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# Anchoring carbon layers and oxygen vacancies endow $\text{WO}_{3-x}/\text{C}$ electrode with high specific capacity and rate performance for supercapacitors†

Juan Xu, \* Chongyang Li, Lulu Chen, Zhongyang Li and Pibin Bing

Herein, novel hierarchical carbon layer-anchored  $\text{WO}_{3-x}/\text{C}$  ultra-long nanowires were developed via a facile solvent-thermal treatment and a subsequent rapid carbonization process. The inner anchored carbon layers and abundant oxygen vacancies endowed the  $\text{WO}_{3-x}/\text{C}$  nanowire electrode with high conductivity, as measured with a single nanowire, which greatly enhanced the redox reaction active sites and rate performance. Surprisingly, the  $\text{WO}_{3-x}/\text{C}$  electrode exhibited outstanding specific capacitance of  $1032.16 \text{ F g}^{-1}$  at the current density of  $1 \text{ A g}^{-1}$  in a  $2 \text{ M H}_2\text{SO}_4$  electrolyte and maintained the specific capacitance of  $660 \text{ F g}^{-1}$  when the current density increased to  $50 \text{ A g}^{-1}$ . Significantly, the constructed  $\text{WO}_{3-x}/\text{C} // \text{WO}_{3-x}/\text{C}$  symmetric supercapacitors achieved specific capacitance of  $243.84 \text{ F g}^{-1}$  at the current density of  $0.5 \text{ A g}^{-1}$  and maintained the capacitance retention of 94.29% after 5000 charging/discharging cycles at the current density of  $4 \text{ A g}^{-1}$ . These excellent electrochemical performances resulted from the fascinating structure of the  $\text{WO}_{3-x}/\text{C}$  nanowires, showing a great potential for future energy storage applications.

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## 1. Introduction

Over the past decades, electrochemical supercapacitors (ESs) have gradually stood out from other electrochemical energy storage devices, profiting from their distinguishing advantages of high power density, rational energy density and long-term cycle stability.<sup>1–3</sup> As is well-established, the electrochemical performance of ESs is heavily dependent on their electrode materials.<sup>4–7</sup> Apart from commercial carbon and conducting polymer materials, transition metal oxides have received considerable attention owing to their good electrochemical reversibility and high specific capacitance in aqueous electrolytes.<sup>8–11</sup> Nanostructured tungsten-based materials ( $\text{WO}_3$  and  $\text{W}_{18}\text{O}_{49}$ ) are distinctly appealing in this regard owing to their multiple oxidation states, high electronic conductivity ( $10 \times 10^{-6} \text{ S cm}^{-1}$ ), small radii and suitable crystalline phases for fast ion insertion and superior electrochemical performance.<sup>12–15</sup>

To induce more active sites during the redox reaction process, strategies for the nanostructures of different dimensionalities such as nanoparticles, nanowires, nanotubes, and nanosheets as well as 3D porous structures have been reported.<sup>16–20</sup> Among them, nanowires are considered to be the

most promising structures due to their sufficient interfacial contact areas with the electrolyte as well as the easy percolation of the nanowire network. Furthermore, the electrical conductivity can be improved by compositing/doping  $\text{WO}_{3-x}$  with conducting alien species.<sup>21–23</sup> Recently, Gong *et al.* reported the growth of carbon-encapsulated  $\text{WO}_{3-x}$  nanowires via a facile hydrothermal and annealing treatment, achieving areal specific capacitance of  $786.8 \text{ mF cm}^{-2}$  at the current density of  $20 \text{ mA cm}^{-2}$ , but their rate properties were not satisfactory.<sup>24</sup> Tian *et al.* reported the production of  $\text{W}_{18}\text{O}_{49}$  nanofibers by the addition of ethanol and electrodeposition of a polyaniline film, displaying specific capacitance of  $440 \text{ F g}^{-1}$  at the current density of  $1 \text{ A g}^{-1}$ . However, they could not display a long cycling life.<sup>14</sup> In all, all these reported structures cannot satisfy the commercial requirements of high specific capacitance, high rate properties and long lifespan. The major obstacle is that all these reported carbon post-coated methods yield  $\text{WO}_{3-x}$  nanowires with only surface-coated carbon materials rather than being confined to a single nanowire and thus, the inner nanowire matrix fails to contact with the exterior conductive carbon materials.

