

## Supporting Information

### **Mesoporous Single-Crystalline MnO<sub>x</sub> Nanofibers@Graphene for Ultra-High Rate and Long-Life Lithium-Ion Battery Anodes**

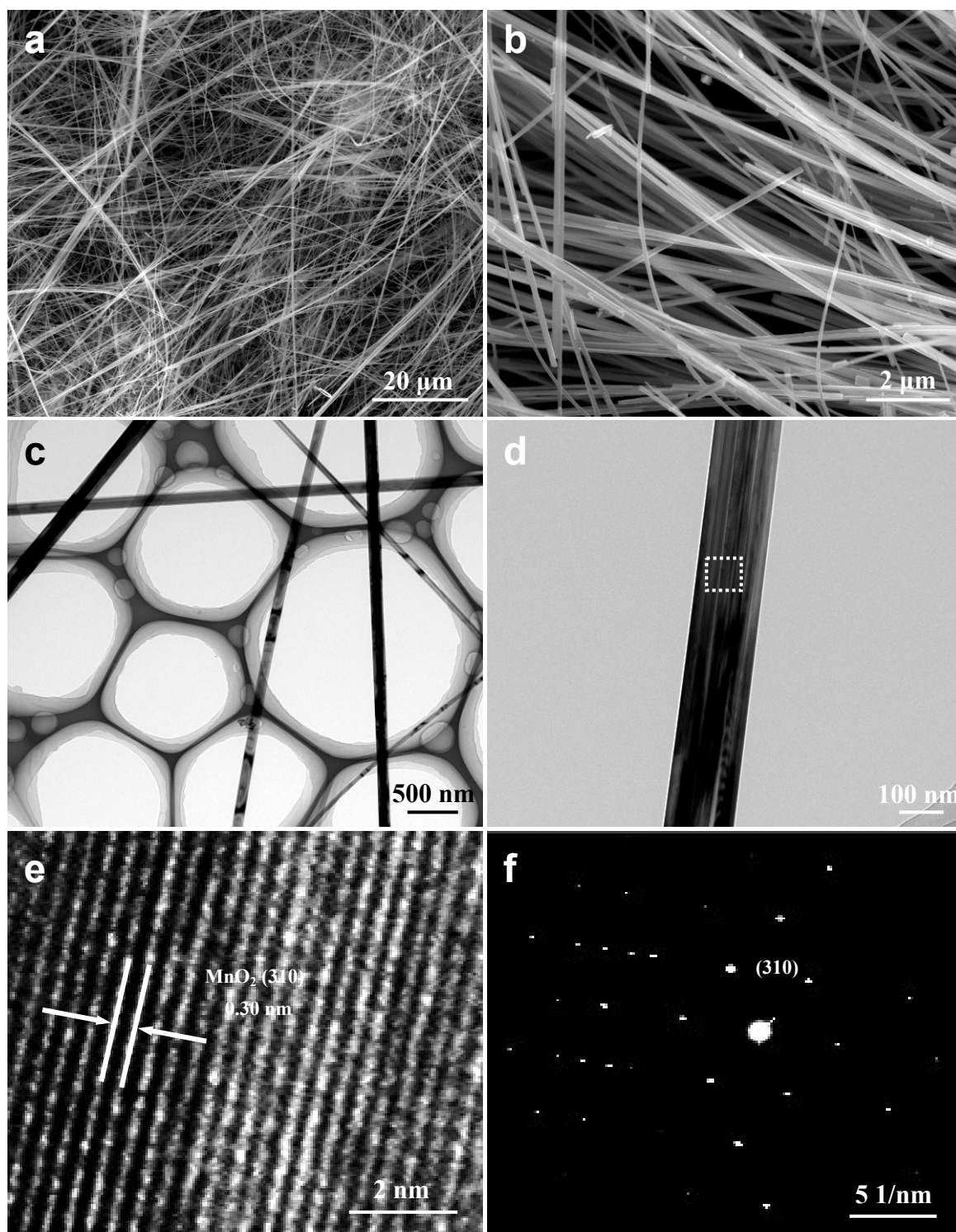
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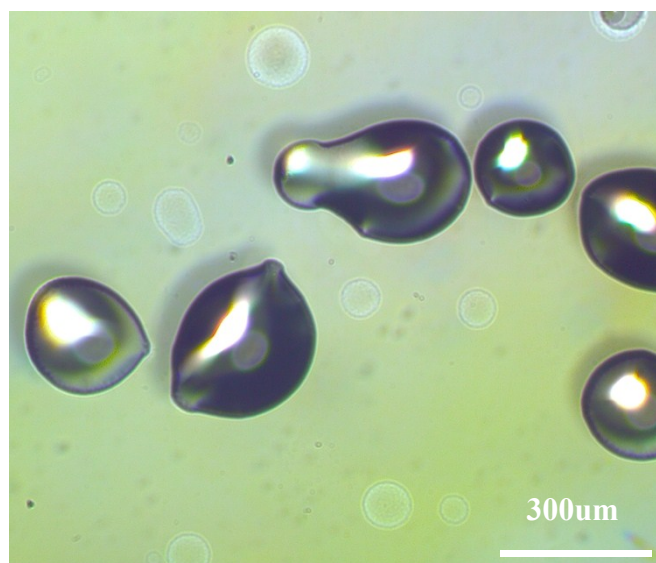
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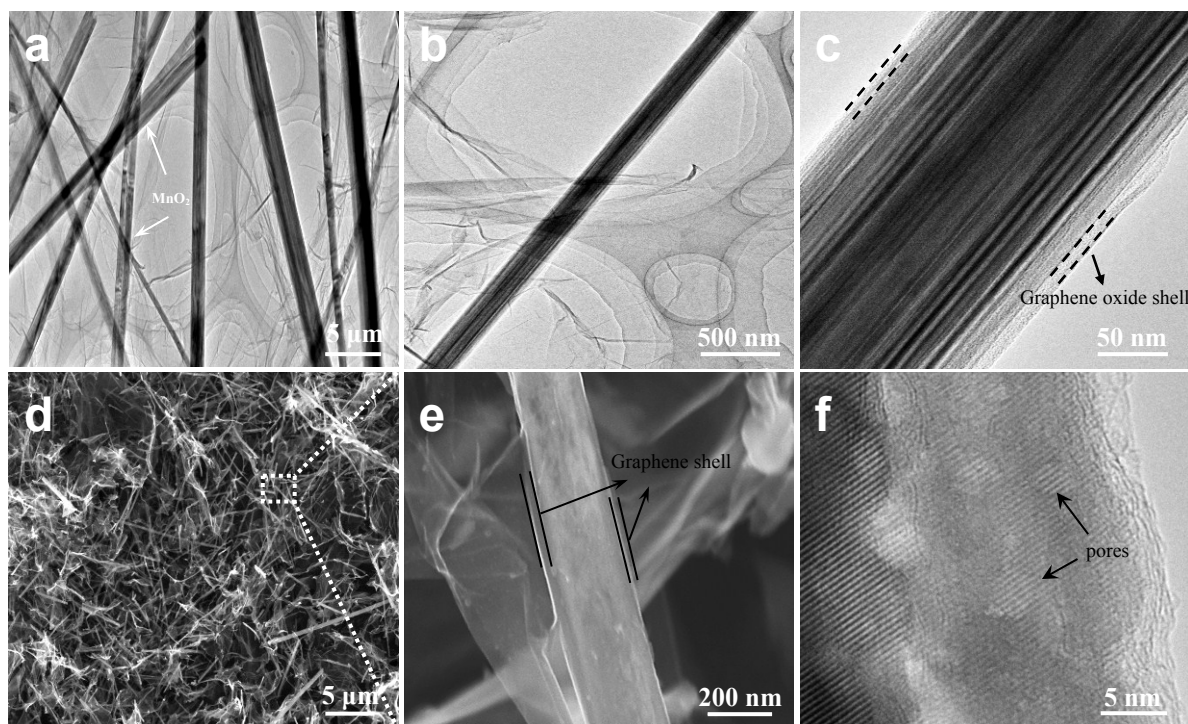
*<sup>†</sup> These authors contributed equally to this work.*



