High-performance aqueous asymmetric supercapacitor based on $K_{0.3}WO_3$ nanorods and nitrogen-doped porous carbon

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Abstract

A novel asymmetric supercapacitor device for energy storage is fabricated using $K_{0.3}WO_3$ nanorods as negative electrode and nitrogen-doped porous carbon (CBC-1) based on agricultural wastes corn bract as positive electrode. The $K_{0.3}WO_3$ nanorods are composed of some thinner needle-shaped nanorods which are parallel to each other, and the CBC-1 reveals rough surface of coral-like frameworks with abundant nanopores. The structures can provide high surface area, low diffusion paths and intercalation/de-intercalation of electrolyte ions between the electrode/electrolyte interfaces. Thus, the asymmetric supercapacitor exhibits high energy density about 26.3 Wh kg^{-1} at power density of 404.2 W kg^{-1} in the wide voltage region of 0-1.6 V, as well as a good electrochemical stability (80% capacitance retention after 1000 cycles). Such outstanding electrochemical behaviors imply the CBC-1// $K_{0.3}WO_3$ asymmetric supercapacitor is a promising practical energy-storage system.

KEYWORDS: Supercapacitor; Tungstate; Biomass carbon; Electrodes

Introduction

In the 21st century, due to the increase of energy consumption, global warming and rapid depletion of fossil fuels, the development of clean and renewable energy sources has been one of the most important tasks of scientists [1]. Electrochemical energy storage systems are promising candidates such as lithium-ion batteries and supercapacitors (SCs). Among them, SCs as efficient, clean and sustainable energy devices have attracted a great deal of attention for the applications in portable electronics and hybrid electric vehicles [2]. This is due to their bridge function for the power/energy gap between traditional dielectric capacitors (which have high power output) and batteries/fuel cells (which have high energy storage) [3].

Normally, supercapacitors are categorized into two types depending on the charge storage mechanism: one is electrochemical double layer capacitors (EDLCs) and the other one is faradic supercapacitors (FS) [4]. A typical EDLC is charged by the physisorption of electrolyte ions at the interface of the electrode and electrolyte, while the capacitance occurs in the FS is from the underpotential deposition, surface redox reactions and ion intercalation [5]. Underpotential deposition occurs when metal ions form an adsorbed monolayer at a surface of different metal well above their redox potential, for example, underpotential deposition is that of lead on the surface of a gold electrode [6]. Redox pseudocapacitance occurs when ions are electrochemically adsorbed onto the surface or near surface of a material with a concomitant faradaic charge-transfer. Intercalation pseudocapacitance occurs when ions intercalate into the layers or tunnels of a redox-active material accompanied by a faradaic charge-transfer. Among the three pseudocapacitive mechanisms, underpotential deposition and surface redox reaction pseudocapacitance exhibit kinetics indicative of surface-controlled electrochemical processes:

$i=Cv$, where i is the current (A) and v is the sweep rate (mV s^{-1}) of a cyclic voltammetry experiment. However, charge storage in intercalation pseudocapacitance occurs in the bulk material, in which the kinetics is limited by surface processes and the overall behavior seems capacitive. Moreover, due to charge storage is limited by solid-state diffusion and the peak currents scale with $v^{1/2}$ in most intercalation materials, intercalation pseudocapacitance is rarely observed [7]. And these processes are illustrated in Fig. S1. Thus, electrode material is a key factor to affect the electrochemical properties of supercapacitors.

Currently, activated carbons especially derived from agricultural byproducts for EDLC applications have attracted considerable interest during the development of carbon-based supercapacitors because of their large surface area, low cost, non-toxicity and easy processability [8]. However, the practical applications of most symmetric supercapacitor based on carbon electrodes were still seriously hindered due to the relatively low energy density less than 10 Wh kg^{-1} , which is significantly lower than that of conventional batteries [9]. Therefore, more effort is still desired to build advanced SCs with both high power and energy densities. Due to faster charging/discharging than batteries and higher energy densities than traditional EDLCs, asymmetric supercapacitors (ASCs) have become promising energy storage devices.

Based on the electrochemical properties of the electrode materials, the asymmetric supercapacitors can generally be divided into two major kinds: (1) the two electrodes are different materials exhibiting capacitive behavior with different potential windows to enlarge the overall operation voltage window and energy density of the supercapacitor [10]; (2) the two electrodes are a battery electrode and a capacitor electrode [11, 12], when the battery electrode charges/discharges at a plateau potential, the supercapacitor can store a greater amount of energy

than the symmetric supercapacitor even with the same operating voltage window. Most of the existing examples of this category, such as Yen-Po Lin et al. synthesized and characterized a new type of asymmetric supercapacitor containing a LiMn_2O_4 positive electrode and a MnFe_2O_4 negative electrode [13]; Nicolas et al. synthesized nanocrystalline FeWO_4 as a pseudocapacitive electrode material for supercapacitors using two low-temperature routes, which exhibit attractive electrochemical performance [14]. In addition, currently, among the high energy faradaic electrode materials, alkali metal tungsten bronzes (M_xWO_3 M: Na, K, Rb, Cs; x: 0-1) have attracted much interest due to their low cost, crystal chemistry and a class of latest developing electrical, optical and magnetic properties [15]. Like all tungsten bronzes, the hexagonal structure of M_xWO_3 is built up by rigid tungsten-oxygen layers, which comprises corner-sharing WO_6 octahedron arranged in six-membered ring and M ions positioned at the centers of these octahedral perovskite units. It is believed that the oxygen vacancies and alkali-metal dopants in M_xWO_3 largely improve free-electron concentrations and thus increase electron mobility [16]. An extensive study of their electrochemical properties were initiated by Sepa et al. [17] and J. Vondrak et al. [18] who studied reduction of oxygen and evolution of hydrogen on tungsten bronzes. And the $\text{K}_{0.3}\text{WO}_3$ nanomaterials were also applied in dye-sensitized solar cells using an improved CVD method [19], but its electrochemical properties in supercapacitors have not yet been reported.

In addition, it has been proven to be an effective strategy to utilise nanostructure engineering, including nanoparticles, hollow nano-architectures and one dimensional (1D) nanostructures. Especially, the 1D nanostructures can contribute greatly to the optimization of electrode properties with higher **capacitance** because of the high surface area, low diffusion paths and easy intercalation/de-intercalation of electrolyte ions which consequently improves the

electrochemically active surface area [20]. In this work, we aim to develop an aqueous electrolyte based ASC with high performance by using one dimensional nanostructures pseudo-capacitive materials $K_{0.3}WO_3$ as the negative electrode and nitrogen doped porous carbon based on corn bract as positive electrode in aqueous H_2SO_4 electrolyte.

2. Experimental

2.1 Materials

Corn bract derived from the local environment (Lanzhou city, Gansu province, China), zinc chloride ($ZnCl_2$), ammonium sulfate ($(NH_4)_2SO_4$) (Yantai Shuangshuang Chemical Co., Ltd, China), Nafion solution (DuPont, USA), sodium tungstate ($Na_2WO_4 \cdot 2H_2O$, Aladdin Industrial Corporation, China), potassium rhodanide (KSCN) and N-methyl-2-pyrrolidone (Shanghai Zhongqin Chemical Co., Ltd, China) were in analytical grade and used as produced without any further treatment.