Herein, the structure of hierarchical carbon layer-anchored ultra-long nanowires was proposed as a promising platform to achieve high electronic conductivity and superior electrochemical performance. We projected that the  $\text{WO}_3$ -ethylenediamine ( $\text{WO}_3\text{-EDA}$ ) inorganic-organic hybrid nanowire framework with a unique structure and high specific surface area can provide large contact areas with the electrolyte. After

Institute of Electric Power, North China University of Water Resources and Electric Power, Zhengzhou, Henan, 450000, China. E-mail: xujuan@ncwu.edu.cn

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a facile rapid thermal treatment, the anchored carbon layers could be uniformly and tightly distributed in the inside of the  $\text{WO}_{3-x}$  nanowires through oxygen bridges, which not only significantly contributed to the enhanced conductivity but also helped enable an outstanding rate performance. Significantly, the reduction of carbon to  $\text{WO}_3$  resulted in the formation of a large amount of oxygen vacancies in  $\text{WO}_{3-x}$  to achieve promising conductivity. Notably, the as-obtained carbon layer-anchored ultra-long  $\text{WO}_{3-x}$  nanowire ( $\text{WO}_{3-x}/\text{C}$ )-based electrode exhibited specific capacitance of  $1032.16 \text{ F g}^{-1}$  at the current density of  $1 \text{ A g}^{-1}$ . Amazingly, when the current density was increased to  $50 \text{ A g}^{-1}$ , the specific capacitance of  $660 \text{ F g}^{-1}$  could still be maintained. This extraordinary performance is superior to previously reported values for  $\text{WO}_{3-x}$ -based electrodes, thus demonstrating the advantage of the carbon layer-anchored nanowire configuration.

## 2. Experimental section

### 2.1. Material preparation

The precursor of organic-inorganic hybrid  $\text{WO}_3$ -EDA nanowires was obtained *via* a facile and low-cost solvent-thermal treatment. In a typical experiment,  $1 \text{ g}$   $\text{WO}_3$  was first slowly added to  $75 \text{ mL}$  ethylenediamine (EDA) to form a uniform and yellow solution. Subsequently, the solution was transferred to a Teflon-lined stainless steel autoclave and then heated in an electric oven at  $180 \text{ }^\circ\text{C}$  for  $12 \text{ h}$ , followed by naturally cooling to room temperature. The product was collected by centrifugation, washed thoroughly with deionized water and ethanol several times and then dried in vacuum at  $60 \text{ }^\circ\text{C}$  overnight. Finally, the hierarchical carbon layer-anchored  $\text{WO}_{3-x}$  nanowires were achieved by the rapid pyrolysis of the as-obtained organic-inorganic hybrid nanowire precursor at  $600 \text{ }^\circ\text{C}$  for  $2 \text{ h}$  under an Ar flow. The pure  $\text{WO}_3$  nanowires were produced by annealing the precursor at  $600 \text{ }^\circ\text{C}$  for  $2 \text{ h}$  under an Air flow.

### 2.2. Material characterization

X-ray powder diffraction (XRD) patterns were recorded using a Philips X'Pert Pro (PANalytical B.V., Netherlands) Super diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54118 \text{ \AA}$ ). SEM images were obtained *via* field-emission scanning electron microscopy (FE-SEM, FEI Nova NanoSEM 450) equipped with an X-ray energy dispersive spectrometer (EDS). Transmission electron microscopy (TEM, FEI Tecnai G20), Raman scattering (InVo-RENISHAW), Fourier transform infrared spectroscopy (FT-IR, Bruker Vertex 80 V) and X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra DLD-600 W) were also performed. The thermogravimetric-differential analysis (TG-DSC) was performed on Perkin Elmer Diamond TG-DTA at a temperature ramping rate of  $10 \text{ }^\circ\text{C min}^{-1}$  under air. A four-point probe on a Si template was then designed and fabricated to measure the conductivity of a single hierarchical  $\text{WO}_{3-x}/\text{C}$  nanowire and pure  $\text{WO}_3$  nanowire.

