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

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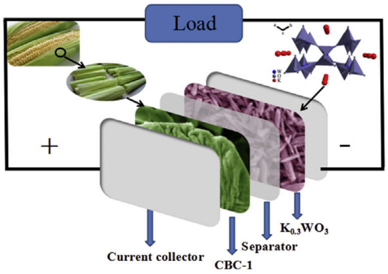
HIGHLIGHTS

- The nanorods $K_{0.3}WO_3$ electrode has high specific capacitance and cycling stability.
- Agricultural wastes corn bract is used to preparation nitrogen-doped porous carbon.
- The special structures of the electrodes is conducive to the diffusion of the electrolyte.
- The aqueous asymmetric supercapacitor exhibit high energy density and stability.

GRAPHICAL ABSTRACT



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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.

1. 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

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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 leading 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 sand 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 $K_{0.3}WO_3$ 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 Zhonqin 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 min 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 min 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