2.2. Synthesis of $K_{0.3}WO_3$ nanorods

The $K_{0.3}WO_3$ nanorods were synthesized using hydrothermal method by twice step. Firstly, the detailed synthesis method of tungsten oxide (WO_3) could be found in our previous work [21]. Secondly, 0.29 g of WO_3 was dispersed in the 30 ml of distilled water with stir uniformly for 20 minutes with assistance by ultrasonic vibration. And then 0.49 g of KSCN was added dropwise to the above solution under violent stirring to form a homogeneous solution. After 30 minutes approximately, the greyish white solution was transferred into a 50 ml Teflon-lined stainless steel autoclave and heated at 180 °C for 24 h. After cooled to room temperature naturally, the resulting precipitates of $K_{0.3}WO_3$ were collected by filtration, washed with distilled water and absolute

ethanol several times to remove the residue of the reactants, finally dried in vacuum at 60 °C for 24 h and characterized further.

2.3. Synthesis of activated carbon

Activated carbon CBC-1 was prepared by carbonization of corn bract as raw materials and the ZnCl_2 as activating agent. Specifically, 1.0 g of dried corn bract was thoroughly mixed with the same quality powder of ZnCl_2 in the crucible, and carbonized in a tubular furnace at 800 °C for 2 h with the heating rate of 5 °C min^{-1} in nitrogen atmosphere. For comparison purpose, the raw material was carried out under the same conditions without mixing activating agent, and the resulting sample was named as CBC. The two samples were washed in 2 M HCl at room temperature for 6 h to remove the impurities, and then washed with distilled water until the pH reached neutral. In final, CBC and CBC-1 are dried at 60 °C overnight.

2.4. Materials characterization

The morphology of the carbons and $\text{K}_{0.3}\text{WO}_3$ materials were performed using the field emission scanning electron microscopy (FE-SEM, Ultra Plus, Carl Zeiss) at an accelerating voltage of 5.0 kV. The structure of CBC-1 and $\text{K}_{0.3}\text{WO}_3$ were further carried out by a transmission electron microscopy (TEM, JEM-2010 Japan). The Brunauer-Emmett-Teller surface area (S_{BET}) and pore structure of the carbon samples were analyzed by nitrogen adsorption/desorption in a Micromeritics ASAP 2020 nitrogen adsorption apparatus (U.S.A.), and all samples were degassed at 200 °C prior to nitrogen adsorption measurements. X-ray diffraction (XRD) of samples was recorded by a Rigaku D/Max-2400 diffractometer with Cu $\text{K}\alpha$ radiation ($\lambda = 0.15418$ nm) at 40 kV and 100 mA and Raman spectra was examined on an in Via Raman spectrometer (Renishaw) at ambient temperature with an Argon ion laser ($\lambda = 514.5$ nm). The relative energy-dispersive

X-ray spectrometry (EDS) elemental mapping in the SEM was operated with a probe focused to 0.2 nm and camera length of 20 cm. X-ray photoelectron spectroscopy (XPS) measurement was performed on an Escalab 210 system (Germany).

2.5. Electrochemical measurements

2.5.1 Three-electrode systems

The electrochemical performance of the carbons and $K_{0.3}WO_3$ materials were investigated using three-electrode systems in 1 M H_2SO_4 solution. A high purity carbon rod was used as the counter electrode while saturated calomel electrode (SCE) was used as the reference electrode. The working electrodes were fabricated as following: 4 mg of electrode materials were dispersed in 0.4 mL of 0.25 wt% Nafion ethanol solutions with assistance by ultrasonic vibration. Then, 8 μ L of above suspension were dropped onto the glassy carbon electrode with a diameter of 5 mm as work electrode and dried for 10 minutes at room temperature.

The specific capacitances of the carbon or $K_{0.3}WO_3$ sample were calculated from the charge-discharge curves based on the following equation:

$$C = I\Delta t / (m\Delta V) \quad (1)$$

Where, C ($F\ g^{-1}$) is the specific capacitance; I (A) refers to the discharge current, ΔV (V) represents the potential change within the discharge time Δt (s), and m (g) corresponds to the total weight of the carbon CBC-1 and $K_{0.3}WO_3$.

2.5.2 Two-electrode systems

Electrochemical measurements were further taken using two-electrode systems consisting of $K_{0.3}WO_3$ and porous carbon electrodes in 1 M H_2SO_4 electrolyte. Firstly, the electrodes were prepared as following: in general, 80 wt% electrodes materials (8.0 mg), 10 wt% PTFE (1.0 mg),

and 10 wt% acetylene black (1.0 mg) were mixed with some N-methyl-2-pyrrolidone to form homogeneous slurry. The as-prepared slurry was spread onto the rounded stainless steel mesh current collector with an area of 2.3 cm² uniformly, and the coating was left in an oven at 60 °C for overnight. Afterward, the coating was pressed with a pressure of up to 10 MPa to ensure adherence between the active materials and the current collector. To construct an ASC, the loading mass ratio of active materials (m(CBC-1)/m(K_{0.3}WO₃)) was estimated to be 1.0 according to their specific capacitance and potential range for the charge/discharge process at a current density of 1 A g⁻¹, and the mass of the single electrode coated on one stainless steel mesh after pressed was calculated to be 4.0 mg (excluding the mass of carbon black and PTFE).

Finally, the asymmetric symmetric supercapacitors was assembled using nanorods pseudo-capacitive materials K_{0.3}WO₃ as the negative electrode, the porous carbon CBC-1 as positive electrode and aqueous 1 M H₂SO₄ solution as electrolyte, separated by a filter paper.

The cell capacitance (C_{cell}), single electrode (C_s), energy density (E) and power density (P) at different current densities are calculated based on these curves and using the following equations:

$$C_{\text{cell}} = I\Delta t / (m\Delta V) \quad (2)$$

$$C_s = 4 \times C_{\text{cell}} \quad (3)$$

$$E = 1000 \times C_{\text{cell}} \Delta V^2 / (2 \times 3600) \quad (4)$$

$$P = E / \Delta t \quad (5)$$

where C_{cell} (F g⁻¹) is the specific capacitance of the ASC device, C_s (F g⁻¹) is the specific capacitance of the single electrode, I represents the discharge current, m is the total mass of the active materials in both electrodes (about 8 mg), Δt is the discharge time; ΔV refers to the voltage window, E (Wh kg⁻¹) corresponds to the energy density and P (kW kg⁻¹) is the power density.

The electrochemical performance of the all electrodes materials in both three-electrode system and two-electrode system were characterized by cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrical impedance spectroscopy (EIS) measurements with an electrochemical workstation (CHI 660D). In addition, the cycle-life stability was obtained on the cycling testing equipment (CT2001A, Wuhan Land Electronic Co. Ltd., China).