### 2.3. Electrochemical measurements

Electrodes were prepared by mixing the collected samples (80%), Super P (10%) and polyvinylidene fluoride (10%) in *N*-methyl,2-pyrrolidone to form a slurry. The slurry was stirred uniformly and pasted on the carbon current collector. The collector was cut into a square shape with  $1 \text{ cm} \times 1 \text{ cm}$  dimensions for electrodes and placed into a vacuum oven ( $80 \text{ }^\circ\text{C}$ ) overnight to remove moisture and residual hydrocarbons. The three-electrode electrochemical cell was fabricated with a platinum foil as the counter electrode, a saturated calomel electrode as the reference electrode and the hierarchical  $\text{WO}_{3-x}/\text{C}$  nanowire electrode as the working electrode. The symmetric supercapacitor was measured with a two-electrode configuration, including two slices of electrode material with the same size ( $1 \times 1 \text{ cm}^2$ ) and the same mass loading ( $1.8 \text{ mg}$ ), a cellulose membrane as the separator, and  $2 \text{ M H}_2\text{SO}_4$  solution as the electrolyte. All the electrochemical measurements in both the three-electrode and two-electrode systems were performed on a CHI660D electrochemical workstation.

## 3. Results and discussion

The above-mentioned organic-inorganic hybrid  $\text{WO}_3$ -EDA nanowires were acquired in high yields *via* a facile hydrothermal treatment with a small quantity of  $\text{WO}_3$  as the raw material and EDA as the solvent. As shown in Fig. 1, EDA plays a vital role in the production of the hierarchical organic-inorganic hybrid nanowires. In the  $\text{WO}_3$ -EDA hybrid nanowires, the organic EDA molecules intercalated into the inorganic  $\text{WO}_3$  framework on a sub-nanometer-scale.<sup>25</sup> The inorganic units are connected by H-bonding of  $\text{N-H}\cdots\text{O-W}$ .<sup>26-28</sup> Following the facile rapid pyrolysis of these hybrid  $\text{WO}_3$ -EDA nanowires in a pure Ar atmosphere, we finally achieved uniform thin carbon layer-anchored  $\text{WO}_{3-x}$  nanowires owing to the instant carbonization of EDA and confined effects. In addition, the formation of abundant oxygen vacancies was induced because of the reduction of carbon to  $\text{WO}_3$ .

Fig. 2a and b show the typical scanning electron microscopy (SEM) images of the hierarchical  $\text{WO}_{3-x}/\text{C}$  nanowires. Fig. 2a

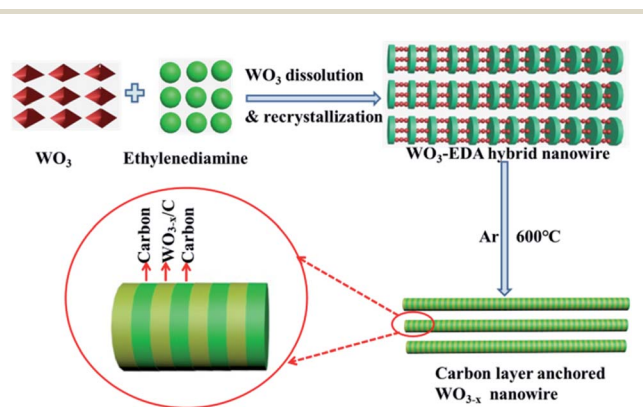
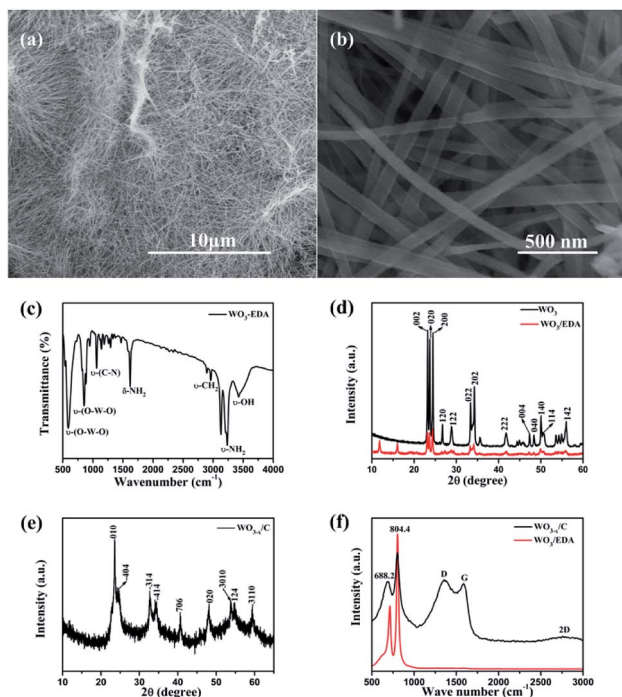


