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Electronic Supplementary Information (ESI)

Graphite Felts Modified by Vertical Two-Dimensional WO_3 Nanowall Arrays: High-Performance Electrode Materials for Cerium-Based Redox Flow Batteries

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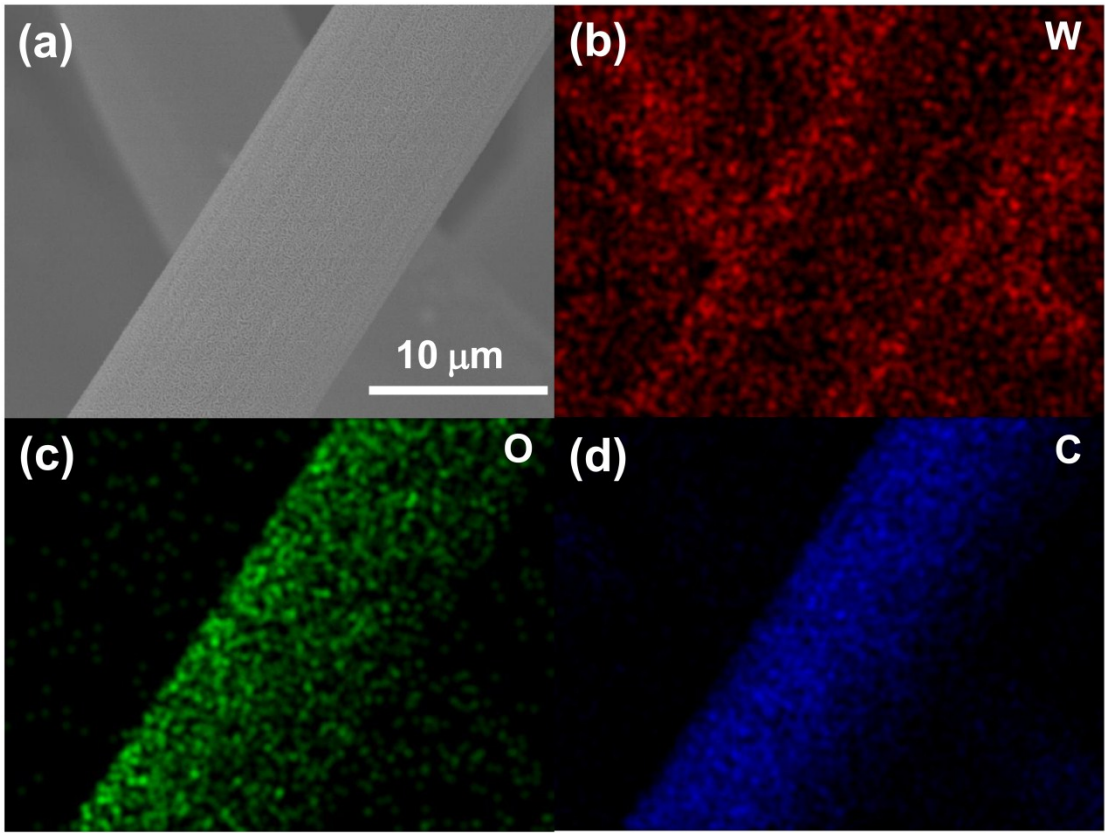

Fig. S1. EDS elemental mapping images of the WGF electrode.