3. Results and discussion

3.1. Negative electrode

FE-SEM and TEM are employed to investigate the morphology and microstructure of the $K_{0.3}WO_3$ negative electrode. As **seen** from the Fig. 1a, the as-prepared $K_{0.3}WO_3$ has nanorods structure, and it also can be clearly observed from high magnification SEM image (Fig. 1b) that the nanorods are composed of some thinner one-dimensional (1D) needle-shaped nanorods which are well aligned together until the final $K_{0.3}WO_3$ took shape. This can be further **proved** by TEM (Fig. 1c). Furthermore, a high-resolution TEM (HRTEM) image (Fig. 1d) illustrates clear lattice fringes, indicating that the nanorods with high crystallinity. The spacing between adjacent lattice planes is 0.384 nm, corresponding to the [002] planes of hexagonal phase $K_{0.3}WO_3$ nanorods. Moreover, the corresponding selected-area electron diffraction (SAED) pattern (the inset of Fig. 1d) selected from random $K_{0.3}WO_3$ nanorods exhibits a crystalline characteristic. And **measuring the electrochemically active surface area of any electrode material has proven to be extremely difficult even though it is one of the most basic properties of electrified interface. However, there are some measurements of surface area that can be obtained, for example, BET surface area, which can be and has been used as an approximation for the electrochemically active surface area, although with some reservation [22]. The BET surface area of the $K_{0.3}WO_3$ determined using the**

Brunauer-Emmett-Teller method is $18.5 \text{ m}^2 \text{ g}^{-1}$, which is similar to that of the pure Co_3O_4 sample ($18.5 \text{ m}^2 \text{ g}^{-1}$) [23] and close to that of emeraldine-di-hydrogensulfate ($22.1 \text{ m}^2 \text{ g}^{-1}$) [24]. Thus, the $\text{K}_{0.3}\text{WO}_3$ nanorods are believed to possess excellent electrode properties with higher capacitance because of the high electrochemically active surface area, low diffusion paths and easy intercalation/de-intercalation of electrolyte ions.

Fig. 1 (a) Low and (b) high magnification high-resolution SEM images, (c) low and (d) high magnification high-resolution TEM images of $\text{K}_{0.3}\text{WO}_3$ negative electrode.

It is well known that the crystal structure of M_xWO_3 is built up by corner-sharing WO_6 octahedra forming channels where the A^+ cations are located. And the structure of potassium tungsten bronzes K_xWO_3 with $0.19 \leq x \leq 0.33$ can be described with a hexagonal symmetry showing trigonal cages and hexagonal tunnels [25]. The as-prepared $\text{K}_{0.3}\text{WO}_3$ nanorods were studied by XRD, revealing all the reflections of the as-synthesized $\text{K}_{0.3}\text{WO}_3$ nanorods are well indexed to the hexagonal potassium tungsten bronze of $\text{K}_{0.3}\text{WO}_3$ (JCPDS card, no. 49-0541). The characteristic peaks of $\text{K}_{0.3}\text{WO}_3$ at the 2θ angle of 13.95, 23.81, 27.94 are observed in Fig. 2a, which are assigned to the [100], [002] and [200] lattice fringes, respectively [26]. To analyze the

elemental distribution, the $K_{0.3}WO_3$ was further characterized by energy dispersive X-ray spectroscopy (EDS) and the homogeneous distribution of oxygen (Fig. 2c), potassium (Fig. 2d) and tungsten (Fig. 2e) in the nanomaterials can be unambiguously confirmed from the corresponding mapping images (Fig. 2b).

Fig. 2 (a) XRD patterns, (b) SEM image of $K_{0.3}WO_3$ nanorods and the corresponding element mapping images (selected from the square region) for the oxygen (Fig. 2c), potassium (Fig. 2d) and tungsten (Fig. 2e), (f) XPS survey spectra and (g) High- resolution XPS spectra of W4f peak of $K_{0.3}WO_3$.

The surface chemical composition of $K_{0.3}WO_3$ was analyzed by XPS and the peaks at binding energy corresponding to potassium, tungsten and oxygen are detected (Fig. 2f). The curves of

tungsten can be fitted to four spin-orbit doublets as shown in Fig. 2g: the two peaks exhibited at 37.7 and 35.6 eV can be assigned to the $W4f_{5/2}$ and $W4f_{7/2}$ of W^{6+} with the interval of 2.1 eV, and the other two peaks centered at 34.5 and 36.5 eV should be attributed to the $W4f_{5/2}$ and $W4f_{7/2}$ of W^{5+} , implying the existence of both W^{5+} and W^{6+} in the materials [27, 28]. The concomitant presence of W^{5+} and W^{6+} ions occupy the same crystallographic position and its direct correlation to the concentration and type of the A^{+} cations, which are associated with the electrical, optical and magnetic properties [15].

Linear scanning voltammetry (LSV) was swept at a scan rate of 5 mV s^{-1} from the open circuit potential vs. reversible hydrogen electrode (RHE), and the potential at which the current crossed zero is taken to be the thermodynamic potential for the hydrogen electrode reactions [29]. The linear sweep voltammogram of $K_{0.3}WO_3$ electrode material in 1 M H_2SO_4 is as shown in the Fig. S2, and the thermodynamic potential for hydrogen evolution is -0.75 V vs. RHE, indicating the potential window of the negative electrode in 1 M H_2SO_4 tested and cycled in the range between -0.6-0 V is stable. In addition, the potential/pH diagram can be used to analyze potential-forming reactions and the chemical state of the material surface in aqueous solutions. Furthermore, the potential/pH diagram of the tungsten has been reported in the literature [30] and the tungsten is passivated at low pH and dissolved above pH=5, whereas it is stable in all pH ranges under -1.3 V/SCE. Thus, the electrochemical behavior of $K_{0.3}WO_3$ about the injection of holes to the valence or (most likely) impurity band in a tungsten oxide bronze was investigated by CV and GCD test within a potential window of -0.6-0 V and 1 M H_2SO_4 aqueous electrolyte. As can be presented in the Fig. 3a, there are characteristic redox peaks of the electrode were observed from -0.2 to -0.6 V which correspond to the reversible intercalation/deintercalation of H^{+} ions

occurring in the $K_{0.3}WO_3$ bulk and at the **interface** of $K_{0.3}WO_3$ and electrolyte [31]. During the charge process, it can be expressed as the hydrogen ions H^+ adsorbed in the $K_{0.3}WO_3$ bulk and at the $K_{0.3}WO_3$ /electrolyte interface and insertion process takes place according to the reaction: $H^+ + e^- \rightarrow H_{ads}^0$. Then the extraction process consequently happens during the discharge process which may occur only when hydrogen adsorbs in the atomic form H^0 in accompany with the reaction: $H^+ \rightarrow H_{ads}^0 + e^-$ [32]. The reactions are possible only when an elementary event of transition of an electron to a hydrogen. **That is, the electrochemical mechanism of $K_{0.3}WO_3$ in H_2SO_4 electrolyte can be expressed as the H^+ insertion process takes place during the charge process, and consequently the extraction process happens during the discharge process: $K_{0.3}WO_3 + xe^- + xH^+ \leftrightarrow H_xK_{0.3}WO_3$.** The reactions are possible only when an elementary event of transition of an electron to a hydrogen. According to the literatures, alkali metal atoms drift from the surface layer to depths from 1 to 30 nm and no passage of alkali metal into electrolyte has been found. In addition, J.P. Randinet al. had also proved using proton radiography that the alkali metal atoms changed their position in the tungsten oxide bronzes cell instead of escaping from the octahedral void [33, 34]. In addition, the larger the scan rates become, the higher/lower potentials the anode/cathode peak potentials move, indicating the excellent electrochemical behavior (Fig. 3b).

The GCD curves of $K_{0.3}WO_3$ electrode show slight deviation from the ideal line with some very short plateaus indicative of faradic processes. This is in agreement with results from CV (see above). As presented in Fig. 3c, the specific capacitance of $K_{0.3}WO_3$ electrode at various current densities of 0.8, 1.0, 2.0, 3.0, and 5.0 $A\ g^{-1}$ are found to be 223.7, 215, 178.3, 161.2, and 142.8 $F\ g^{-1}$, respectively, showing a good rate capability [35]. For evaluation of the cycling stability, $K_{0.3}WO_3$ electrode was subjected to galvanostatic charge/discharge cycling at a current density of

2 A g^{-1} . As presented in Fig. 3d, the specific capacitance of the pure $\text{K}_{0.3}\text{WO}_3$ electrode retains about 67% of its initial capacitance after 4500 cycles and then remains almost constant in the 1 M H_2SO_4 electrolyte. In summary, $\text{K}_{0.3}\text{WO}_3$ with high capacitance and capacitance retention has been successfully prepared via a facile, effective and scaled-up hydrothermal method without tedious step involvement.

