Supplementary Information

Synergistic Effect of Bifunctional Polydopamine-Mn_3O_4 Composite Electrocatalyst for Vanadium Redox Flow Batteries

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Contents

I. Calculation of diffusion coefficient (D) from Randles-Sevcik equation

According to Randles-Sevcik equation, for a redox reaction, the peak current i_p is calculated in Eq. (S1) and Eq. (S2) [1]:

$$i_p = 2.69\times 10^5\, n^{3/2}\, A\, D^{1/2}\, C\, \nu^{1/2} \text{ (reversible system)} \qquad \text{Eq. S1}$$

$$i_p = 2.99\times10^5\, n^{3/2}\, \alpha^{1/2}\, A\, D^{1/2}\, C\, \nu^{1/2} \text{ (irreversible system)} \qquad \text{Eq. S2}$$

where n is the number of electron transfer in redox reaction, A is the area of the working electrode, C is the primary concentration of reactant, D is the diffusion coefficient, V is the scan rate and α is the transfer coefficient (0.5). Since the reaction is quasi-reversible process, the real value of D should be in the range between the calculated values obtained from Eq. S1 and S2.

II. Calculation of average size of Mn_3O_4 crystal from XRD

The average size of the Mn_3O_4 crystallites can be calculated by using the Scherrer equation shown below [2]:

$$D=\frac{k\lambda}{\beta\cos\theta} \qquad \text{Eq. S3}$$

where D is the mean crystalline size, λ the X-ray wavelength, β is the full width at half-maximum of the peak (in radians), θ the Bragg angle at which the peak is observed, and K the shape factor, which is dependent on the shape of the particle (0.9 is usually used for particles of unknown geometry).

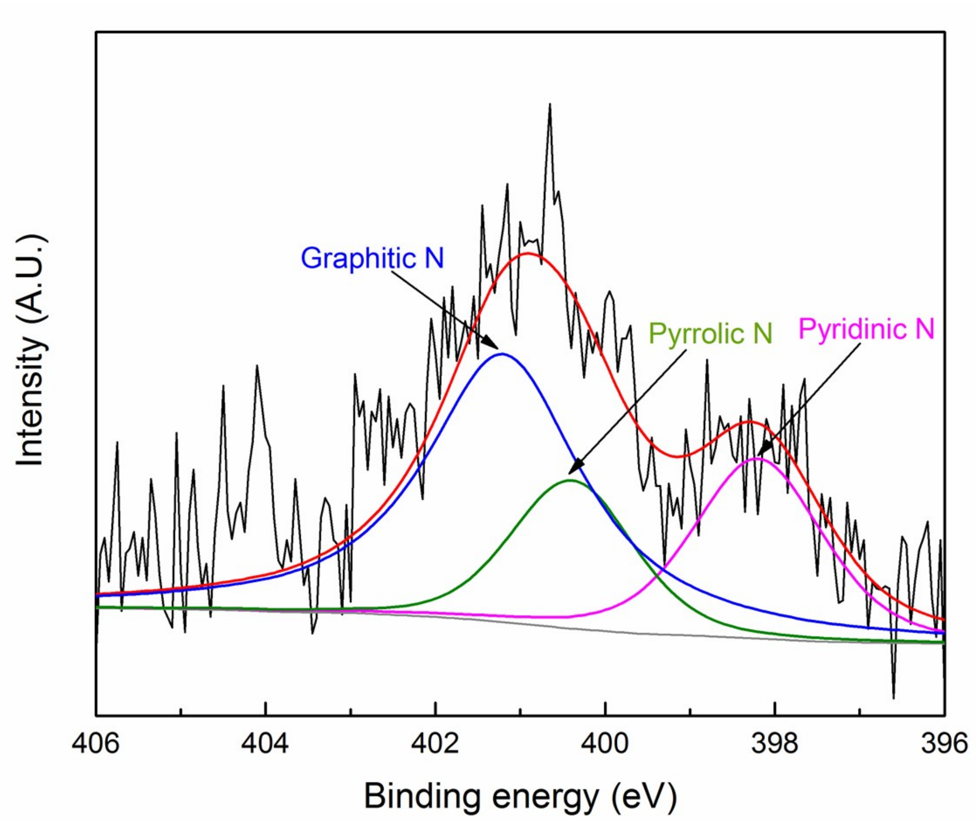

Figure S1. N 1s XPS spectrum of PDA modified GF.

