Supplementary Information

Temperature controlled hydrothermal synthesis of γ -MnOOH, Mn₃O₄ and

MnCO₃ on carbon cloth for supercapacitor application

Shujuan Meng, Qiong Su, Ping Zhang, Wanhong Sun, Yanbin Wang

School of Chemical Engineering, Key Laboratory for Utility of Environment-Friendly Composite Materials and Biomass in University of Gansu Province, Northwest Minzu

University, Lanzhou, 730030, China. E-mail: mengshujuan@126.com



Fig. S1 Photograph of (a) SC100 and (b) unreacted KMnO₄ solution after reaction at 100 °C for 15 h. After reaction at 100 °C, only part of carbon cloth was covered with Mn_7O_{13} ·5H₂O (red quasi-circular area) and most of the carbon cloth are clean without Mn_7O_{13} ·5H₂O covering.



Fig. S2 Photograph of unreacted KMnO₄ solution after reaction at (a) 100 $^{\circ}$ C and (b) 140 $^{\circ}$ C for 15 h without carbon cloth growth substrate.



Fig. S3 The photograph of the products and solution after reacted at 220°C for 15h without carbon cloth substrate. No unreacted KMnO₄ was left in the autoclave.



Fig. S4 SEM images of SC100 with different magnifications.



Fig. S5 SEM images of SC140 with different magnifications.



Fig. S6 SEM images of SC180 with different magnifications.



Fig. S7 SEM images of SC220 with different magnifications.



Fig. S8 EDS mapping of (b) Mn, (c) O and (d) C taken from a selected nanowire exfoliated from SC220 on Si substrate in (a).



Fig. S9 The (a, b) low magnification TEM images, (c, d) SAED patterns, (e, f) HR-TEM images of (a, c, e) γ -MnOOH nanowires and (b, d, f) Mn₃O₄ irregular particle obtained in SC180 and SC220, respectively.

Note S1: Calculation of mass difference of carbon cloth before and after reaction at different temperatures

We weighted the mass of carbon cloth before reaction and after dissolving the Mn species grown on carbon cloth at 140°C, 180°C and 220°C, respectively. In order to investigate the mass change of carbon cloth, we placed one piece of carbon cloth ($\sim 2.5 \times 4 \text{ cm}^2$) into Teflon-line autoclave containing 40mL KMnO₄ (0.5 g) solution, then the autoclave was heated at 220°C for 15 hours. After cooling down to room temperature, we collected the carbon cloth with corresponding products covering on its surface. We dissolved the γ -MnOOH, MnCO₃ and Mn₃O₄ particles on the carbon cloth surface by using 4 M HCl solution and washed the left carbon cloth with distilled water for several times and dried it. The mass of carbon cloth before reaction and after dissolving the γ -MnOOH, MnCO₃ and Mn₃O₄ particles is M₁ and M₂, respectively. The mass difference is defined as $\Delta M=M_1-M_2$. The same procedure was also carried out for 140 °C and 180 °C cases. At every temperature point, two sets of experiments were carried out.



Fig. S10 SEM images of (a, b) carbon cloth before reaction, (c, d) carbon cloth after dissolving Mn_3O_4/γ -MnOOH composites (by 4M HCl) grown at 180 °C and (e, f) SEM images of carbon cloth after dissolving γ -MnOOH, MnCO₃ and Mn₃O₄ composites (by 4M HCl) grown at 220 °C.



Fig. S11 (a) XPS survey of carbon cloth. Fine-scan XPS spectra of (b) O 1s and (c) C 1s on carbon cloth and (d) fitted curves for C 1s XPS spectra with four synthetic peaks.

Fig. S11a shows the XPS survey of carbon cloth, and we found that the main elemental composition of carbon cloth surface is C and O. Fig. S11b and c gives the fine-scan rate of O 1s and C 1s spectra, respectively, and the evident O 1s signal indicates that there are oxygen-containing functional groups on the carbon cloth surface. The oxygen ratio [defined as O/(O+C), where O and C represent the number of oxygen and carbon atoms, respectively] on the carbon cloth surface calculated based on XPS survey spectra is 6.41%, which is consistent with the reported data $(7\%)^1$. We also fitted the C 1s spectrum with four synthetic peaks centered at 284.6, 286.2, 287.3, and 288.7 eV, which are assigned to the C=C, C-O, C=O, and O-C=O bonds¹, respectively, with the results shown in Fig. S11d. The carbon atoms existed by formation of oxygen-containing functional groups is 14.1%.

Next, we will testify that the oxygen-containing functional groups may only contribute small part of carbon atoms for the formation of $MnCO_3$ on carbon cloth because of their very low content compared with the all carbon atoms in carbon fibres. Fig. S12 shows the SEM image of carbon cloth and a single carbon fibre and we can



Fig. S12. SEM images of (a) carbon cloth and (b) a single carbon fibre.

see that the radii of the carbon fibre is ~8µm. It is known that the XPS can only detect the elemental composition with a very thin surface and we assume the thickness of detected carbon cloth surface is 20 nm and the number of carbon atoms in unit volume (1nm³) is N_c . Fig. S13 schematically the cross section of a carbon fibre and the radii of carbon fibre is r_c =8µm=8000nm, the detection thickness of carbon cloth surface for XPS is r_s =20nm and the length of carbon fibre is H nm. So, the number of carbon atoms existed by formation of oxygen-containing functional groups can be calculated as follow: N_{oc} = $\pi \cdot (r_c^2 - r_t^2) \cdot H \cdot N_c$. The number of all carbon atoms in this carbon fibre is N_{all} = $\pi \cdot r_c^2 \cdot H \cdot N_c$. Thus, the ratio of carbon atoms in oxygen-containing functional groups compared with the all carbon atoms in carbon cloth is $R=N_{oc}/N_{all}=1-(r_t/r_c)^2=1 0.99500625=0.00449375 \approx 0.45\%$. So, the carbon atoms in oxygen-containing functional groups as well as the amount of oxygen-containing functional groups are very low.



Fig. S13 The schematic diagram for the cross section of a carbon fibre in carbon cloth.



Fig. S14 SEM images of (a, b) SC180-5, (c, d) SC180-10 and (e, f) SC180-20.

References:

1. G. Wang, H. Wang, X. Lu, Y. Ling, M. Yu, T. Zhai, Y. Tong and Y. Li, *Adv. Mater.*, 2014, **26**, 2676-2682.