



A single-walled carbon nanotubes/poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)/copper hexacyanoferrate hybrid film for high-volumetric performance flexible supercapacitors

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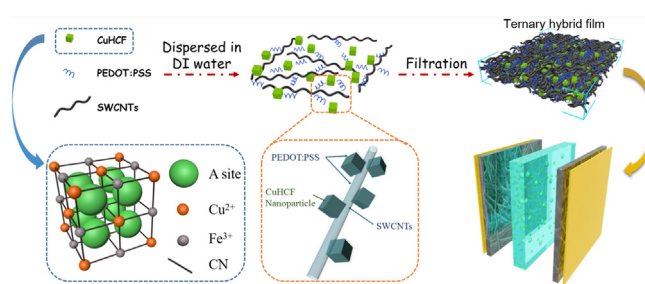
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HIGHLIGHTS

- Ternary electrode with high packing density (2.67 g cm^{-3}) has been fabricated.
- The electrode exhibited high areal and volumetric specific capacitance.
- Asymmetric supercapacitor exhibited volumetric energy density of 30.08 Wh L^{-1} .

GRAPHICAL ABSTRACT



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ABSTRACT

Volumetric energy density is generally considered to be detrimental to the actual application of supercapacitors, which has provoked a range of research work on increasing the packing density of electrodes. Herein, we fabricate a free-standing single-walled carbon nanotubes (SWCNTs)/poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS)/copper hexacyanoferrate (CuHCF) nanoparticles (NPs) composite supercapacitor electrode, with a high packing density of 2.67 g cm^{-3} . The pseudocapacitive CuHCF NPs are decorated onto the SWCNTs/PEDOT:PSS networks and filled in interspace to increase both of packing density and specific capacitance. This hybrid electrode exhibits a series of outstanding performances, such as high electric conductivity, ultrahigh areal and volumetric capacitances (969.8 mF cm^{-2} and 775.2 F cm^{-3} at scan rate of 5 mV s^{-1}), long cycle life and superior rate capability. The asymmetric supercapacitor built by using the SWCNTs/PEDOT:PSS/CuHCF film as positive electrode and Mo-doped WO_3 /SWCNTs film as negative electrode, can deliver a high energy density of 30.08 Wh L^{-1} with a power density of 4.25 kW L^{-1} based on the total volume of the device. The approach unveiled in this study could provide important insights to improving the volumetric performance of energy storage devices and help to reach the critical targets for high rate and high power density demand applications.

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1. Introduction

Owing to unending demand for aesthetic appeal and multi-functionality of electronics, portable, flexible and even wearable electronic devices have attracted great attention and may lead the next revolution in the field of electronics [1–4]. A great many products and prototypes have reached the frontier of current technology research. However, while the computational capability of mobile technologies has increased many orders of magnitude over past decades, the development for high safety, light-weight and flexible energy storage devices of electronics, has significantly lagged the development of portable electronics [4–8]. Supercapacitors are energy storage devices that can often be safely charged or discharged in seconds with extremely long cycle life (> 100,000 cycles) [9,10]. Combined with their properties of high power density (often > 10,000 W kg⁻¹) and simple structure, supercapacitor is one of the most promising candidates for flexible energy storage devices [3–5,11–13].

To enlarge the energy density of supercapacitors, especially volumetric energy density, the electrode material is the key component that largely determines their performance. The general approach is to prepare electrode with large packing density [14,15]. As discussed by Gogotsi and Simon, the mass of the active material and thickness of the electrode play an important role in the final report electrochemical performances of supercapacitors [6,12,16,17]. Some supercapacitors related research works with ultralow active materials loading mass and/or ultrathin electrode film even claimed that their energy density could approach or even exceed that of some batteries, which is calculated only based on the mass or volume of active materials [18–20]. However, if the energy density and power density calculated based on the total mass or volume of the supercapacitor, performance of these active materials could not be totally translated to actual device [21]. The evaluation of electrodes with extremely thin and/or very low amounts of active materials will lead to an over-estimate of electrode material's performance. Thus, in order to achieve true high electrochemical performance by areal and volumetric units, the high loading mass, large thickness and high packing density will be the key factors to achieve this goal [22,23].

Typical pseudocapacitive materials, such as transition metal oxides (e.g. RuO₂ [24–26], MnO₂ [27,28], and Nb₂O₅ [23]) and conducting polymers (e.g. polyanilines [29–31], polypyrroles [32] and polythiophenes [33]) generally showed large specific capacitances (500–1300 F g⁻¹), which far exceeds that of electric double-layer capacitors (EDLC) active materials (< 500 F g⁻¹) [5,17,34,35]. In addition, due to their relative high density, these pseudocapacitive materials generally can store a large amount of energy in a small packing space. That is to say, electrodes with pseudocapacitive performance are more favorable for achieving the high volumetric or areal capacitances.