Fig. 1 The formation process of hierarchical carbon layer-anchored ultra-long  $\text{WO}_{3-x}$  nanowires from the organic-inorganic hybrid  $\text{WO}_3$ -EDA precursor.





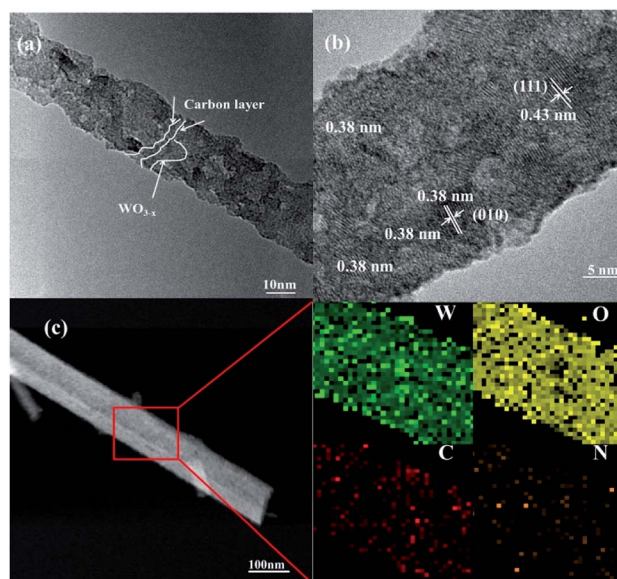
**Fig. 2** (a and b) SEM images of different magnifications of hierarchical  $\text{WO}_{3-x}/\text{C}$  nanowires. (c) FTIR spectrum of the  $\text{WO}_3$ -EDA organic-inorganic hybrid precursor. (d) XRD patterns of the raw material  $\text{WO}_3$  and the  $\text{WO}_3$ -EDA precursor. (e) XRD pattern of the hierarchical  $\text{WO}_{3-x}/\text{C}$  nanowires. (f) Raman spectra of the  $\text{WO}_3$ -EDA hybrid precursor and hierarchical  $\text{WO}_{3-x}/\text{C}$  nanowires.

