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A novel aqueous asymmetric supercapacitor based on petal-like cobalt selenide nanosheets and nitrogen-doped porous carbon networks electrodes

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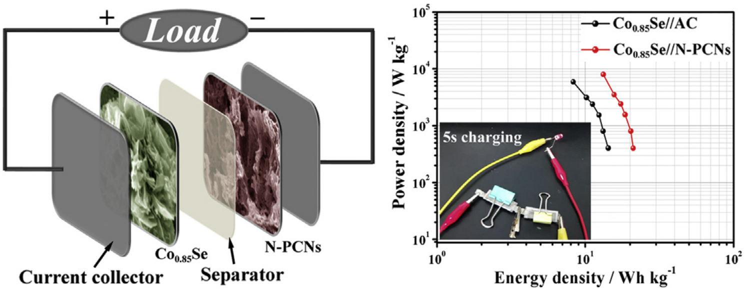
HIGHLIGHTS

- Asymmetric supercapacitor is assembled based on novel $Co_{0.85}Se$ and N-PCNs electrodes.
- Petal-like $Co_{0.85}Se$ nanosheets are synthesized *via* a simple solvothermal method.
- N-PCNs are prepared by integrating polymerization and catalytic carbonization method.
- $Co_{0.85}Se$//N-PCNs aqueous ASC with an extended operating voltage window of 1.6 V.
- The ASC exhibits a high energy density, high rate ability and good cycle stability.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel asymmetric supercapacitor (ASC) is assembled based on petal-like cobalt selenide ($Co_{0.85}Se$) nanosheets as positive electrode and nitrogen-doped porous carbon networks (N-PCNs) as negative electrode in a 2 M KOH aqueous electrolyte. The $Co_{0.85}Se$ nanosheets are synthesized *via* a simple low-temperature solvothermal method without any template and surfactant, and the N-PCNs are prepared by integrating in-situ oxidation polymerization and catalytic carbonization methods directly from the *p*-phenylenediamine monomers. Thanks to their unique structures and high capacitive performance, the as-assembled $Co_{0.85}Se$//N-PCNs ASC device possesses an extended operating voltage window of 1.6 V, high energy density of 21.1 W h kg^{-1} at a power density of 400 W kg^{-1} and outstanding cycling stability (93.8% capacitance retention after 5000 cycles) in aqueous electrolyte.

1. Introduction

As the increasing fossil energy serious depletion and the emergence of global warming issues, researchers around the world

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are not only striving to exploit renewable and clean resources, e.g., solar, wind, and tidal power, but also developing low-cost and high performance energy storage devices. Among various energy storage devices, supercapacitors have drawn considerable attention in recent years due to their high power density and outstanding cycle stability [1,2]. However, it is unfortunate that they are still not ideal for commercial use since their energy density (E) is inferior to that of batteries [3]. To improve the energy density (E) of supercapacitors and maintain their intrinsic high power density, both the device capacitance (C) and the operating voltage (V) should be improved according to the equation of $E = 0.5CV^2$ [4]. As we all know, the device capacitance is prominently dependent on the inherent properties of electrode materials, including good electronic conductivity, special microtopography (e.g., 2D nanosheets and 3D network), high chemical stability, large specific surface area, existence of two or more oxidation states (for transition metal compounds) and so on [3,5,6]. Therefore, it is feasible to achieve high E for supercapacitors which is firstly originated from high C of the electrodes.

Recently, two dimensional (2D) layer-structured transition-metal chalcogenides have been recognized to have high electrochemical activity, which is due to its unique metallic conductivity, multiple available oxidation states and special geometric structures with weak interlayer Van de Waals coupling [7,8]. Some transition-metal sulfides, including MoS_2 [9], CoS_2 [10], NiS [11] and VS_2 [12], are mainly investigated as novel positive electrode materials for supercapacitors in view of their fascinating physicochemical properties. Similarly, 2D layered metal selenides, such as $GeSe_2$ [13] and $SnSe_2$ [14], also provide potential applications in supercapacitors. As a class of metal selenides, cobalt selenide is also known as a metallic conductor and widely used as transparent counter electrodes for dye-sensitized solar cells [15], electrocatalyst for the oxygen evolution reaction [16–18] and so on. However, to the best of our knowledge, still little attention has been paid to the cobalt selenide as electrode materials for supercapacitor so far [19].