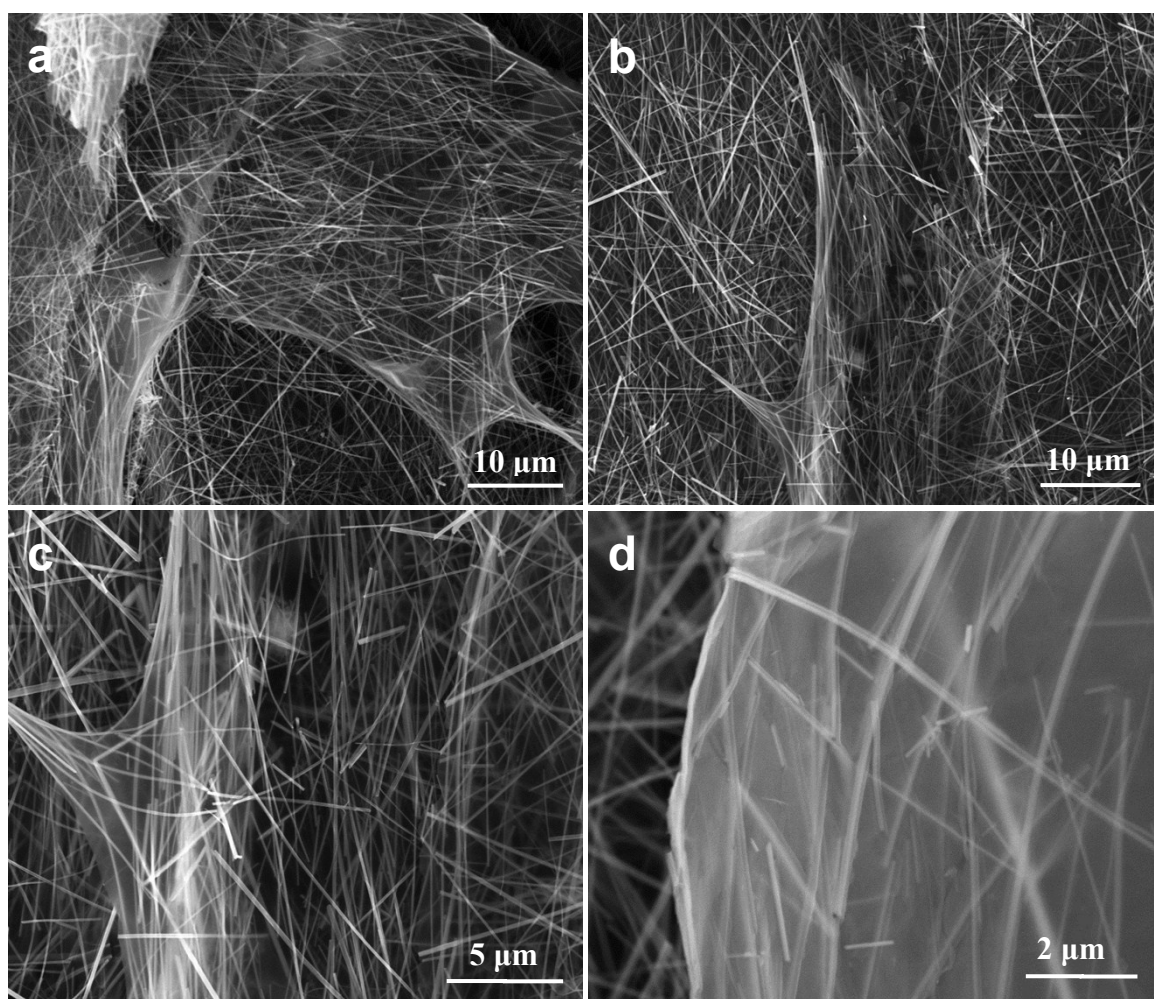
**Fig. S1.** (a,b) SEM images of the as-prepared MnO<sub>2</sub> NFs. (c,d) TEM images of MnO<sub>2</sub> NFs. (e,f) The high resolution TEM (HRTEM) image and selected area diffraction (SAED) pattern of MnO<sub>2</sub> NFs.