shows the hierarchical  $\text{WO}_{3-x}/\text{C}$  nanowires with a uniform length of 10–20  $\mu\text{m}$ . Obviously, the nanowires exhibited a diameter of 50–100 nm. The nanowires possessed the same morphology as that of the  $\text{WO}_3$ -EDA hybrid precursor, which is characterized in Fig. S1.† The presence of EDA molecules in the  $\text{WO}_3$ -EDA hybrid precursor is confirmed by the FTIR spectrum in Fig. 2c, which displays the  $\nu$ -OH stretching mode at  $3433\text{ cm}^{-1}$  and the  $\nu$ - $\text{CH}_2$  bending mode at  $2960\text{ cm}^{-1}$ .<sup>26</sup> The sharp peaks at around  $1620\text{ cm}^{-1}$  and  $3245\text{ cm}^{-1}$  correspond to the  $\delta$ - $\text{NH}_2$  and  $\nu$ - $\text{NH}_2$  stretching modes, indicating that the interlayer organic molecules were intercalated as ammonium cations rather than neutral amines. In addition, the absorption peaks at around  $590\text{ cm}^{-1}$  and  $850\text{ cm}^{-1}$  can be attributed to the  $\nu$ -(O-W-O) lattice vibration modes in  $\text{WO}_3$ .<sup>26</sup> These results gave significant evidence that the EDA molecules intercalated into the  $\text{WO}_3$  lattice. Moreover, the XRD pattern in Fig. 2d clearly shows the presence of three level diffraction peaks at  $2\theta = 11.73^\circ$ ,  $15.94^\circ$ , and  $19.13^\circ$  (*i.e.*,  $d_1 = 0.71\text{ nm}$ ,  $d_2 = 0.54\text{ nm}$ , and  $d_3 = 0.44\text{ nm}$ ), respectively, which are owing to the intercalation of the EDA molecules into the  $\text{WO}_3$  nanowires. Furthermore, the other peaks well-matched with the previous results for monoclinic  $\text{WO}_3/\text{EDA}$  (JCPDS Card no. 43-1034).<sup>26</sup> Fig. 2e shows the XRD pattern of the final carbon layer-anchored  $\text{WO}_{3-x}/\text{C}$  nanowire network, which can be indexed to monoclinic  $\text{WO}_{3-x}$  (JCPDS Card no. 36-0103). The Raman spectra in Fig. 2f further confirm the presence of carbon in the  $\text{WO}_{3-x}$  nanowire network.<sup>29</sup> The absorption peaks at around  $688.2\text{ cm}^{-1}$  and

$804.4\text{ cm}^{-1}$  can be attributed to the  $\delta$ -(O-W-O) lattice vibration mode and  $\nu$ -(W=O) lattice vibration mode in  $\text{WO}_3$ , respectively.<sup>30</sup> Moreover, the two broad peaks at  $1360\text{ cm}^{-1}$  and  $1578\text{ cm}^{-1}$  correspond to the D band and G band, which indicate the existence of carbon coating layers originating from the disordered and ordered graphitic carbon, respectively. The  $I_D/I_G$  value was calculated to be about 1.05, which indicated a reasonable degree of graphitization.<sup>31–34</sup>

Fig. 3 further confirms the crystalline structure and element distribution of the  $\text{WO}_{3-x}/\text{C}$  nanowires. The diameter of the  $\text{WO}_{3-x}/\text{C}$  nanowires was about 20 nm. Obviously, Fig. 3a shows the carbon layers tightly anchored on the inside of the  $\text{WO}_{3-x}$  layers, which is consistent with the description in Fig. 1. In addition, the lattice fringes of the  $\text{WO}_3$  layers and carbon layers are very clear in Fig. 3b. Fig. 3c shows the TEM image and X-ray energy dispersive spectroscopy (EDS) maps of a single nanowire, confirming the uniform distribution of W, O, C and N.

The X-ray photoelectron spectroscopy (XPS) results acquired from the pure  $\text{WO}_3$  nanowires (Fig. S2†) and  $\text{WO}_{3-x}/\text{C}$  nanowires are shown in Fig. 4a. The presence of N1s in the XPS spectra of the  $\text{WO}_{3-x}/\text{C}$  nanowires clearly proved the insertion of EDA into the  $\text{WO}_3$  nanowires. Moreover, the ratio of O to W was less than 3, indicating the generation of oxygen vacancies in the hierarchical carbon layer-anchored  $\text{WO}_{3-x}$  nanowires. The fine XPS spectra of N1s are shown in Fig. S3.† The two fine XPS peaks of W of pure  $\text{WO}_3$  (Fig. 4b) at  $36.03\text{ eV}$  and  $38.48\text{ eV}$  correspond to  $4f_{7/2}$  and  $4f_{5/2}$  of  $\text{W}^{6+}$ , which are in agreement with the XRD pattern. However, the binding energy was lower than that for the corresponding fine spectra of  $\text{W}4f_{7/2}$  and  $\text{W}4f_{5/2}$  in the  $\text{WO}_{3-x}/\text{C}$  nanowires by  $0.17\text{ eV}$ .<sup>10,14,24,25</sup> The shifts in the binding energies can provide valuable information. As previously reported, this evidences the introduction of oxygen vacancies and the perturbation of the electronic environment after incorporating a small amount of N anions with different electronegativities. The C content in the hierarchical