Fig. 3 (a) CV curves with various scan rates, (b) GCD curves at different current densities; (c) the change of specific capacitance with the increase of current density and (d) cycling performances of $\text{K}_{0.3}\text{WO}_3$ negative electrode material at the current density of 2 A g^{-1} .

3.2. Positive electrode

The characteristic features regarding the shapes and sizes of the carbon samples were FE-SEM. The SEM images (Fig. 4a-b) show essentially the morphology of CBC as that of 2D thick sheets with relatively smooth surfaces. Whereas in contrast, CBC-1 possesses much rougher surface with numerous distinguishable pores (Fig. 4c), which are beneficial to the fast diffusion of electrolyte

ions from bulk electrolyte into the inner space of carbon materials. At high magnification (Fig. 4d), the CBC-1 looks composed of small carbon fragments and also more loose and less agglomeration than CBC (Fig. 4b), which might result from the thermal decomposition of carbon precursors and the volatilization of ZnCl_2 above 600 °C during activation process [36].

The intrinsic structure of the CBC-1 sample was further investigated by TEM technique. The TEM image (Fig. 4e) of the CBC-1 reveals the rough surface of the coral-like frameworks with abundant nanopores, which can provide a number of interpenetrating channels, allowing the electrolyte to permeate sufficiently into the entire structure and facilitating H^+ transport between the electrode/electrolyte interfaces. The amorphous porous disordered carbon structure in nature of the CBC-1 is also observed in the high resolution TEM image (Fig. 4f).

Fig. 4 (a, c) Low and (b, d) high magnification high-resolution SEM images of CBC and CBC-1 samples, (e) low

and (f) high magnification high-resolution TEM images of CBC-1.

The surface area and porosity of CBC and CBC-1 were determined using the Brunauer-Emmett-Teller (BET) method, and the results are shown in Fig. 5a. As in the case of the as-prepared carbons, the isotherms (Fig. 5a) at relative pressure $p/p^0 < 0.90$ are typical Type I curves with well-defined plateaus according to the IUPAC classification which given by microporous solids [37]. The steep increase in the adsorbed volume at a very low relative pressure ($p/p^0 < 0.05$) of the carbons exhibit the presence of abundant micropores, and the nitrogen uptake of CBC-1 is considerably larger. The pore structure is also confirmed by the pore size distribution profiles, which is recorded from the adsorption branch of the isotherm based on Barrett-Joyner-Halenda (BJH) model (Fig. 5b). As shown in Fig. 5b, the porosity for the two samples indicates the coexistence of predominantly micropores (<2 nm) and mesopores (2-5 nm), and the nitrogen absorption volume of CBC-1 is higher than that of CBC. Moreover, in the case of CBC-1, the activation process has notably increased the BET surface area and the pore volume up to values of $820.6 \text{ m}^2 \text{ g}^{-1}$ and $0.5 \text{ cm}^3 \text{ g}^{-1}$, much higher than those of CBC ($628.4 \text{ m}^2 \text{ g}^{-1}$ and $0.3 \text{ cm}^3 \text{ g}^{-1}$).

X-ray diffraction (XRD) analysis was used to investigate the structure of the carbon samples. As presented from the Fig. 5c, there are two relatively broad diffraction peaks centered at around 25.5° and 43.7° , which were ascribed to the (002) and (100) diffraction of the turbostratic carbon structure [38]. It is also found that the diffraction peak intensity of the CBC-1 has become a little weaker when compared with that of the CBC, indicating the more amorphous structure and defects due to the further harsh ZnCl_2 -activation. Furthermore, the structures of the carbon samples were also studied by Raman spectroscopy, which is believed to be a powerful tool to

characterize the different types of sp^2 carbon nanostructures (such as graphene and nanotube) and disorder structures [39]. Raman spectra of the CBC and CBC-1 samples are shown in Fig. 5d and two feature peaks at 1351 and 1600 cm^{-1} are observed, corresponding to the D band and G band of graphite, respectively [40]. The D band is related to the defects (or disorder structures) while the G band is related to the first-order scattering of the E_{2g} mode observed for sp^2 -carbon domains of the carbon materials [41]. And the integrated intensity ratio of D and G bands (I_D/I_G) can be used for characterizing the density of the defect quantity in graphitic materials. In our case, the I_D/I_G of the CBC sample (0.85) is substantially lower than that of the pristine CBC-1 sample (0.95), indicating that the CBC-1 sample has substantially higher edge/plane defective sites compared to the CBC sample. In conclusion, the I_D/I_G ratios of the corresponding sample increases, which indicated that the ordered crystallite structure decreases during the activation of $ZnCl_2$.

Fig. 5 (a) Nitrogen adsorption-desorption isotherms, (b) and inset (b) pore size distributions, (c) XRD patterns and

(d) Raman spectrum of the as-prepared carbons.

The surface chemical composition of CBC-1 was analyzed by XPS and the survey spectrum (Fig. 6a) shows three peaks with binding energy at 285, 400 and 532 eV, which are characteristics of C1s, N1s and O1s orbital, respectively, indicating the presence of C, N and O elements in CBC-1. In addition, no other impurities can be detected in the range of 200-800 eV, implying the high purity of the as-prepared carbon CBC-1. The contents of oxygen and nitrogen elements of the CBC-1 are calculated from the XPS survey spectrum to be around are 7.40, and 2.44 at.%, respectively. Specifically, five types of carbon species are fitted in C1s spectrum, including graphitic carbon (sp^2 configuration, 284.6 ± 0.1 eV), Csp^2 -N/C-OH (285.6 ± 0.2 eV), Csp^3 -N/C=O (287.1 ± 0.1 eV), and carboxyl (289.2 ± 0.3 eV) groups (Fig. 6b), which clearly reveal the nitrogen atoms and oxygen groups have been doped. Additionally, the band at ca. 291.2 ± 0.3 eV due to π - π^* transitions in aromatic rings is related to shake-up satellite peaks [42]. There are also five main components observed in the O1s core level spectra of CBC-1 (Fig. 6c). They are commonly ascribed to C=O in ketone/carbonyl (530.9 ± 0.1 eV), O-C in lactone, phenol/ether/epoxy (532.5 ± 0.3 eV), C=O in carboxylic acid (534.0 ± 0.3 eV), occluded CO or CO₂ (536 ± 0.2 eV) and adsorbed oxygen (537.9 ± 0.1 eV) [43]. The presence of C-O and C=O species are of critical importance for wettability with the aqueous electrolyte, resulting in efficient surface areas exposed for charge storage [44, 45]. The N1s core level spectra (Fig. 6d) could be decomposed into four different components attributed to N-6 pyridinic (398.5 ± 0.2 eV), N-5 pyrrolic/pyridone (400.4 ± 0.2 eV), N-Q quaternary (401.4 ± 0.1 eV) and pyridine N-oxide (403.4 ± 0.2 eV) [46]. It have demonstrated by previously reported studies that N-Q can significantly increase the electronic conductivity of carbon materials, while N-5 and N-6 could create numerous

extrinsic defects and active sites, which are favourable for the fast diffusion of transporting ions and give rise to pseudocapacitance [47].