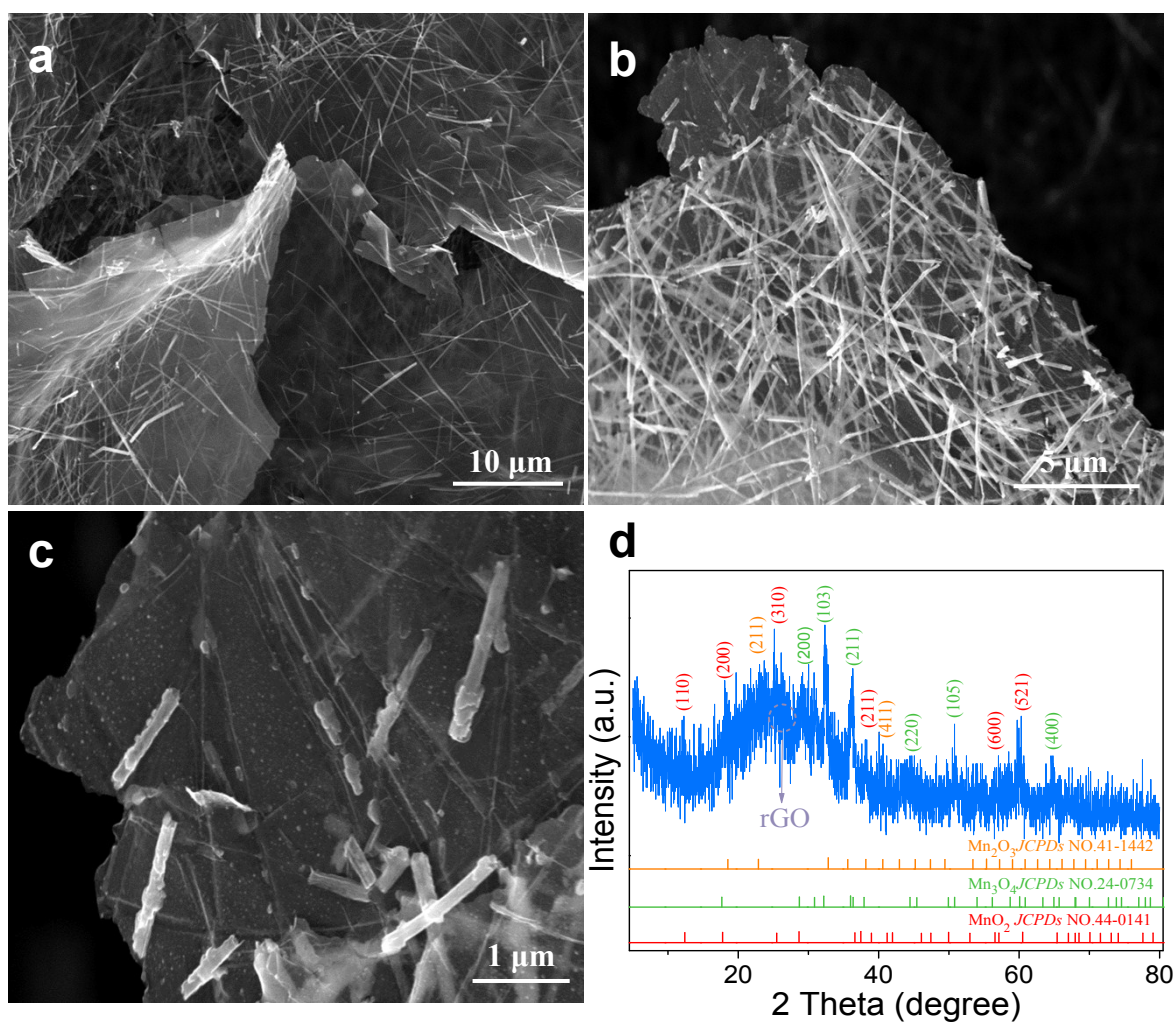
**Fig. S2.** Polarized optical microscope (POM) image of micro-sized droplets of MnO<sub>2</sub> NFs/GO suspension.



