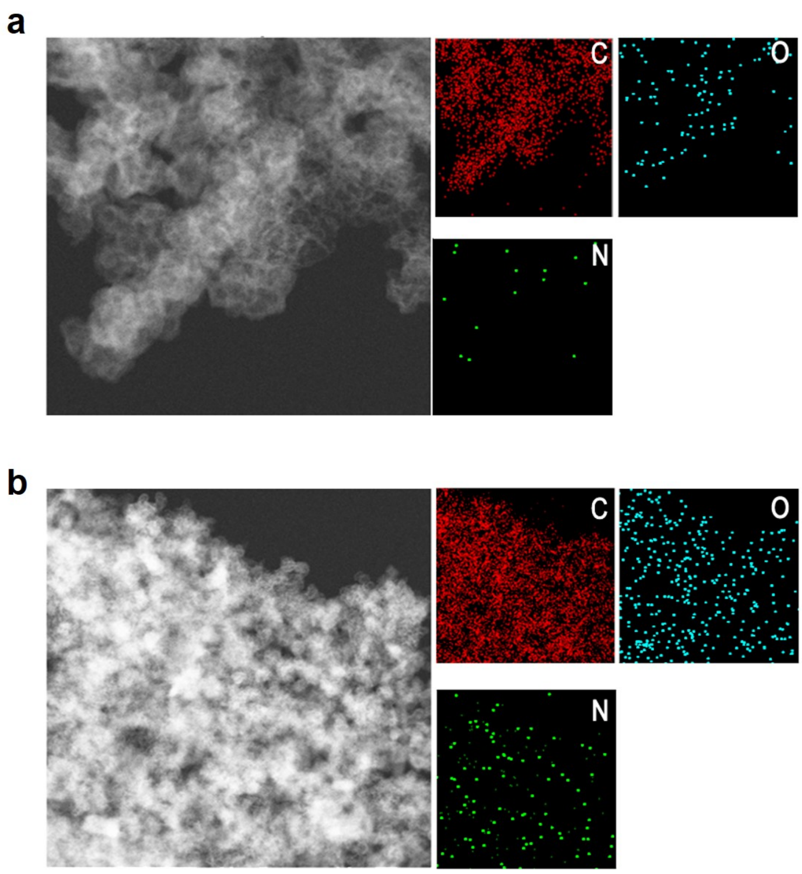

Figure S4. EDXS mapping of carbon, oxygen and nitrogen element of a) CB and b) N-CB catalyst, showing that oxygen and nitrogen atom were substantially increased after N-doped graphene coating on CB compared with untreated one.

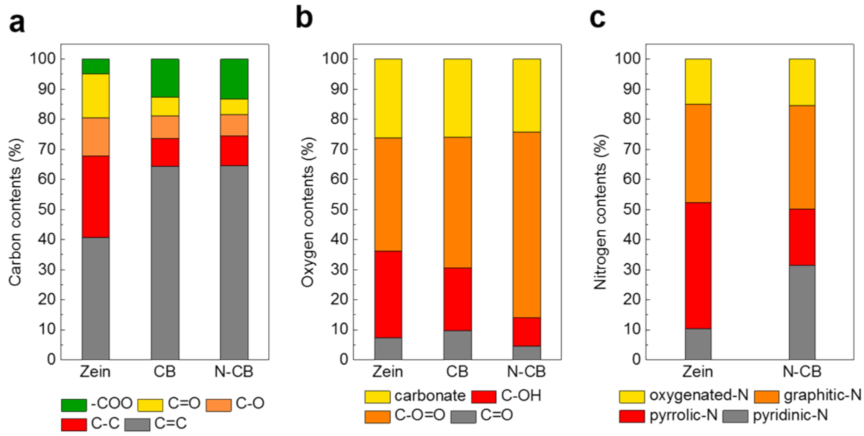

Figure S5. Chemical composition ratio of functional groups from curve fitting of a) C1s, b) O1s, and c) N1s spectra of the pristine zein, CB, and N-CB sample.