Fig. 6 (a) XPS survey spectra and (b, c and d) High-resolution XPS spectra of the deconvoluted C 1s, N 1s and O

1s peak of CBC-1.

The obtained carbons were used as electrode materials of supercapacitor and their electrochemical behaviors have been analyzed in 1 mol L⁻¹ H₂SO₄ electrolyte in a standard three-electrode system within a potential window of 0-1.0 V. There are small redox peaks in the CVs of the two samples are observed at 0.3-0.4 V (Fig. 7a), which might be attributed to pseudo-Faradaic reactions involving the quinone functional groups [48]. Specifically, the pseudocapacitance of the two carbon electrodes can be ascribed to the reversible conversion reactions between different types of oxygen containing functional groups, as following [49]:

In addition, it is well known that the larger for the area of CV curve, the higher for the capacitance of electrode [50]. Comparatively, the CV curve area of CBC-1 is much higher than that of CBC, displaying a higher specific capacitance. Such remarkable improvement in capacitance is mainly due to the oxygen functional groups onto the surface of carbon materials produce the pseudocapacitance and increased surface area after activation enhance the electric double-layer capacitance. In addition, as shown in Fig. 7b, the GCD curves of CBC and CBC-1 at the current density of 0.5 A g⁻¹ exhibit partial arc shaped line contributed by the above pseudofaradic reactions, which is corresponding with the CV curves. As can be seen from the Fig. 7c, the shape of these CV curves remains similar even though the scan rate is up to 500 mV s⁻¹, suggesting the good rate capability of the CBC-1 electrode. And the GCD curve of CBC-1 still remains a curving shape when the current density increases up to 30 A g⁻¹ (Fig. 7d), which indicates excellent capacitive behavior and electrochemical reversibility. In addition, the CBC-1 electrode possesses a specific capacitance obtained from the Fig. 7d ranging from 244.7 F g⁻¹ at 0.5 A g⁻¹ to 156.0 F g⁻¹ at 30 A g⁻¹, implying excellent rate capability of CBC-1. Furthermore, Fig. 7e illustrates the capacitances of the CBC-1 electrode as a function of current densities and it is obvious that the specific capacitance decreases slowly when the current densities are more than 2 A g⁻¹. The CBC-1 sample was operated under the galvanostatic charge-discharge at 5 A g⁻¹ in order to test the stability of the activated carbon electrode (Fig. 7f). The specific capacitance is reduced by only 8% after 5000 cycles, which indicates that the as-synthesized activated carbon electrode with good long-term stability can be operated in practice.

Fig. 7 (a) CV curves at a scan rate of 50 mV s⁻¹ and (b) GCD curves at the current density of 1 A g⁻¹ for all as-prepared carbons; (c) CV curves with various scan rates, (d) GCD curves at different current densities; (e) the change of specific capacitance with the increase of current density and (f) cycling performances at the current density of 5 A g⁻¹ of CBC-1 electrode material.

3.3. Asymmetric supercapacitor

Considering the fast ion-transport property of the electric double-layer storage for the carbon material CBC-1 and the redox character of K_{0.3}WO₃ electrode, an asymmetric supercapacitor was successfully fabricated using the two materials as the positive and negative electrodes,

respectively. To further evaluate the electrochemical properties and estimate the stable potential windows of $K_{0.3}WO_3$ and CBC-1 electrodes, we performed CV measurements on the two electrode materials in 1 M H_2SO_4 solution in a three electrode system (Fig. 8a). The stable potential window is between 0 and 1.0 V for CBC-1 and between -0.6 and 0 V for $K_{0.3}WO_3$. The cell voltage can be expressed as the sum of the potential range of the CBC-1 and $K_{0.3}WO_3$, and consequently, it can be extended up to 1.6 V in aqueous 1 M H_2SO_4 solution for the asymmetric supercapacitor of CBC-1// $K_{0.3}WO_3$. For asymmetric supercapacitors, it is necessary to balance the charges stored at the positive and negative electrodes. The stored charges (q) are related with the specific capacitance (C_m), the voltage window (ΔV), and the mass (m) of the electrode according to equation [51]: $q = C_m \times \Delta V \times m$ (6). In order to obtain $q^+ = q^-$, as well as take advantage of the largest voltage window, the mass balancing will be expressed as following equation: $m^+/m^- = (C_m^+ \times \Delta V^+) / (C_m^- \times \Delta V^-)$ (7). Based on the above analysis of the specific capacitance values and potential ranges found for the carbon material CBC-1 and the $K_{0.3}WO_3$ electrode at a current density of 1 A g^{-1} , the optimal mass ratio between the two electrodes should be $m(CBC-1)/m(K_{0.3}WO_3) \approx 1.0$ in the asymmetric supercapacitor cell.

Fig. 8b showed that CV curves still exhibit a nearly rectangular shape without obvious distortion with increasing voltage scan rates, indicating a pseudo-constant charged/discharged rate process over the entire voltammetric cycle and a desirable fast charge/discharge property for power devices [52]. Meanwhile, as the scan rate increases, the anodic and cathodic peaks in the CV curves shift toward the positive and negative voltage, respectively, leading to a continuous increase of voltage distance between the oxidation and the reduction peaks. The GCD curves of the ASC device at various current densities from 0.5 to 3 A g^{-1} (Fig. 8c) show the highly linear

correlation and the symmetrical shape with a quick I - V response, which also represent an ideal capacitive behavior of the ASC device.

Furthermore, it can be obtained from the Fig. 8c that the specific capacitance of the ASC device electrode ranges from 295.6, 240.4, 222.4, 187.2 and 164.0 F g⁻¹ at 0.5, 0.8, 1.0, 2.0 and 3.0 A g⁻¹, respectively. With the increase of current densities, the capacitance of the sample decreases, this might be caused by the large resistance and the insufficient Faradaic redox reaction of the active material under higher discharge current densities.

To examine the ion transport properties of the CBC-1//K_{0.3}WO₃ ASC, EIS analysis was carried out over the frequency range from 0.1 Hz to 100 kHz. Fig. 8d shows the Nyquist plot including a linear part in the low-frequency region and a small semicircle in the high frequency region. The intercept at the real axis of the plot provides the equivalent series resistance (R_s), which includes the intrinsic resistance of the electroactive materials, the bulk resistance of the electrolyte and the contact resistance at the interface between the electrolyte and electrode. And the charge-transfer resistance (R_{ct}) at the electrode/electrolyte interface is counted from the span of the small semicircle along the Z' axis. Remarkably, as seen from the Fig. 8d, the CBC-1//K_{0.3}WO₃ electrode not only shows a small R_s (5.8 Ω) but also delivers a small R_{ct} (2.0 Ω), indicating that the ASC possesses a fast charge transfer process. In addition, the Bode angle is a measure of the quality of the activated material used in supercapacitors. Furthermore, the Bode plot obtained for the impedance measurement of the CBC-1//K_{0.3}WO₃ ASC is shown in the inset of Fig. 8d, and in the low-frequency region (0.1-10 Hz), the phase angle for the ASC is close to -90°, suggesting that all samples exhibit a good capacitive behavior [53].

Fig. 8 (a) CV curves of the CBC-1 and $\text{K}_{0.3}\text{WO}_3$ electrodes in a three-electrode cell at 50 mV s^{-1} in $1 \text{ M H}_2\text{SO}_4$, (b) CV curves at various scan rates; (c) GCD curves at various current densities; (d) Nyquist plot; the inset of (d) Bode phase angle plot, (e) Cycling stability and (f) Ragone plots related to energy and power densities of the

CBC-1// $\text{K}_{0.3}\text{WO}_3$ ASC in a two-electrode cell.