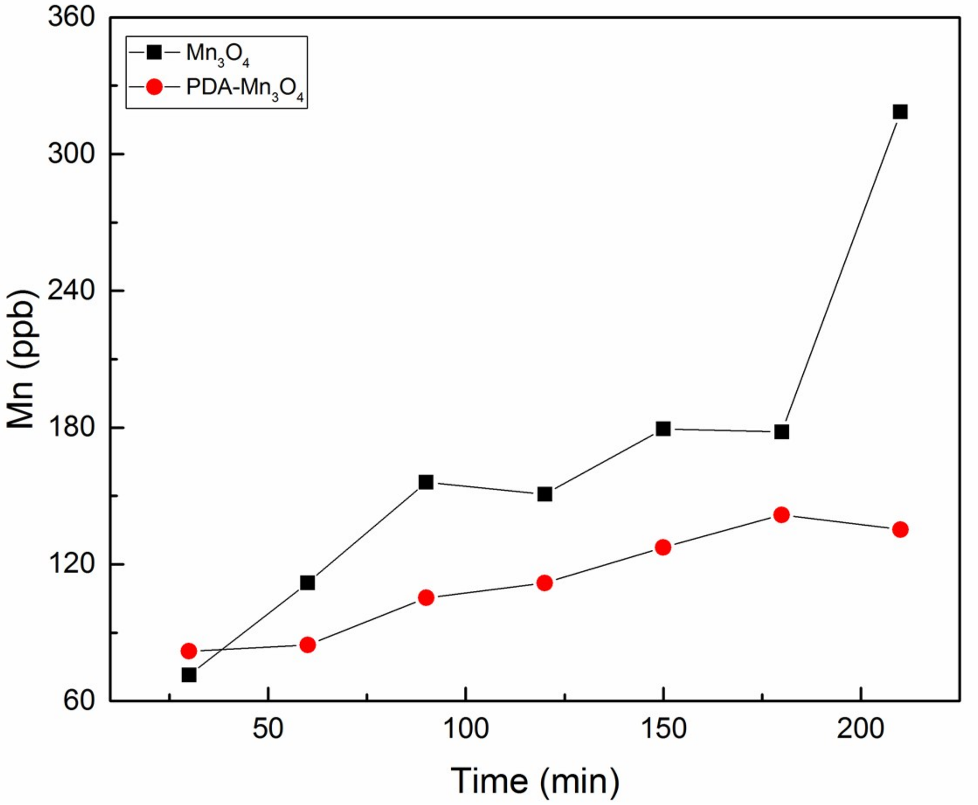

Figure S2. Loss of Mn from PDA-Mn_3O_4 composite GF.