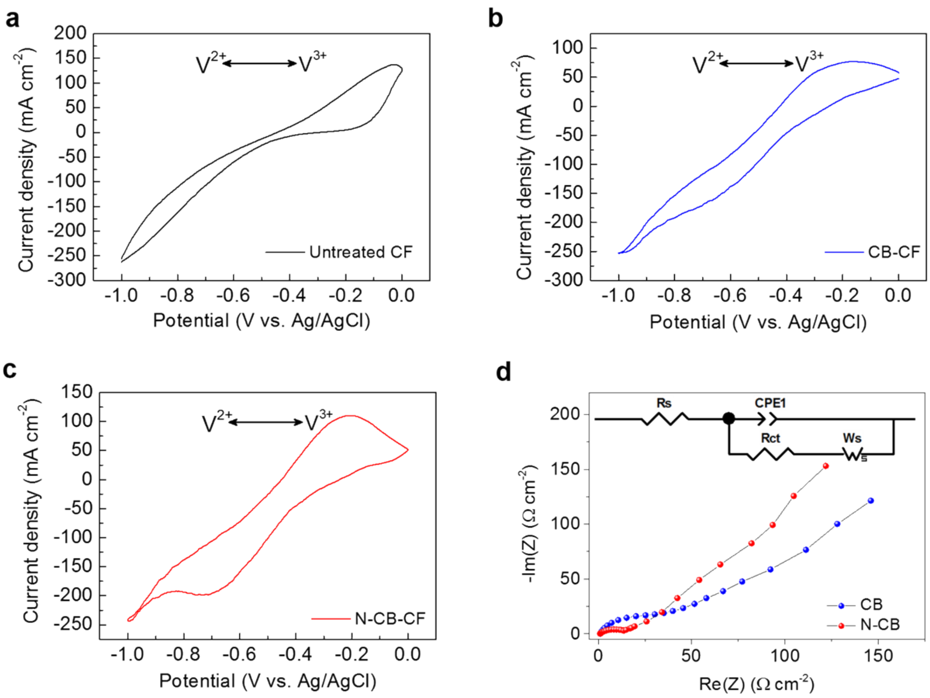

Figure S6. Cyclic voltammograms with a) untreated, b) CB , and c) N-CB carbon felt as working electrode for V^{2+}/V^{3+} redox couple in negative electrolyte. d) Nyquist plot showing electrochemical impedance spectroscopy (EIS) data for CB and N-CB catalyst. CF: carbon felt.

We have selected the general electrochemical analysis method that is widely used in other negative half-cell test at the potential range from 0 to -0.1 V in the negative electrolyte.[8] It is known that the hydrogen evolution reaction occurs under -0.5 V, but the negative vanadium redox reactions occur at -0.2 V.

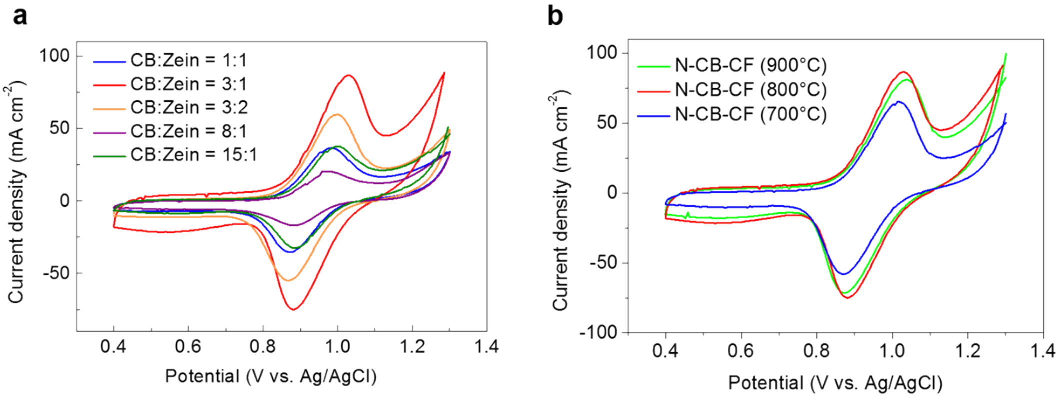

Figure S7. Cyclic voltammetry curves on N-CB carbon felt electrodes with a) various carbon black to zein powder composition (1:1, 3:1, 3:2, 8:1, and 15: 1) and b) different carbonization temperatures (700, 800, and 900 °C) in 0.1 M $VOSO_4$ + 3 M H_2SO_4 electrolyte solution at a scan rate of 5 mV s^{-1}.