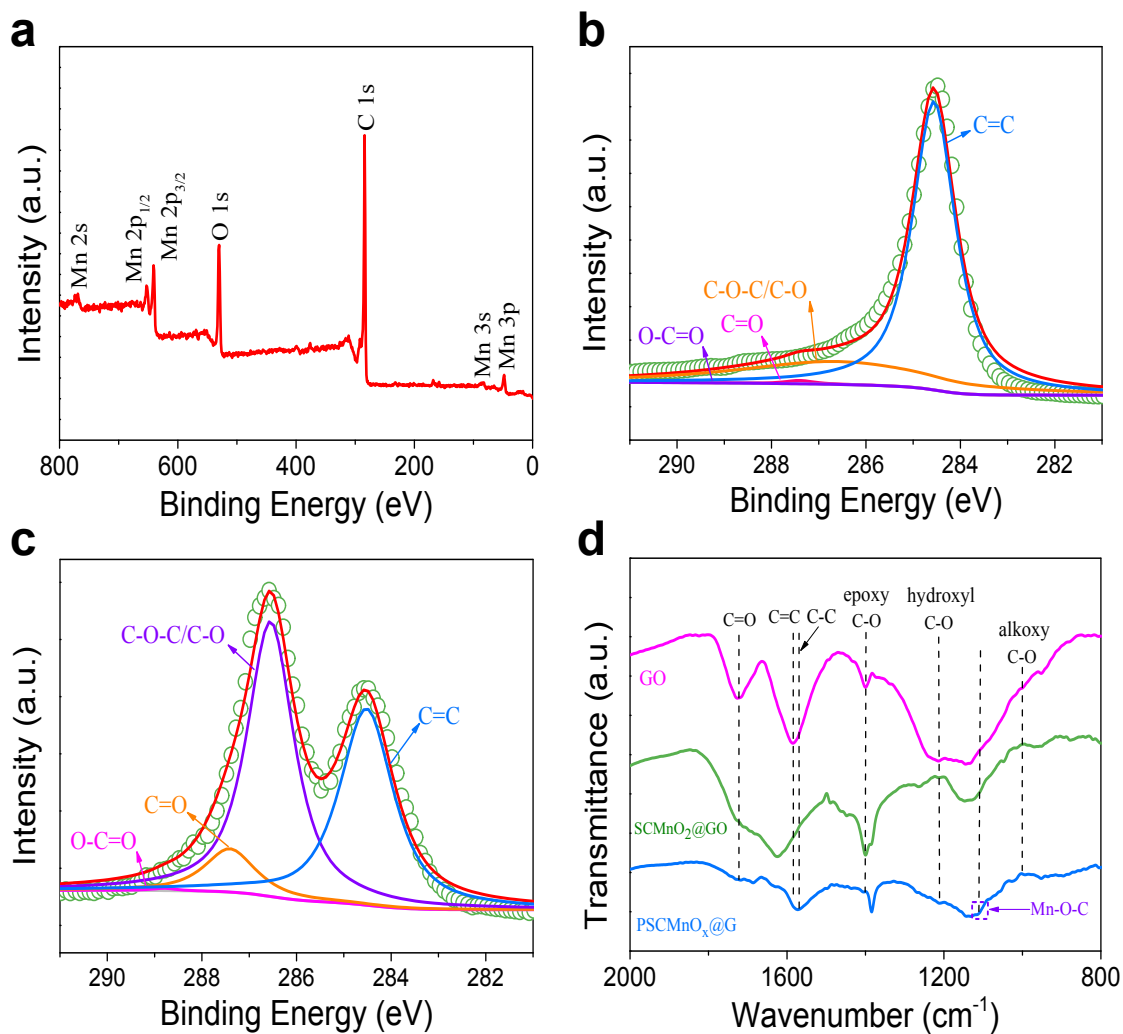
**Fig. S3.** (a,b,c) TEM images of SCMnO<sub>2</sub>@GO. (d,e) SEM images and (f) HRTEM image of PSCMnO<sub>x</sub>@G.