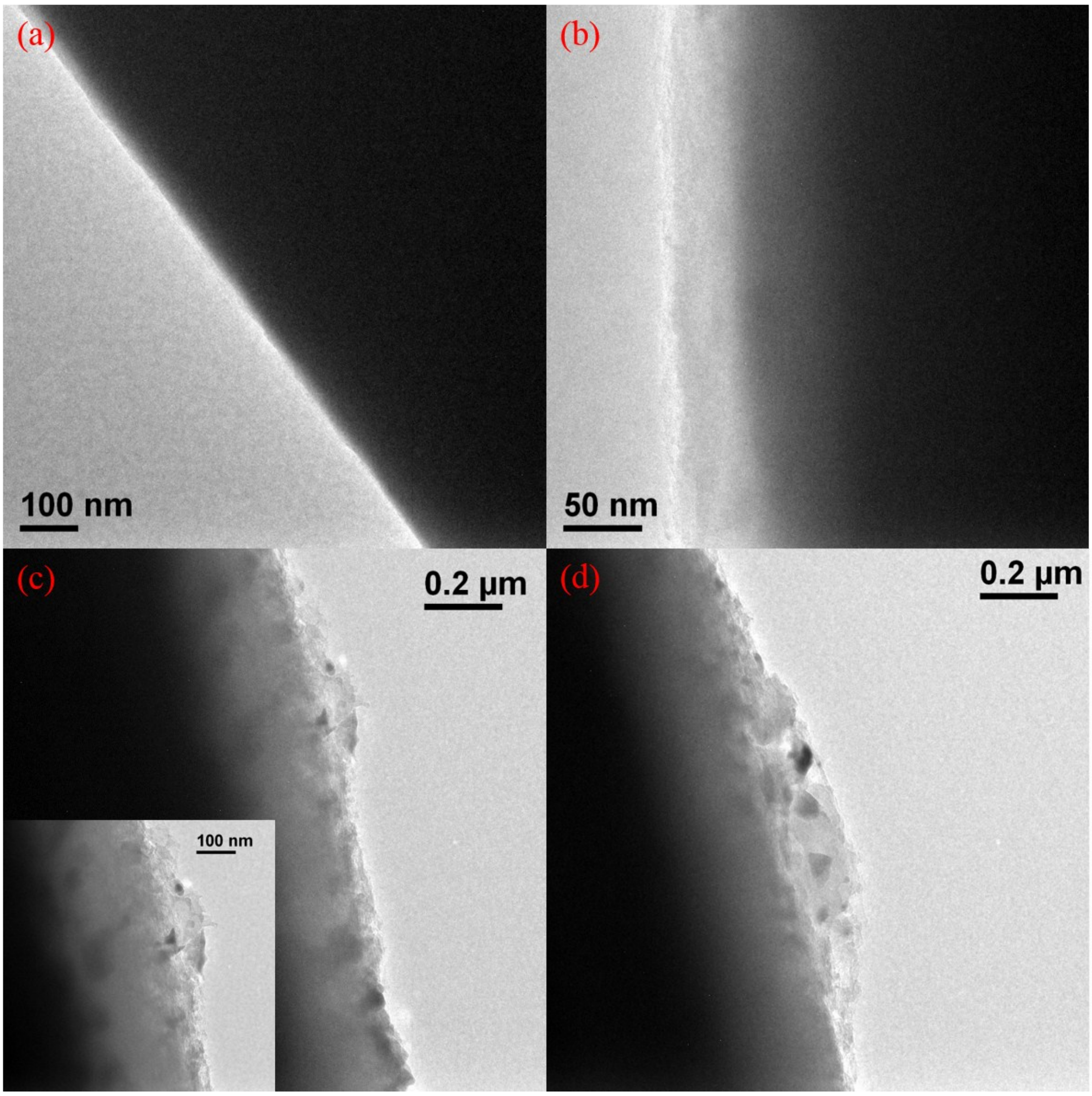

Figure S3. TEM of (a) blank GF, (b) PDA GF, (c) and (d) PDA-Mn_3O_4 composite GF at different spots.