Correspondingly, carbonaceous materials, mainly include activated carbons, graphene and carbon nanotubes, are usually investigated as candidate negative electrode materials for ASCs due to their low cost, high electrical conductivity, high specific surface area and good cycling stability. However, there are still some shortcomings to greatly restrict their application in supercapacitors, such as low capacitive performance of activated carbons, complex and expensive preparation process of graphene and carbon nanotubes [6]. Currently, three-dimensional (3D) carbon-based nanostructures, especially nitrogen-doped porous carbon materials with 3D network architectures, have attracted great interest for high-performance supercapacitors, because they combine most characteristics of conventional carbonaceous materials and unique 3D interconnection structure [20]. Furthermore, the incorporation of nitrogen atoms into the carbon frameworks seems to be the effective strategy for enhancing the surface wettability and electronic conductivity of electrode material and lead to high capacity performance [21].

Apart from device capacitance, the operating voltage is another major parameter that is important in determining high energy density of supercapacitors. The operating voltage (V) is dependent on the electrolytes and device structure (assemble types of device and reasonable match of negative/positive electrodes) [3]. Although the use of organic electrolytes in supercapacitors can effectively improve the operating voltage window, low conductivity and inevitable environmental pollution still limit its application in supercapacitor [22]. In comparison to organic electrolytes, aqueous electrolytes hold many advantages such as low-cost, high ionic conductivity, environmental friendliness, inherently safe and acceptable operating voltage range [23]. The asymmetric supercapacitor (ASC) design is another effective way for extending the operating voltage (more than 1.5 V although in aqueous electrolytes) [3], which is greater than that of traditional symmetric supercapacitors (about 1.0 V). ASC is usually assembled with two differents electrodes and utilizes their different potential windows in the same electrolyte to broaden its overall operating voltage. Great efforts have been devoted to exploring various aqueous ASC systems, such as MnO_2//graphene [24], $Ni(OH)_2$//activated carbon [25], Ni–Co sulfide//activated carbon [26], but most of them still use traditional activated carbon as negative electrodes. Therefore, ASCs are fabricated by novel cobalt selenide as the positive electrode and nitrogen-doped porous carbon materials with network architectures as the negative electrode, which seem to meet these requirements of energy storage devices with large operating voltage window and high energy density.

In this work, we aim to achieve the high energy density of ASC through enhancing the specific capacitance of electrode materials and operating voltage of device. A novel aqueous ASC was fabricated based on petal-like cobalt selenide ($Co_{0.85}Se$) nanosheets as positive electrode and nitrogen-doped porous carbon networks (N-PCNs) as negative electrode. The $Co_{0.85}Se$ nanosheets were synthesized *via* a simple low-temperature solvothermal method without any template and surfactant. The N-PCNs were prepared by integrating in-situ oxidation polymerization and catalytic carbonization methods directly from the *p*-phenylenediamine monomer. Thanks to the excellent performance of the positive and negative materials, the assembled $Co_{0.85}Se$//N-PCNs ASC exhibits outstanding electrochemical properties, including large operating voltage, high energy density and good cycle stability.

2. Experimental section

2.1. Materials

Cobaltous nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, Aladdin Industrial Inc., Shanghai, China), selenium dioxide (SeO_2, Sinopharm Chemical Reagent Co., Ltd., China), *p*-phenylenediamine (*p*PDA, Sinopharm Chemical Reagent Co., Ltd., China), anhydrous ferric chloride ($FeCl_3$, Shanghai Chemical Works, China). All the reagents used in experiments were of analytical grade and without further purification.

2.2. Synthesis of petal-like cobalt selenide ($Co_{0.85}Se$) nanosheets

The petal-like $Co_{0.85}Se$ nanosheets were synthesized by a solvothermal method using benzyl alcohol as solvent. In a typical procedure, $Co(NO_3)_2 \cdot 6H_2O$ (0.349 g, 1.2 mmol) and SeO_2 (0.111 g, 1.0 mmol) were added into 35 mL benzyl alcohol solution. After strongly stirring for about 30 min at room temperature, the solution was transferred into a Teflon-lined stainless steel autoclave and heated at 180 °C for 15 h. After cooling to room temperature, the black precipitate was washed with absolute ethanol for several times to remove the residue of reactants and dried at 60 °C for 24 h.

2.3. Synthesis of nitrogen-doped porous carbon networks (N-PCNs)

The N-PCNs were synthesized similar to our previous reported literature [27]. In a typical procedure, *p*PDA monomer (0.54 g, 5 mmol) was dissolved in 25 mL deionized water with magnetic stirring for 30 min in an ice bath. Then, $FeCl_3$ (2.43 g, 15 mmol) was dissolved in 10 mL deionized water and added into the above solution. The polymerization reaction was performed with continuous stirring at below 5 °C for 12 h. Afterwards, the reaction product was transferred to the porcelain boat and evaporated excess water at 80 °C to form a carbon precursor. Finally, the as-