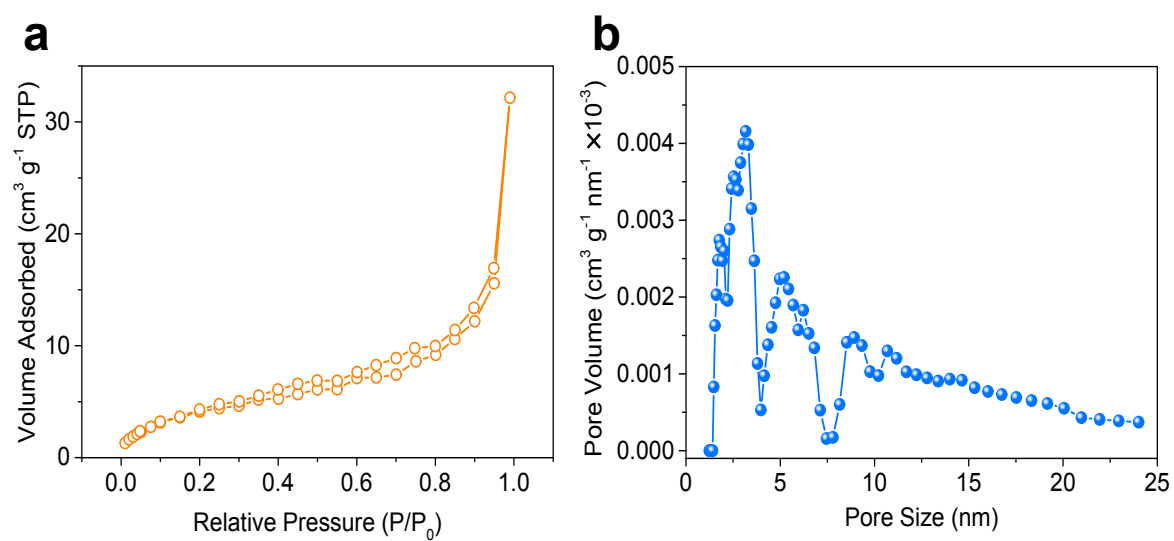
**Fig. S4.** SEM images of MnO<sub>2</sub>/GO at different magnifications.



**Fig. S5.** (a-c) SEM images of MnO<sub>x</sub>/G at different magnifications. (d) XRD pattern of MnO<sub>x</sub>/G.



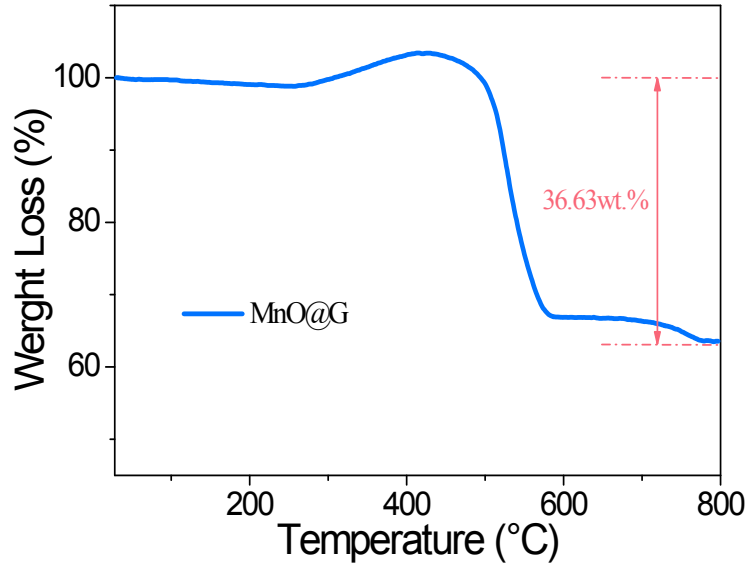
**Fig. S6.** (a) XPS survey spectrum and (b) high-resolution C 1s XPS spectra of PSCMnO<sub>x</sub>@G. (c) High-resolution C 1s XPS spectra of SCMnO<sub>2</sub>@GO. (d) FTIR spectra of PSCMnO<sub>x</sub>@G, SCMnO<sub>2</sub>@GO and GO.



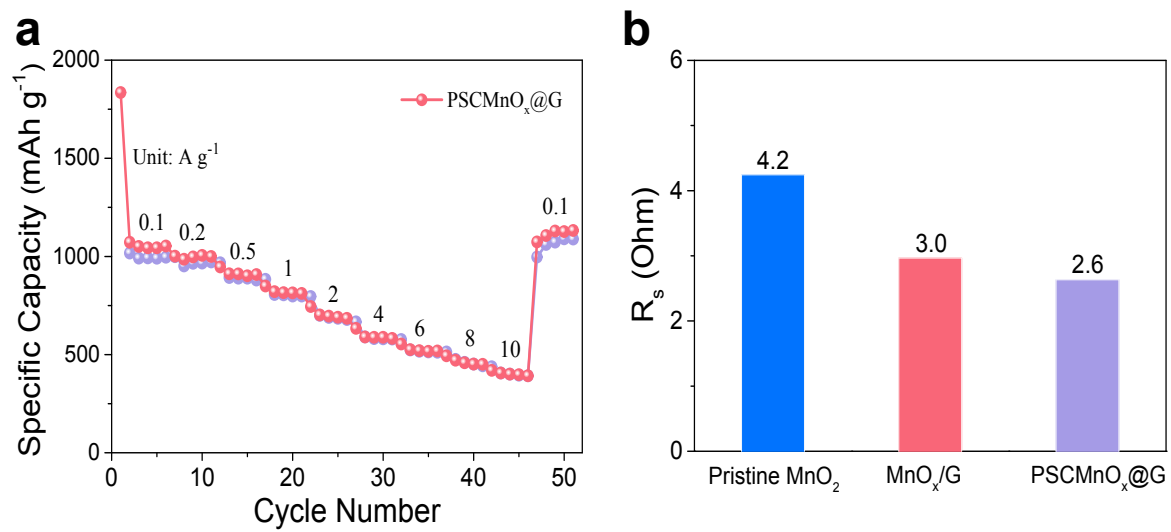
**Fig. S7.** (a) Nitrogen adsorption and desorption isotherm and (b) pore-size distribution plot of pristine MnO<sub>2</sub>.