**Fig. 3** (a and b) TEM images and (c) EDS mapping results of the carbon layer-anchored  $\text{WO}_{3-x}$  nanowires.



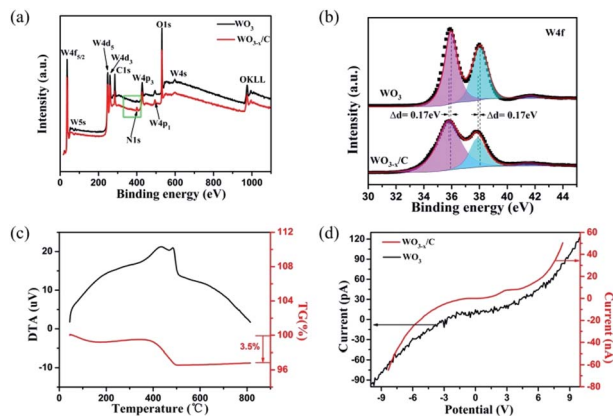


Fig. 4 (a) Survey XPS of pure  $\text{WO}_3$  nanowires and  $\text{WO}_{3-x}/\text{C}$  nanowires. (b) High-resolution W4f spectra of  $\text{WO}_3$  nanowires and  $\text{WO}_{3-x}/\text{C}$  nanowires. (c) TGA and DSC profiles of the  $\text{WO}_{3-x}/\text{C}$  nanowires. (d) Electrical conductivity of the  $\text{WO}_3$  nanowires and  $\text{WO}_{3-x}/\text{C}$  nanowires.

$\text{WO}_{3-x}/\text{C}$  nanowires was measured to be 3.5 wt% according to the TG curve in Fig. 4c. According to the calculation in Fig. 4d, the electrical conductance is  $1.64 \times 10^{-3} \text{ S cm}^{-1}$  for a single hierarchical  $\text{WO}_{3-x}/\text{C}$  nanowire, which is approximately three orders of magnitude higher than that of a single pure  $\text{WO}_3$  nanowire with  $1.00 \times 10^{-6} \text{ S cm}^{-1}$ . This is consistent with the prominent role of the anchoring of carbon layers, which can indicate the excellent electrochemical performance of the  $\text{WO}_{3-x}/\text{C}$  nanowire electrodes.

The electrochemical performance of the as-prepared  $\text{WO}_{3-x}/\text{C}$  nanowire electrode in comparison with that of the pure  $\text{WO}_3$  nanowire electrode was evaluated using three-electrode cell configuration in 2 M  $\text{H}_2\text{SO}_4$  electrolyte. The results are clearly given in Fig. 5a–f. Notably, the  $\text{WO}_{3-x}/\text{C}$  nanowire electrode delivered larger CV curve areas and wider voltage window than the pure  $\text{WO}_3$  nanowire electrode at the same scan rate and current density (Fig. 5a–d), which indicated its enhanced specific capacitance and good redox reaction kinetics. Obviously, broad peaks were detected in the CV curves of the two samples, which corresponded to the slightly sloping plateaus in the GCD curves at different current densities, indicating redox-active  $\text{WO}_{3-x}$  with reversible Faradaic reactions as the dominant charge storage mechanism.<sup>35–38</sup> The voltage window was 0.9 eV for the  $\text{WO}_{3-x}/\text{C}$  electrode, which was larger than that for the pure  $\text{WO}_3$  electrode (0.6 eV) (Fig. 5c and d). Prominently, this was ascribed to the introduction of oxygen vacancies in the  $\text{WO}_{3-x}/\text{C}$  nanowires.<sup>25,26,28,29</sup> The gravimetric specific capacitances were calculated from the GCD curves and the result was plotted *vs.* mass current density (Fig. 5e). Ultra-high specific capacitance of  $1032.16 \text{ F g}^{-1}$  was acquired at  $1 \text{ A g}^{-1}$  for the  $\text{WO}_{3-x}/\text{C}$  electrode, which was much higher than that for the pure  $\text{WO}_3$  electrode ( $308.15 \text{ F g}^{-1}$ ) at  $1 \text{ A g}^{-1}$ . When the current density increased to 2, 5, 10, 20, and  $50 \text{ A g}^{-1}$ , the specific capacitances gradually reduced to 896.96, 886.61, 835.67, 765.33, and  $660 \text{ F g}^{-1}$ , respectively. Obviously, the pure  $\text{WO}_3$  electrode exhibited a much poorer rate performance (Fig. 5e). The cyclic performance of the  $\text{WO}_{3-x}/\text{C}$  electrode was much better than that of the pure  $\text{WO}_3$  electrode (Fig. 5f), and the