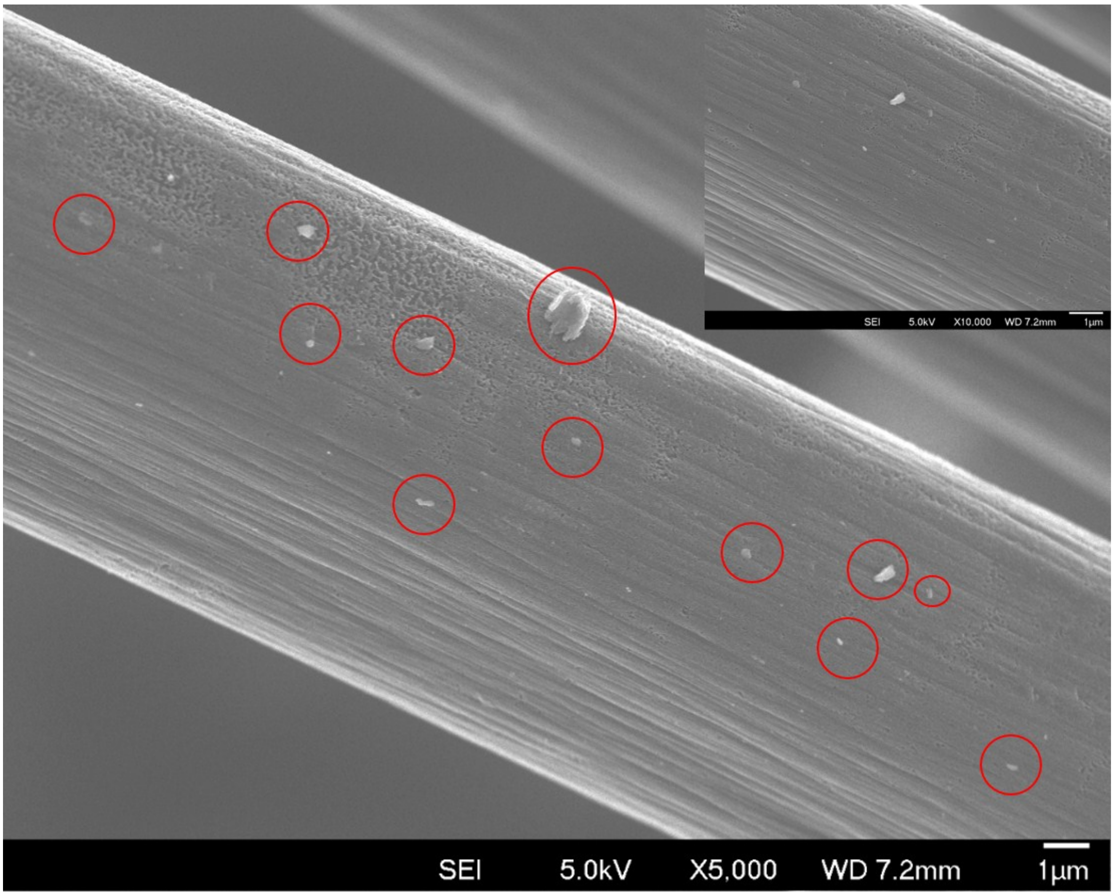

Figure S4. SEM of PDA-Mn_3O_4 composite GF after VRFB single cell test for 50 cycles.

Table S1. Efficiency comparison between this work and literatures [3-7]

Positive Electrode type	Current density/ mA cm^{-2}	EE/%	Ref
PDA-Mn_3O_4 GF	50	84.6	this work
PDA-Mn_3O_4 GF	100	73.7	this work
CNF-CNT GF	100	65.6	ref 3
Mn_3O_4-MWCNT GF	20	84.6	ref 4
MWCNT GF	50	82.0	ref 5
porous carbon GF	100	68.7	ref 6
Water activated GF	50	83.1	ref 7

Reference

1. A. J. Bard, L. R. Faulkner, J. Leddy and C. G. Zoski, *Electrochemical methods: fundamentals and applications*, Wiley New York, 1980.
2. A. Ejigu, M. Edwards and D. A. Walsh, *ACS Catalysis*, 2015, **5**, 7122-7130.
3. M. Park, Y.-j. Jung, J. Kim, H. I. Lee and J. Cho, *Nano letters*, 2013, **13**, 4833-4839.
4. Z. He, L. Dai, S. Liu, L. Wang and C. Li, *Electrochimica Acta*, 2015, **176**, 1434-1440.
5. G. Wei, C. Jia, J. Liu and C. Yan, *Journal of Power Sources*, 2012, **220**, 185-192.
6. J. Liu, Z. Wang, X. Wu, X. Yuan, J. Hu, Q. Zhou, Z. Liu and Y. Wu, *Journal of Power Sources*, 2015, **299**, 301-308.
7. D. M. Kabtamu, J.-Y. Chen, Y.-C. Chang and C.-H. Wang, *Journal of Power Sources*, 2017, **341**, 270-279.