**Table S1.** Specific surface area obtained from N<sub>2</sub> adsorption/desorption test.

| Samples                   | Specific surface area<br>m <sup>2</sup> g <sup>-1</sup> | Micropore area<br>m <sup>2</sup> g <sup>-1</sup> | Mesopore area<br>m <sup>2</sup> g <sup>-1</sup> |
|---------------------------|---------------------------------------------------------|--------------------------------------------------|-------------------------------------------------|
| Pristine MnO <sub>2</sub> | 16.2                                                    | 1.5                                              | 11.3                                            |
| SCMnO <sub>2</sub> @GO    | 31.9                                                    | 1.2                                              | 30.6                                            |
| PSCMnO <sub>x</sub> @G    | 58.8                                                    | 8.5                                              | 50.3                                            |



**Fig. S8.** TGA curve of MnO@G. The  $\text{SCMnO}_2\text{@GO}$  was annealed at 800 °C under a hydrogen atmosphere for 2 h to obtain the MnO@G. The content of graphene in MnO@G is the same as in  $\text{PSCMnO}_x\text{@G}$ . The final product of MnO@G after annealing at 800 °C in air can be assigned to the tetragonal structure of  $\text{Mn}_3\text{O}_4$  phase, indicating that the MnO was oxidized to  $\text{Mn}_3\text{O}_4$ . In theory, this oxidation process will give rise to a 7.5wt.% weight increase. Assuming that the total mass is 1 and the carbon content is  $x$ , then the MnO content is  $(1-x)$ . As shown in the TGA curve, the weight loss can be calculated using the following formula:  $x - 7.5 \text{ wt.}\%(1-x) = 36.63 \text{ wt.}\%$ . Thus, the carbon content  $x$  is equal to 41.05wt%.