Long cycling life is an important requirement for supercapacitors. The long-term stability of the CBC-1// $\text{K}_{0.3}\text{WO}_3$ ASC was examined by galvanostatic charge-discharge cycling at a current density of 1 A g^{-1} between 0 and 1.6 V. As a whole, the CBC-1// $\text{K}_{0.3}\text{WO}_3$ ASC shows excellent

cycling behavior (Fig. 8e) and the specific capacitance of the ASC remains 80.0% after 1000 cycles. The attenuation of the electrochemical performance of the ASC may be due to the active materials on the positive and negative electrode fall off or are dissolved in the electrolyte. Fig. 8f shows the energy density of the CBC-1//K_{0.3}WO₃ ASC reaches to 26.3 Wh kg⁻¹ at a power density of 404.2 W kg⁻¹ and still remains 14.6 Wh kg⁻¹ at a power density of 2396.3 W kg⁻¹. The maximum energy density obtained for CBC-1//K_{0.3}WO₃ ASC with a cell voltage of 1.6 V is much higher than those of symmetrical and asymmetric supercapacitors in the previous reports, as shown in Fig. 8f and Table 1. By virtue of the high energy density and good stability feature, the CBC-1//K_{0.3}WO₃ ASC can serve as a promising power supply device for next-generation storage systems.

Table 1. Performances comparison of asymmetric cells in the references

samples	energy density	power density	number	Ref.
	Wh kg ⁻¹	W kg ⁻¹		
Co _{0.85} Se//N-PCNs	21.1	400	1	54
AC//Co(OH) ₂	20.3	90.6	2	55
AC//CQDs/NiCo ₂ O ₄	27.8	128	3	56
Cu _{1.79} Co _{0.21} CH/NF//graphene/NF	21.5	200	4	57
MCMSs//RGO	21.5	759	5	58
MnO ₂ @CCNs//CCNs	23.6	188.8	6	59
AC//CQDs/NiCo ₂ O ₄	28.3	245	7	60
CNT@NiO//PCPs	25.4	400	8	61
Our work	26.3	404.2	9	

4. Conclusions

The concept of an asymmetric CBC-1//K_{0.3}WO₃ electrochemical capacitor in 1 M H₂SO₄ aqueous electrolyte is presented for the first time, in which the K_{0.3}WO₃ nanorods as the negative electrode and CBC-1 as the positive electrode. The as-prepared ASC delivers an energy density 26.3 Wh kg⁻¹ at a power density of 404.2 W kg⁻¹ with an output voltage of 1.6 V. The electrode

material $\text{K}_{0.3}\text{WO}_3$ nanorods are prepared by a facile and effective hydrothermal procedure and exhibits superior electrochemical performance, such as high specific capacitance (295.6 F g^{-1} at 0.8 A g^{-1}). A nitrogen-doped biomass activated carbon (CBC-1) is prepared using the agricultural wastes corn bract as raw materials and ZnCl_2 as activating agent carbonized at 800°C . And CBC-1 possesses large specific capacitance (244.7 F g^{-1} at 0.5 A g^{-1}) and 92 % of initiatory specific capacitance after 5000 consecutive cycles. The results presented here may pave the way for promising applications in easy preparation and high energy density storage systems based on the alkali metal tungsten bronzes and porous carbons.

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References

- [1] S. E. Moosavifard, S. Fani, M. Rahmanian, Hierarchical CuCo_2S_4 hollow nanoneedle arrays as novel binder-free electrodes for high-performance asymmetric supercapacitors, Chem. Commun. 52 (2016) 4517-4520
- [2] C. Liu, F. Li, L. P. Ma, H. M. Cheng, Advanced materials for energy storage, Adv. Mater. 22

(2010) E28–E62.

[3] Y. Shao, M. F. El-Kady, L. J. Wang, Q. Zhang, Y. Li, H. Wang, M. F. Mousavi, R. B. Kaner, Graphene-based materials for flexible supercapacitors, *Chem. Soc. Rev.* 44 (2015) 3639-3665.

[4] G. Wang, L. Zhang, J. Zhang, A review of electrode materials for electrochemical supercapacitors, *Chem. Soc. Rev.* 41 (2012) 797-828.

[5] T. Brezesinski, J. Wang, S. H. Tolbert, B. Dunn, Ordered mesoporous $[\alpha]$ - MoO_3 with iso-oriented nanocrystalline walls for thin-film pseudocapacitors, *Nat. Mater.* 9 (2010) 146-151.

[6] E. Herrero, L. J. Buller, H. D. Abruna, Underpotential deposition at single crystal surfaces of Au, Pt, Ag and other materials, *Chem. Rev.* 101 (2001) 1897–1930.

[7] V. Augustyn, J. Come, M. A. Lowe, J. W. Kim, P. L. Taberna, S. H. Tolbert, H. D. Abruña, P. Simon, B. Dunn, High-rate electrochemical energy storage through Li^+ intercalation pseudocapacitance, *Nat. Mater.* 12 (2013) 518-522.

[8] A. Kurniawan, C. Effendi, L. K. Ong, F. Kurniawan, C. X. Lin, A. E. Angkawijaya, Y. H. Juc, S. Ismadjia, X. S. Zhao, Preparation of nanoporous carbon microspheres by subcritical water carbonization and electro capacitive study, *Electrochim. Acta* 111 (2013) 99.

[9] N. S. Choi, Z. Chen, S. A. Freunberger, X. Ji, Y. K. Sun, K. Amine, G. Yushin, L. F. Nazar, J. Cho, P. G. Bruce, Challenges Facing Lithium Batteries and Electrical Double-Layer Capacitors, *Angew. Chem., Int. Ed.* 51 (2012) 9994-10024.

[10] P. J. Hall, M. Mirzaeian, S. I. Fletcher, F. B. Sillars, A. J. Rennie, G. O. Shitta-Bey, G. Wilson, A. Cruden, R. Carter, Energy storage in electrochemical capacitors: designing functional materials to improve performance, *Energy Environ. Sci.* 3 (2010)1238-1251.

- [11] Y. G. Wang, Y. Y. Xia, A new concept hybrid electrochemical supercapacitor: Carbon/LiMn₂O₄ aqueous system, *Electrochem. Commun.* 7 (2005) 1138-1142.
- [12] W. G. Pell, B. E. Conway. Peculiarities and requirements of asymmetric capacitor devices based on combination of capacitor and battery-type electrodes, *J. Power Sources* 136 (2004) 334-345.
- [13] Y. P. Lin, N. L. Wu, Characterization of MnFe₂O₄/LiMn₂O₄ aqueous asymmetric supercapacitor, *J. Power Sources* 196 (2011) 851-854.
- [14] N. Goubard-Bretesché, O. Crosnier, C. Payen, F. Favier, T. Brousse, Nanocrystalline FeWO₄ as a pseudocapacitive electrode material for high volumetric energy density supercapacitors operated in an aqueous electrolyte, *Electrochem. Commun.* 57 (2015) 61-64.
- [15] Y. Zhang, B. Li, Y. Cao, J. Qin, Z. Peng, Z. Xiao, X. Huang, R. Zou, J. Hu, Na_{0.3}WO₃ nanorods: a multifunctional agent for in vivo dual-model imaging and photothermal therapy of cancer cells, *Dalton Transactions* 44 (2015) 2771-2779.
- [16] A. Hjelm, C. G. Granqvist, J. M. Wills, Electronic structure and optical properties of WO₃, LiWO₃, NaWO₃, and HWO₃, *Phys. Rev. B* 54 (1996) 2436.
- [17] K. Sasaki, H. Urata, K. Uneyama, S. Nagaura, Anodic methoxylation of alkylbenzenes, *Electrochim. Acta* 12 (1967) 137-146..
- [18] J. Vondrak, J. Balej, Electrochemical properties of tungsten bronzes-II. Hydrogen evolution on sodium tungsten bronzes, *Electrochim. Acta* 20 (1975) 283-287.
- [19] J. Qin, G. Zhang, J. Liang, H. Xia, Y. Xing, W. Sun, Completely Different Performances of the Dye-Sensitized Solar Cells Based on Potassium-Tungsten-Oxide and-Bronze Nanobranches, *Sci. Adv. Mater.* 6 (2014) 141-150.