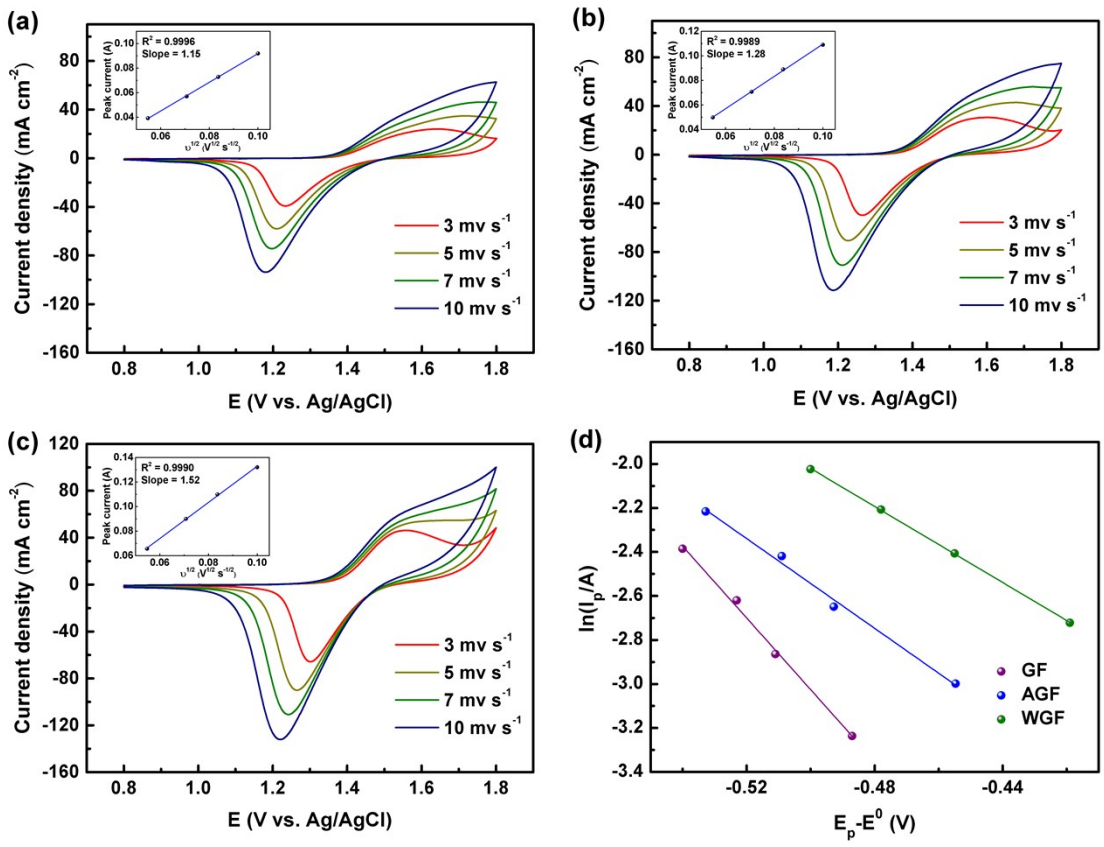

Fig. S2. CV curves of the (a) GF, (b) AGF and (c) WGF electrodes in 0.05 M Ce(III) methanesulfonate + 1.0 M MSA electrolyte at various scan rate. Insets: the plot of the peak current *vs.* the square root of each scan rate. (d) Comparison of standard rate constant (k_0) for GF, AGF and WGF.

S1. The electrochemical surface area (ECSA)

The electrochemical surface area (ECSA) can be estimated from the Randles-Sevcik equation, what relates the peak current with the square root of the scan rate, as follows:

$$i_p = 2.99\times10^5 n(\alpha n)^{1/2} A D_0^{1/2} C_0 v^{1/2}$$

where i_p is the peak current, n is the number of electrons involved in the electrode reaction, α is the transfer coefficient (0.5), A is the ECSA (cm^2),

C_0 is the concentration of the electroactive species in the bulk solution (mol cm^{-3}), D_0 is the diffusion coefficient (cm^2 s^{-1}) and v is the scan rate (V s^{-1}). The values of the diffusion coefficients were obtained from bibliography, 0.69×10^{-6} cm^2 s^{-1}.[1]

S2. The standard rate constant, k_0

The standard rate constants can be determined using the following equation:

$$i_p = 0.227nFAC_0k_0 \exp\left[\frac{-\alpha nF\left(E_p - E^0\right)}{RT}\right]$$

where i_p is the peak current, n is the number of electrons involved in the reaction, F is the Faraday constant, A is the active surface area of the electrode, C_0 is the bulk concentration of the electroactive species, α is the transfer coefficient (0.5), E_p is the peak potential, E^0 is the formal potential, R is the gas constant and T is the electrolyte temperature. Therefore, a plot of ln (i_p) *vs.* E_p-E^0 for different scan rates, should yield a straight line with a slope of $-\alpha nF/(RT)$ and an intercept proportional to k_0. Figure S2d depicts the plots of ln (i_p) *vs.* E_p-E^0 obtained from the CV data, from which k_0 values can be calculated.