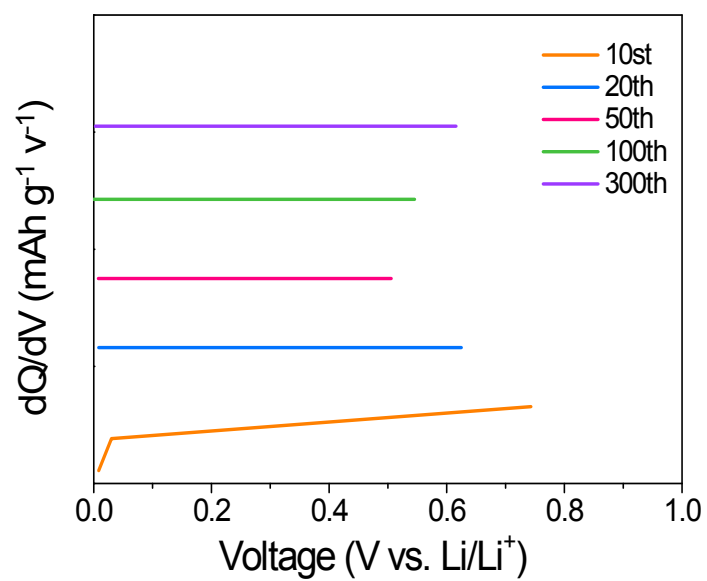


**Fig. S9.** (a) Rate capabilities of PSCMnO<sub>x</sub>@G at the current densities from 0.1 to 10.0 A g<sup>-1</sup>.

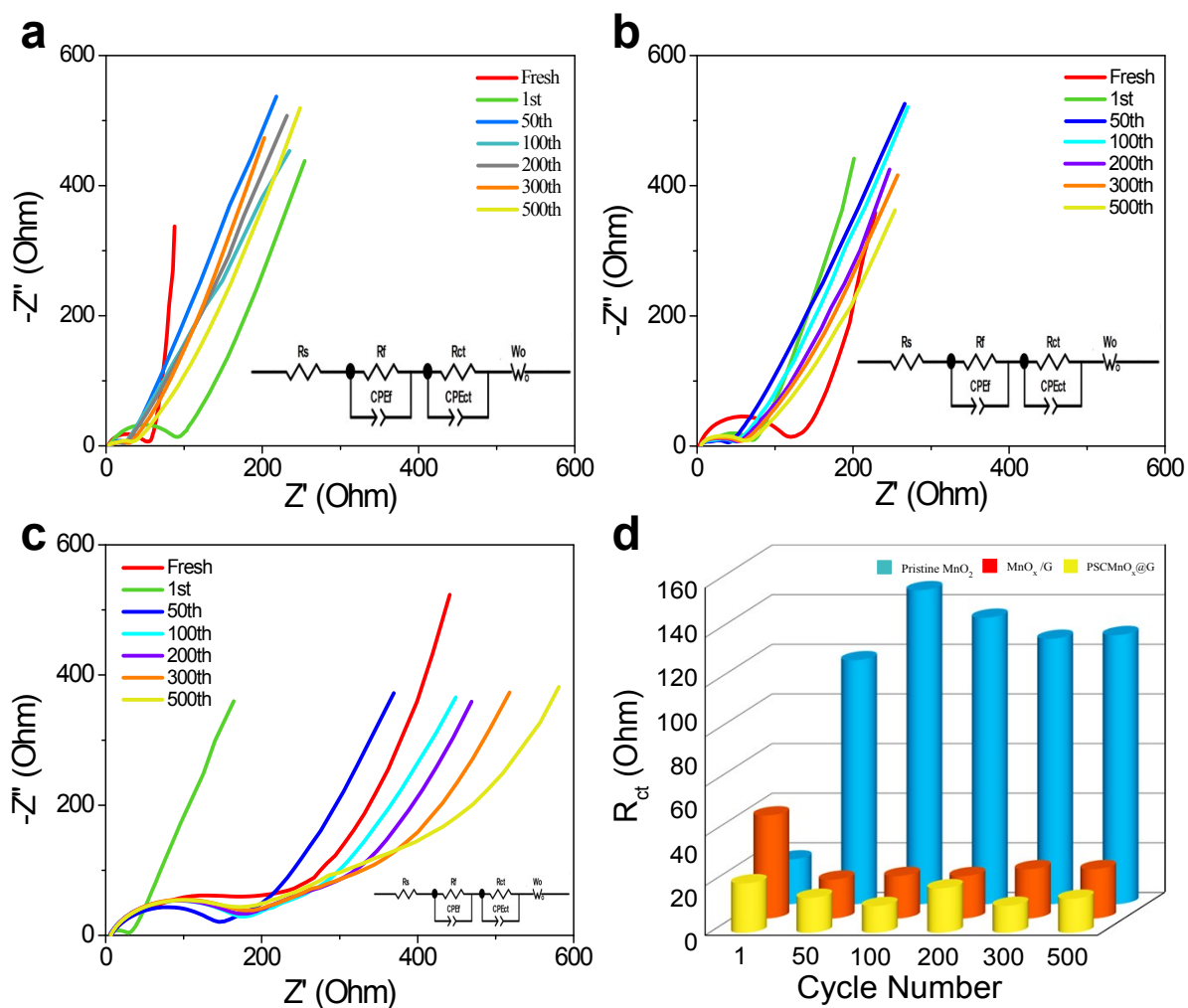
(b) The R<sub>s</sub> of the PSCMnO<sub>x</sub>@G, MnO<sub>x</sub>/G and pristine MnO<sub>2</sub> electrodes.

**Table S2.** Comparison of the electrochemical performance of PSCMnO<sub>x</sub>@G with previously reported MnO<sub>x</sub> based electrodes.