- [20] D. P. Dubal, P. Gomez-Romero, B. R. Sankapal, R. Holze, Nickel cobaltite as an emerging material for supercapacitors: An overview, *Nano Energy* 11 (2015) 377-399.
- [21] H. Peng, G. Ma, K. Sun, J. Mu, M. Luo, Z. Lei, High-performance aqueous asymmetric supercapacitor based on carbon nanofibers network and tungsten trioxide nanorod bundles electrodes, *Electrochim. Acta* 147 (2014) 54-61.
- [22] M. Dupont, A. F. Hollenkamp, S. W. Donne, Electrochemically active surface area effects on the performance of manganese dioxide for electrochemical capacitor applications, *Electrochim. Acta* 104 (2013) 140-147.
- [23] A. Abdolmaleki, H. Kazerooni, M. B. Gholivand, H. Heydari, A. Pendashteh, Facile electrostatic coprecipitation of f-SWCNT/Co₃O₄ nanocomposite as supercapacitor material, *Ionics* 21 (2015) 515-523.
- [24] D. Vonlanthen, P. Lazarev, K. A. See, F. Wudl, A. J. Heeger, A Stable Polyaniline-Benzoquinone-Hydroquinone Supercapacitor, *Adv. Mater.* 26 (2014) 5095-5100.
- [25] R. T. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica Section A: Crystal Physics, Diffraction, Theoretical and General Crystallography* 32 (1976) 751-767.
- [26] Y. P. Wang, B. B. Zhou, L. Y. Liu, Synthesis of K_{0.3}WO₃ tungsten bronze with gaseous permeation of K₃PW₁₂O₄₀ by Sm and electrical properties of K_{0.3}WO₃ tungsten bronze, *J. Alloy. Compd.* 463 (2008) 333-337.
- [27] C. Guo, S. Yin, L. Huang, T. Sato, Synthesis of one-dimensional potassium tungsten bronze with excellent near-infrared absorption property, *ACS Appl. Mater. Inter.* 3 (2011) 2794-2799
- [28] Z. Gu, Y. Ma, T. Zhai, B. Gao, W. Yang, J. Yao, A Simple Hydrothermal Method for the

Large-Scale Synthesis of Single-Crystal Potassium Tungsten Bronze Nanowires, Chemistry-A European Journal 12 (2006) 7717-7723.

[29] Y. Li, W. Zhou, H. Wang, L. Xie, Y. Liang, F. Wei, J. Idrobo, S. J. Pennycook, H. Dai, An oxygen reduction electrocatalyst based on carbon nanotube-graphene complexes, Nat. Nanotechnol. 7 (2012) 394-400.

[30] Y. J. Seo, S. W. Park, W. S. Lee, Application of Potential-pH Diagram and Potentiodynamic Polarization of Tungsten. IEEJ T. Electr. Electr. 7 (2006) 108-111.

[31] C. K. Kwan, W. Hwang, Electrical transport in solids with particular reference to organic semiconductors, Pergamon Press: Oxford, England (1981).

[32] A. Y. Gokhshtein, Poverkhnostnoe natyazhenie tverdykh tel i adsorbtsiya (The Surface Stress in Solids and the Adsorption), Nauka Moscow (in Russian) (1976).

[33] J. P. Randin, Interpretation of the relative electrochemical activity of various metal phthalocyanines for the oxygen reduction reaction, Electrochim. Acta 19 (1974) 83-85.

[34] B. M. Khubolov, V. P. Podlinov, Injection of holes and their localization in defect states at the interface between an electrochromically sensitive single crystal and an amorphous thin film of a complex tungsten oxide, Bulletin of the Russian Academy of Sciences: Physics 71 (2007) 1164-1167.

[35] Z. Fan, J. Yan, T. Wei, L. Zhi, G. Ning, T. Li, F. Wei, Asymmetric supercapacitors based on graphene/MnO₂ and activated carbon nanofiber electrodes with high power and energy density, Adv. Funct. Mater. 21 (2011) 2366-2375.

- [36] Z. J. Zhang, C. Dong, X. Y. Ding, Y. K. Xia, A generalized ZnCl_2 activation method to produce nitrogen-containing nanoporous carbon materials for supercapacitor applications, *J. Alloy. Compd.* 636 (2015) 275-281.
- [37] B. Li, F. Dai, Q. Xiao, L. Yang, J. Shen, C. Zhang, M. Cai, Nitrogen-doped activated carbon for a high energy hybrid supercapacitor, *Energy Environ. Sci.* 9 (2016) 102-106.
- [38] D. N. Futaba, K. Hata, T. Yamada, T. Hiraoka, Y. Hayamizu, Y. Kakudate, O. Tanaike, H. Hatori, M. Yumura, S. Iijima, Shape-engineer able and highly densely packed single-walled carbon nanotubes and their application as super-capacitor electrodes, *Nat. Mater.* 5 (2006) 987-994.
- [39] P. A. Goodman, H. Li, Y. Gao, Y. F. Lu, J. D. Stenger-Smith, J. Redepenning, Preparation and characterization of high surface area, high porosity carbon monoliths from pyrolyzed bovine bone and their performance as supercapacitor electrodes, *Carbon* 55 (2013) 291–298
- [40] D. Aradilla, M. Delaunay, S. Sadki, J. M. Gérard, G. Bidan, Vertically aligned graphene nanosheets on silicon using an ionic liquid electrolyte: towards high performance on-chip micro-supercapacitors, *J. Mater. Chem. A* 3 (2015) 19254-19262.
- [41] J. Hwang, S. H. Woo, J. Shim, C. Jo, K. T. Lee, J. Lee, One-Pot Synthesis of Tin Embedded Carbon/Silica Nanocomposites for Anode Materials in Lithium-Ion Batteries, *ACS Nano* 7 (2013) 1036–1044.
- [42] D. Q. Yang, J. F. Rochette, E. Sacher, Spectroscopic evidence for π - π interaction between poly (diallyl dimethylammonium) chloride and multiwalled carbon nanotubes, *J. Phys. Chem. B* 109 (2005) 4481-4484.
- [43] G. Zhang, S. Sun, D. Yang, J. P. Dodelet, E. Sacher, The surface analytical characterization

of carbon fibers functionalized by H₂SO₄/HNO₃ treatment, Carbon 46 (2008) 196-205.

[44] D. Hulicova-Jurcakova, M. Seredych, G. Q. Lu, T. J. Bandosz, Combined Effect of Nitrogen-and Oxygen-Containing Functional Groups of Microporous Activated Carbon on its Electrochemical Performance in Supercapacitors, Adv. Funct. Mater. 19 (2009) 438-447.