Table S1 – Summary of representative WO_3-based materials for RFBs.

Sample	Application system	Increase in EE over pristine GF (%)	Reference
WO_3 modified GF	All-vanadium	12.5	39
Nb-doped WO_3 modified GF	All-vanadium	16.4	32
WO_3 coated carbon paper	All-vanadium	23.7	42
WGF	Cerium-based	42.1	This work

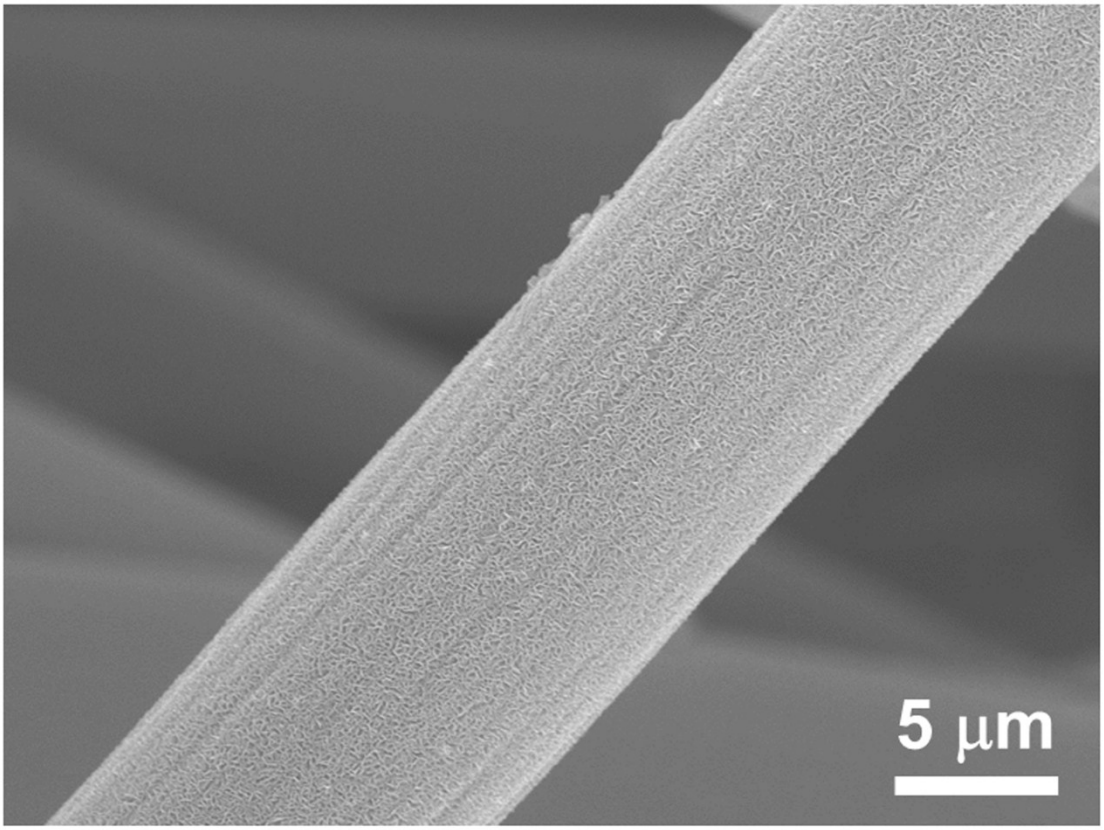

Fig. S3. SEM images of the WGF electrode after 200 charge/discharge cycles.

Supplementary Reference

(S1) P. K. Leung, C. Ponce-de-León, C. T. J. Low and F. C. Walsh, *Electrochim. Acta*, 2011, **56**, 2145–2153.