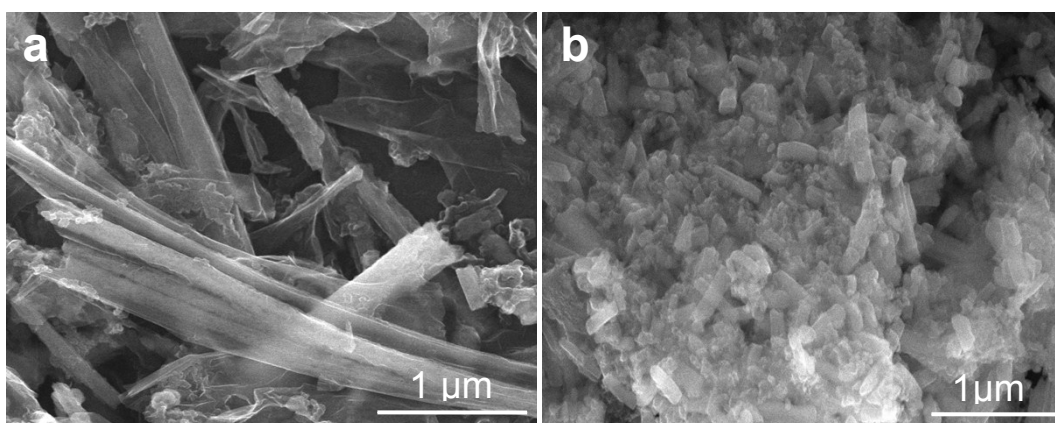
| Manganese oxide -based materials                       | Rate performance<br>[ mA h g <sup>-1</sup> ]                  | Cycling performance<br>[mA h g <sup>-1</sup> ] | Ref.             |
|--------------------------------------------------------|---------------------------------------------------------------|------------------------------------------------|------------------|
| GNS@MnO@N-C                                            | 873 (0.1 A g <sup>-1</sup> ); 165 (2.0 A g <sup>-1</sup> )    | 754 (0.1 A g <sup>-1</sup> , 350 cycles)       | [19]             |
| $\alpha$ -Mn <sub>2</sub> O <sub>3</sub> nanocrystals  | 780 (0.1 A g <sup>-1</sup> ); 425 (3.2 A g <sup>-1</sup> )    | 780 (0.1 A g <sup>-1</sup> , 100 cycles)       | [23]             |
| Carbon NFs/MnO                                         | 1006 (0.1 A g <sup>-1</sup> ); 409 (2.0 A g <sup>-1</sup> )   | 992 (0.2 A g <sup>-1</sup> , 50 cycles)        | [8]              |
| MnCO <sub>3</sub> /Mn <sub>3</sub> O <sub>4</sub> /RGO | 800 (0.1 A g <sup>-1</sup> ); 150 (3.2 A g <sup>-1</sup> )    | 532 (1.0 A g <sup>-1</sup> , 800 cycles)       | [17]             |
| MnO/C nanopeapods                                      | 845 (0.1 A g <sup>-1</sup> ); 320 (5.0 A g <sup>-1</sup> )    | 525 (2.0 A g <sup>-1</sup> , 1000 cycles)      | [25]             |
| Coaxial MnO/N-C nanorods                               | 828 (0.2 A g <sup>-1</sup> ); 372 (5.0 A g <sup>-1</sup> )    | 982 (0.5 A g <sup>-1</sup> , 100 cycles)       | [34]             |
| MnO@Mn <sub>3</sub> O <sub>4</sub> /NPCF               | 660 (0.2 A g <sup>-1</sup> ); 280 (2.0 A g <sup>-1</sup> )    | 1500 (0.2 A g <sup>-1</sup> , 270 cycles)      | [14]             |
| GO-MnO <sub>2</sub> -GO NRBs                           | 680 (0.1 A g <sup>-1</sup> ); 280 (2.0 A g <sup>-1</sup> )    | 612 (0.4 A g <sup>-1</sup> , 250 cycles)       | [9]              |
| MnO <sub>2</sub> /RGO                                  | 964 (0.1 A g <sup>-1</sup> ); 115 (10 A g <sup>-1</sup> )     | 1574 (1.0 A g <sup>-1</sup> , 500 cycles)      | [10]             |
| MnO <sub>x</sub> /SWCNT                                | 866 (0.2 A g <sup>-1</sup> ); 437 (0.8 A g <sup>-1</sup> )    | 850 (0.1 A g <sup>-1</sup> , 36 cycles)        | [28]             |
| MnNCN                                                  | 792 (0.1 A g <sup>-1</sup> ); 320 (3.2 A g <sup>-1</sup> )    | 385 (5.0 A g <sup>-1</sup> , 500 cycles)       | [16]             |
| MnO@N-C                                                | 1097 (0.1 A g <sup>-1</sup> ); 438 (2.0 A g <sup>-1</sup> )   | 690 (1.0 A g <sup>-1</sup> , 150 cycles)       | [15]             |
| MnO@CF                                                 | 895 (0.2 A g <sup>-1</sup> ); 513 (4.0 A g <sup>-1</sup> )    | 1040 (0.2 A g <sup>-1</sup> , 500 cycles)      | [42]             |
| G/MnO-800                                              | 1000 (0.1 A g <sup>-1</sup> ); 270 (8.0 A g <sup>-1</sup> )   | 620 (1.0 A g <sup>-1</sup> , 600 cycles)       | [29]             |
| MnO@C CSNWs                                            | 880 (0.1 A g <sup>-1</sup> ); 356 (5.0 A g <sup>-1</sup> )    | 750 (1.0 A g <sup>-1</sup> , 200 cycles)       | [18]             |
| Mn <sub>3</sub> O <sub>4</sub> /N-C fiber              | 1058 (0.05 A g <sup>-1</sup> ); 320 (2.5 A g <sup>-1</sup> )  | 1007 (0.1 A g <sup>-1</sup> , 160 cycles)      | [26]             |
| MnO nanowires/graphene                                 | 780 (0.05 A g <sup>-1</sup> ); 300 (1.0 A g <sup>-1</sup> )   | 930 (0.5 A g <sup>-1</sup> , 500 cycles)       | [33]             |
| <b>PSCMnO<sub>x</sub>@G</b>                            | <b>1072 (0.1 A g<sup>-1</sup>); 420 (10 A g<sup>-1</sup>)</b> | <b>1163 (2.0 A g<sup>-1</sup>, 500 cycles)</b> | <b>This work</b> |



**Fig. S10.** Differential capacities ( $dQ/dV$ ) versus voltage plots of pristine  $\text{MnO}_2$  for different cycles at  $2.0 \text{ A g}^{-1}$ .



**Fig. S11.** Nyquist impedance plots of (a) PSCMnO<sub>x</sub>@G, (b) MnO<sub>x</sub>/G and (c) pristine MnO<sub>2</sub> for different cycles at 2.0 A g<sup>-1</sup>. (d) R<sub>ct</sub> of PSCMnO<sub>x</sub>@G, MnO<sub>x</sub>/G and pristine MnO<sub>2</sub> for different cycles at 2.0 A g<sup>-1</sup>.



**Fig. S12.** SEM images of (a) the PSCMnO<sub>x</sub>@G and (b) MnO<sub>2</sub> nanofibers after 500 cycles at 2.0 A g<sup>-1</sup>.