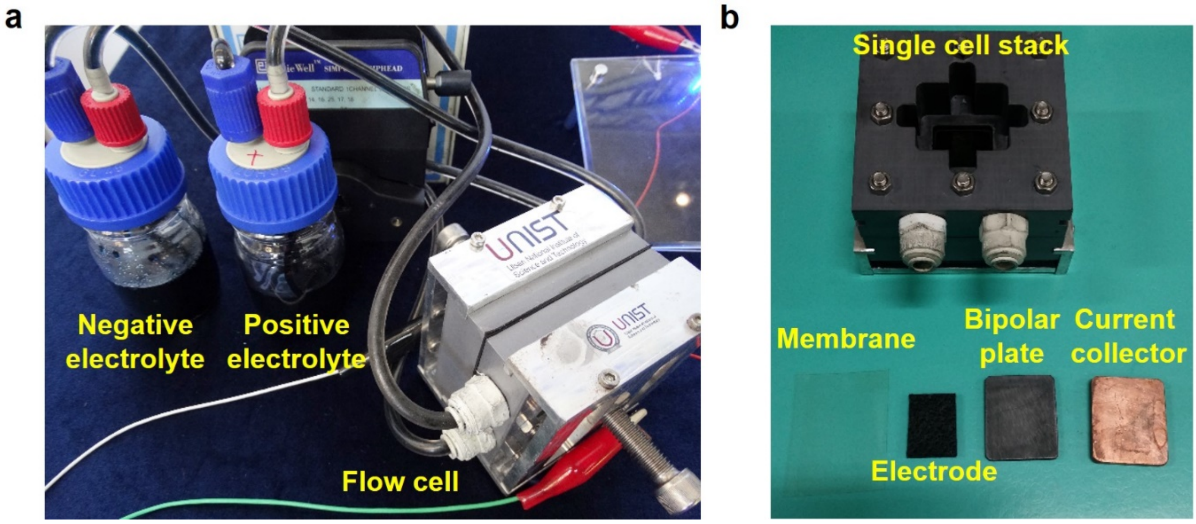

Figure S8. a) Digital photograph of vanadium redox flow battery system, which includes a single stack cell, two electrolyte tank, and flow pump. b) Details of flow cell components.

The experimental conditions, such as electrolyte concentrations, membrane thickness, and other parameters, have been identically set in flow cell tests. The Nafion117 membrane is generally used in the VRFB field and considered as a reference membrane, as shown in various papers as below. Although the Nafion117 (183 μm) is thicker than other one, it can prevent the vanadium ion crossover more properly.

Reference

1. S. Zhang, B. Zhang, G. Zhao and X. Jian, *Journal of Materials Chemistry A*, 2014, **2**, 3083-3091.
2. T. M. Tseng, R. H. Huang, C. Y. Huang, K. L. Hsueh and F. S. Shieu, *J. Electrochem. Soc.*, 2013, **160**, A690-A696.
3. M. Park, Y. J. Jung, J. Kim, H. I. Lee and J. Cho, *Nano Lett.*, 2013, **13**, 4833-4839.
4. Wang, Yufei, et al., RSC Advances 3.35 (2013): 15467-15474.

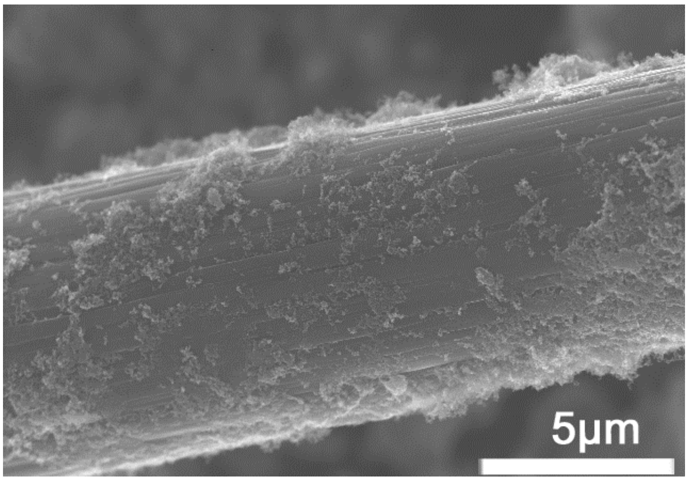

Figure S9. The N-CB catalyst coated carbon felt electrode after 100 cycle charge/discharge test.