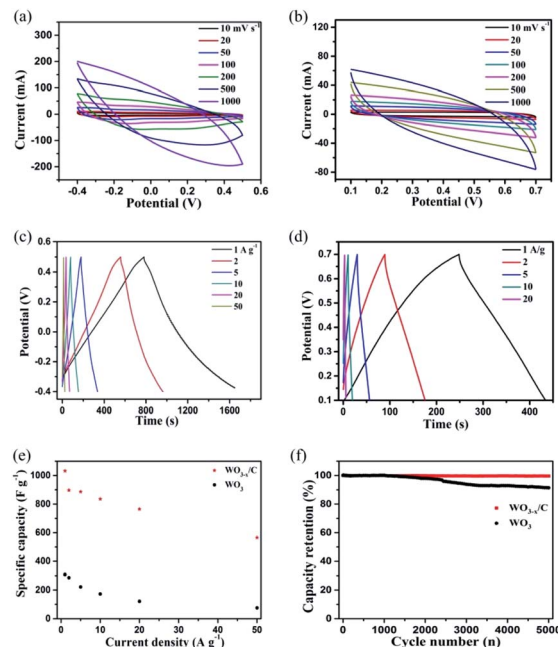


Fig. 5 (a and b) Typical CV curves at different scan rates and (c–e) GCD profiles at different current densities and corresponding rate performance of the  $\text{WO}_{3-x}/\text{C}$  nanowire electrode and pure  $\text{WO}_3$  nanowire electrode in the three-electrode configuration. (f) Cycle stability of the hierarchical  $\text{WO}_{3-x}/\text{C}$  nanowire and pure  $\text{WO}_3$  nanowire electrodes for 5000 cycles.

capacitance retention of 100% could be maintained after 5000 cycles. This significant electrochemical performance was attributed to the carbon layer-anchored nanowire structure and the introduction of numerous oxygen vacancies. In fact, the excellent structure with high electrical conductivity makes a substantial contribution to the high specific capacitance of the  $\text{WO}_{3-x}/\text{C}$  electrode, and this 1D nanowire morphology offers more electro-active sites, which are easily accessible by the electrolyte ions during the redox reactions even at high rates.

Fig. 6 shows the electrochemical performance of the as-assembled hierarchical  $\text{WO}_{3-x}/\text{C}/\text{WO}_{3-x}/\text{C}$  symmetric supercapacitor (SSC). A schematic of the SSC device is clearly shown in Fig. 6a. The CV profiles (Fig. 6b) of the SSC device measured at different scan rates implied a very stable electrochemical performance with symmetric rectangular curves at the voltage window of 1.2 V. Obviously, the GCD curves (Fig. 6c) of the device obtained at a series of current densities ranging from  $0.5 \text{ A g}^{-1}$  to  $5 \text{ A g}^{-1}$  exhibited a nearly perfect symmetric triangular shape with a prominent charge/discharge capacitive performance, which corresponded to the coulombic efficiency of nearly 100% at every charge/discharge cycle. The gravimetric capacitances were calculated using the results from the GCD profiles and plotted *versus* current density (Fig. 6d). The devices showed outstanding specific capacitance of  $243.84 \text{ F g}^{-1}$  at the current density of  $0.5 \text{ A g}^{-1}$ . When the current density increased to 1, 2, 4, and  $5 \text{ A g}^{-1}$ , the specific capacitances gradually decreased to 194.64, 150.32, 100.97, and  $59.46 \text{ F g}^{-1}$ , respectively. The cell also demonstrated outstanding capacitance