[45] X. Hong, K. S. Hui, Z. Zeng, K. N. Hui, L. Zhang, M. Mo, M. Li, Hierarchical nitrogen-doped porous carbon with high surface area derived from endothelium corneum gigeriae galli for high-performance supercapacitor, Electrochim. Acta 130 (2014) 464-469.

[46] J. Wang, H. Liu, J. Diao, X. Gu, H. Wang, J. Rong, B. Zong, D. S. Su, Size-controlled nitrogen-containing mesoporous carbon nanospheres by one-step aqueous self-assembly strategy, J. Mater. Chem. A 3 (2015) 2305-2313.

[47] C. Yuan, X. Liu, M. Jia, Z. Luo, J. Yao, Facile preparation of N-and O-doped hollow carbon spheres derived from poly (o-phenylenediamine) for supercapacitors, J. Mater. Chem. A 3 (2015) 3409-3415.

[48] H. A. Andreas, B. E. Conway, Examination of the double-layer capacitance of an high specific-area C-cloth electrode as titrated from acidic to alkaline pHs, Electrochim. Acta 51 (2006) 6510-6520.

[49] X. Fan, Y. Lu, H. Xu, X. Kong, J. Wang, Reversible redox reaction on the oxygen-containing functional groups of an electrochemically modified graphite electrode for the pseudo-capacitance, J. Mater. Chem. 21 (2011) 18753-18760.

[50] X. Wu, J. Zhou, W. Xing, G. Wang, H. Cui, S. Zhuo, Q. Xue, Z. Yana, S. Z. Qiao, High-rate capacitive performance of graphene aerogel with a super high C/O molar ratio, J. Mater. Chem. 22 (2012) 23186-23193.

- [51] M. Kaempgen, C. K. Chan, J. Ma, Y. Cui, G. Gruner, Printable thin film supercapacitors using single-walled carbon nanotubes, *Nano Lett.* 9 (2009) 1872–1876.
- [52] M. Kim, I. Oh, J. Kim, Effects of different electrolytes on the electrochemical and dynamic behavior of electric double layer capacitors based on a porous silicon carbide electrode, *Phys. Chem. Chem. Phys.* 17 (2015) 16367-16374.
- [53] T. F. Hsieh, C. C. Chuang, W. J. Chen, J. H. Huang, W. T. Chen, C. M. Shu, Hydrous ruthenium dioxide/multi-walled carbon-nanotube/titanium electrodes for supercapacitors, *Carbon* 50 (2012) 1740-1747.
- [54] H. Peng, G. Ma, K. Sun, Z. Zhang, J. Li, X. Zhou, Z. Lei, A novel aqueous asymmetric supercapacitor based on petal-like cobalt selenide nanosheets and nitrogen-doped porous carbon networks electrodes, *J. Power Sources* 297 (2015) 351-358.
- [55] S. Yang, K. Cheng, K. Ye, Y. Li, J. Qu, J. Yin, G. Wang, D. Cao, A novel asymmetric supercapacitor with buds-like $\text{Co}(\text{OH})_2$ used as cathode materials and activated carbon as anode materials, *J. Electroanal. Chem.* 741 (2015) 93-99.
- [56] Y. Zhu, Z. Wu, M. Jing, H. Hou, Y. Yang, Y. Zhang, X. Yang, W. Song, X. Jia, X. Ji, Porous NiCo_2O_4 spheres tuned through carbon quantum dots utilised as advanced materials for an asymmetric supercapacitor, *J. Mater. Chem. A* 3 (2015) 866-877.
- [57] S. Liu, K. S. Hui, K. N. Hui, V. V. Jadhav, Q. X. Xia, J. M. Yun, Y. R. Choa, R. S. Mane, K. H. Kim, Facile Synthesis of Microsphere Copper Cobalt Carbonate Hydroxides Electrode for Asymmetric Supercapacitor, *Electrochim. Acta* 188 (2016) 898-908.

- [58] Q. Ruibin, H. Zhongai, Y. Yuying, L. Zhimin, A. Ning, R. Xiaoying, H. Haixiong, W. Hongying, Mono disperse carbon microspheres derived from potato starch for asymmetric supercapacitors, *Electrochim. Acta* 167 (2015) 303-310.
- [59] Y. Li, N. Yu, P. Yan, Y. Li, X. Zhou, S. Chen, G. Wang, T. Wei, Z. Fan, Fabrication of manganese dioxide nanoplates anchoring on biomass-derived cross-linked carbon nanosheets for high-performance asymmetric supercapacitors, *J. Power Sources* 300 (2015) 309-317.
- [60] Y. Zhu, Z. Wu, M. Jing, X. Yang, W. Song, X. Ji, Mesoporous NiCo_2S_4 nanoparticles as high-performance electrode materials for supercapacitors, *J. Power Sources* 273 (2015) 584-590.
- [61] H. Yi, H. Wang, Y. Jing, T. Peng, X. Wang, Asymmetric supercapacitors based on carbon nanotubes@NiO ultrathin nanosheets core-shell composites and MOF-derived porous carbon polyhedrons with super-long cycle life, *J. Power Sources* 285 (2015) 281-290.

Figure captions

Fig. 1 (a) Low and (b) high magnification high-resolution SEM images, (c) low and (d) high magnification high-resolution TEM images of $\text{K}_{0.3}\text{WO}_3$ negative electrode.

Fig. 2 (a) XRD patterns, (b) SEM image of $\text{K}_{0.3}\text{WO}_3$ nanorods and the corresponding element mapping images (selected from the square region) for the oxygen (Fig. 2c), potassium (Fig. 2d) and tungsten (Fig. 2e), (f) XPS survey spectra and (g) High-resolution XPS spectra of W4f peak of $\text{K}_{0.3}\text{WO}_3$.

Fig. 3 (a) CV curves with various scan rates, (b) GCD curves at different current densities; (c) the change of specific capacitance with the increase of current density and (d) cycling performances of $\text{K}_{0.3}\text{WO}_3$ negative electrode material at the current density of 2 A g^{-1} .

Fig. 4 (a, c) Low and (b, d) high magnification high-resolution SEM images of CBC and CBC-1 samples, (e) low and (f) high magnification high-resolution TEM images of CBC-1.

Fig. 5 (a) Nitrogen adsorption-desorption isotherms, (b) and inset (b) pore size distributions, (c) XRD patterns and (d) Raman spectrum of the as-prepared carbons.

Fig. 6 (a) XPS survey spectra and (b, c and d) High-resolution XPS spectra of the deconvoluted C 1s, N 1s and O 1s peak of CBC-1.

Fig. 7 (a) CV curves at a scan rate of 50 mV s^{-1} and (b) GCD curves at the current density of 1 A g^{-1} for all as-prepared carbons; (c) CV curves with various scan rates, (d) GCD curves at different current densities; (e) the change of specific capacitance with the increase of current density and (f) cycling performances at the current density of 5 A g^{-1} of CBC-1 electrode material.

Fig. 8 (a) CV curves of the CBC-1 and $\text{K}_{0.3}\text{WO}_3$ electrodes in a three-electrode cell at 50 mV s^{-1} in $1 \text{ M H}_2\text{SO}_4$, (b) CV curves at various scan rates; (c) GCD curves at various current densities; (d) Nyquist plot; the inset of (d) Bode phase angle plot, (e) Cycling stability and (f) Ragone plots

related to energy and power densities of the CBC-1//K_{0.3}WO₃ ASC in a two-electrode cell.

Table 1. Performances comparison of asymmetric cells in the references.

Load