Because of its tunable, open channels which allow the rapid insertion of ions, Copper hexacyanoferrate (CuHCF), as an analogue of Prussian Blue, is one type of promising pseudocapacitive materials [36–40]. The general formula for these materials is A_xPR(CN)₆, and their crystal structure is analogous to the ABX₃ perovskites, in which the P^{m+} and Rⁿ⁺ ions are in the ordered arrangement on the B sites. The occupancy of the tetrahedrally coordinated A sites in the large cages of the crystallographic framework (Fig. 1c) may vary from x = 0 to x = 2, which result in the changes of the valence for one or more of the P and R species. As a result, species of the appropriate size can be reversibly inserted into the A sites [40,41], thus they can exhibit high electrochemical activity for the highly reversible pseudocapacitive redox reactions.

Herein, we demonstrate a compact ternary single-walled carbon nanotubes (SWCNTs)/PEDOT:PSS/CuHCF hybrid supercapacitor electrode for high volumetric energy storage performance. In this ternary hybrid electrode, the pseudocapacitive PEDOT:PSS coated onto SWCNTs networks, while the CuHCF NPs were deposited and filled the interspaces between the conductive networks. The as-prepared 3D

multiple-ion-channel hybrid film exhibits a combination of the significant properties, such as good electrical conductivity (1.47 × 10³ S cm⁻¹), high bulk density (2.67 g cm⁻³), and extreme high specific capacitances (areal capacitance of 969.8 mF cm⁻² and volumetric capacitance of 775.2 F cm⁻³ under a scan rate of 5 mV s⁻¹). Furthermore, an asymmetric supercapacitor was assembled by using SWCNTs/PEDOT:PSS/CuHCF film as a positive electrode and Mo-doped WO₃/SWCNTs film as a negative electrode. The device achieved an outstanding energy density of 30.08 Wh L⁻¹ with a high power delivery (4.25 kW L⁻¹) and a long cycling life of 10,000 cycles.

2. Result and discussion

2.1. Materials synthesis and characterization

As illustrated in Fig. 1d, the fabrication process of the 3D interconnected SWCNTs/PEDOT:PSS/CuHCF generally involves two steps. Firstly, the CuHCF crystal was prepared by a co-precipitation method [40]. As shown in the SEM image of Fig. 1a, the size of as-prepared CuHCF NPs is in the range of 20–50 nm. Secondly, after vacuum filtration assembly of the homogeneous mixture of SWCNTs, PEDOT:PSS dispersion and CuHCF NPs, the 3D interconnected SWCNTs/PEDOT:PSS/CuHCF structure was obtained. And the mass ratio of SWCNTs, PEDOT:PSS and CuHCF NPs is about 30:30:40. As shown in the optical image of Fig. 1e the hybrid film exhibited good flexibility with the help of highly mechanical support of SWCNTs.

The X-ray diffraction (XRD) patterns of the pure CuHCF NPs, SWCNTs/PEDOT:PSS and the SWCNTs/PEDOT:PSS/CuHCF hybrid films are showed in Fig. 1b. The peaks located at 17.7, 25.2, 35.7 and 40.4° can be indexed as (200), (220), (400) and (420) reflections (JCPDS No. 02–0381) of cubic phase CuHCF. The broad peaks are ascribed to components of SWCNTs and PEDOT:PSS in these hybrid film. The crystallite size (*D*) based on the (220) diffraction peak is calculated using Scherrer's equation (1):

$$D = \kappa\lambda/\beta\cos\theta \quad (1)$$

where $\kappa = 0.9$, $\lambda = 1.5406 \text{ \AA}$, and β is the full width at half maximum length of a diffraction peak, respectively. The *D* value is calculated to be 16.1 nm resulting from Scherrer's equation. Such small size of the crystal grain will also affect the electrolyte ion transport behavior as discussed in following electrochemical and kinetic part.

The well-dispersivity of CuHCF NPs and its decoration onto the interconnected SWCNTs was confirmed by the cross-section and top-view SEM images of SWCNTs/PEDOT:PSS/CuHCF film of Fig. 2b and Fig. S1a. As shown in the cross-section SEM image of Fig. 2i, the hybrid film showed dense and homogeneous structure, which thanks to co-decoration of CuHCF NPs and the conductive polymer component PEDOT:PSS. PSS is a type of polymer derived from polystyrene but containing sulfonate functional groups. Thus, it exhibited amphiphilic property and enhanced the dispersibility of SWCNTs, which hydrophobic part of the polymer chains (polystyrene) connected well with SWCNTs and hydrophilic part (sulfonate functional groups) could disperse well in water. Thus, the SWCNTs can form into a uniform interconnected structure, resulting in a very good electronic conductivity and mechanical strength. In addition, the CuHCF NPs were also wrapped by the PEDOT:PSS layer and dispersed well in as-prepared dispersion.

The schematic of Fig. 2a illustrated the spatial distribution of SWCNTs, PEDOT:PSS and CuHCF NPs. The wrapped effect of PEDOT:PSS on SWCNTs and CuHCF NPs can be intuitively proved by the STEM mapping test (Fig. 2c–f) of the SWCNTs/PEDOT:PSS/CuHCF hybrid film. PEDOT:PSS is the only component, which contain sulfur in this hybrid system. Thus, the S mapping showed in Fig. 2e provide evidence for the homogenous wrapping of PEDOT:PSS onto SWCNTs and CuHCF NPs.

The packing density is the key factor to determine the volumetric

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