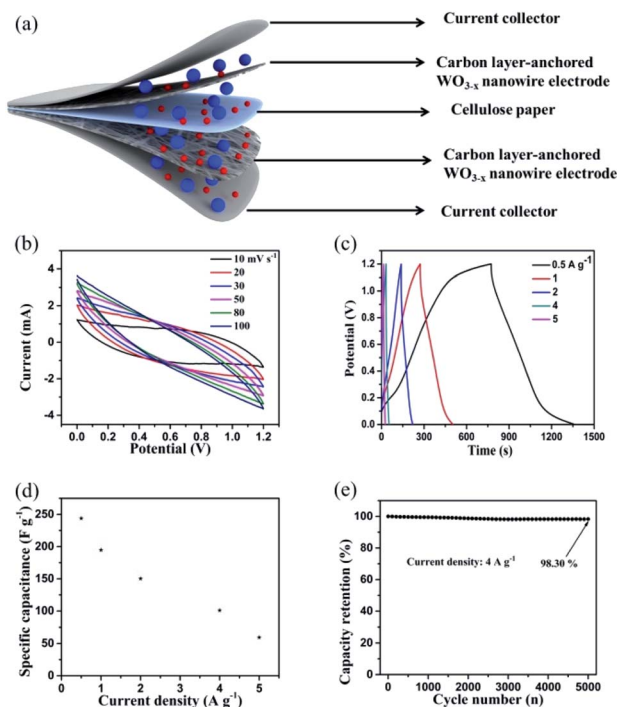


Fig. 6 Electrochemical properties of the assembled hierarchical  $\text{WO}_{3-x}/\text{C} // \text{WO}_{3-x}/\text{C}$  symmetric supercapacitor (SSC): (a) schematic illustration of the SSC device, where the blue spheres represent  $(\text{SO}_4)^{2-}$  and the red spheres represent  $\text{H}^+$ . (b) CV curves at different scan rates. (c and d) GCD curves and specific capacitance plots at various current densities, respectively. (e) Cyclic stability at the current density of  $4 \text{ A g}^{-1}$ .

retention of 94.29% even after 5000 charge/discharge cycles at the high current density of  $4 \text{ A g}^{-1}$  (Fig. 6e). These results are considerably superior to that for previously reported  $\text{WO}_3$ -based symmetric supercapacitors.<sup>10,12,24,29</sup> The prominent electrochemical performance of the developed SSC device implied that the hierarchical carbon layer-anchored  $\text{WO}_{3-x}/\text{C}$  nanowire electrode is a promising candidate for practical applications in next-generation energy storage devices, presenting a new solution of carbon layers and oxygen vacancies integrated into metal oxides in the process of material preparation.

## 4. Conclusions

In summary,  $\text{WO}_{3-x}/\text{C}$  ultra-long nanowires with *in situ* anchored carbon layers were successfully achieved *via* a facile hydrothermal treatment and a subsequent rapid carbonization process; they were also employed as promising electrode materials for supercapacitors. The hierarchical  $\text{WO}_{3-x}/\text{C}$  nanowire electrode achieved outstanding specific capacitance of  $1032.16 \text{ F g}^{-1}$  at the current density of  $1 \text{ A g}^{-1}$  owing to its enhanced electrochemical active sites and improved conductivity due to the introduction of abundant oxygen vacancies and inner anchored carbon layers. Amazingly, the assembled  $\text{WO}_{3-x}/\text{C} // \text{WO}_{3-x}/\text{C}$  symmetric supercapacitors exhibited an excellent electrochemical performance of  $243.84 \text{ F g}^{-1}$  at the current density of  $0.5 \text{ A g}^{-1}$  and maintained the specific

capacitance retention of 94.29% even after 5000 charging/discharging cycles. This synthetic strategy exhibits a new protocol to develop carbonization-engineered metal oxides as electrode materials for applications in supercapacitors.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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