



Tetra-heteroatom self-doped carbon nanosheets derived from silkworm excrement for high-performance supercapacitors

Shuijin Lei^{a,*}, Lianfu Chen^a, Wei Zhou^a, Peiqin Deng^a, Yan Liu^b, Linfeng Fei^b, Wei Lu^b, Yanhe Xiao^a, Baochang Cheng^a

^a School of Materials Science and Engineering, Nanchang University, Nanchang, Jiangxi 330031, PR China

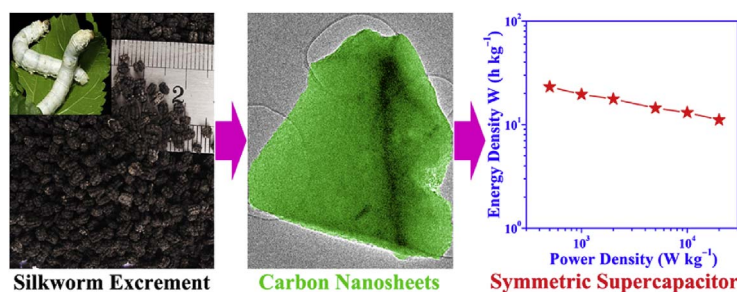
^b Department of Applied Physics, The Hong Kong Polytechnic University, Hong Kong SAR, PR China



HIGHLIGHTS

- N-, P-, S-, O-self-doped carbon nanosheets are prepared from silkworm excrement.
- The obtained carbon nanosheets have high surface area and hierarchical porosity.
- The fabricated carbon-based electrode exhibits high capacitive performance.
- The as-assembled symmetric supercapacitor delivers high energy density.

GRAPHICAL ABSTRACT



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ABSTRACT

Carbon materials are deemed to be competitive candidate electrode materials for energy storage systems. It is still a great challenge to explore advanced carbon-based electrode materials for high-performance supercapacitors by a facile, economical and efficient method. In this work, N-, P-, S-, O-self-doped carbon nanosheets with high surface area and well-developed porosity are successfully prepared by pyrolysis carbonization and post KOH activation from silkworm excrement, a novel abundant, low-cost and eco-friendly agricultural waste. Thanks to their unique multi-heteroatom doping and porous structure, the obtained carbon materials exhibit high charge storage capacity with a specific capacitance of 401 F g^{-1} at a current density of 0.5 A g^{-1} in 6 M KOH and good cycling stability with a capacitance retention of 93.8% over 10000 cycles. A symmetric supercapacitor device using $1 \text{ M Na}_2\text{SO}_4$ aqueous solution as the electrolyte can deliver a specific capacitance of 41.7 F g^{-1} at a current density of 0.5 A g^{-1} , and a high energy density of 23.17 Wh kg^{-1} at a power density of 500 W kg^{-1} with a wide voltage window of 2.0 V . This work develops a new strategy to produce favorable carbon-based electrode materials for supercapacitors with high electrochemical performances.

1. Introduction

Supercapacitor, a promising candidate for energy storage system, has attracted immense interest due to its high power density, long cycle life, good reversibility, as well as its extensive applications in hybrid electrical vehicles, portable electronics, and power back-up devices

[1–4]. Based on the established charge storage mechanism, supercapacitors can be categorized into pseudocapacitor and electrical double layer capacitor (EDLC). The former stores charges through fast reversible Faradaic reaction or surface redox at the electrode/electrolyte interfaces, while the latter is based on the non-Faradic charge accumulation in the double layers at the electrode/electrolyte interfaces.

* Corresponding author.

E-mail address: shjlei@ncu.edu.cn (S. Lei).

Therefore, pseudocapacitors usually utilize transition metal oxides, hydroxides, nitrides, carbides and conducting polymers as the electroactive materials, whereas EDLCs are generally focused on carbonaceous materials [5–9]. Pseudocapacitors can deliver relatively higher capacitance and energy density than EDLCs due to their fast redox reactions, but they usually suffer from the disadvantages of low conductivity, inferior stability, and high cost. Conversely, EDLCs have significant superiorities of high power density, good rate performance and long cycling stability over pseudocapacitors thanks to the pure electrostatic charge accumulation [10,11]. In this regard, carbon-based materials are the most commonly employed electrode materials for supercapacitors.

Up to now, various carbon-based materials, including activated carbons, graphene, carbon nanotubes, carbon nanofibers, carbon aerogels and carbide-derived carbons, have been extensively developed for supercapacitors [12–20]. Thereinto, activated carbons are the most widely adopted electrode materials for EDLCs due to their high specific surface area, low cost and good chemical stability [21–23]. In order to win the high supercapacitive performances, it is crucial to prepare the advanced carbon-based electrode materials with enhanced characteristics such as high specific surface area, appropriate pore size distribution, excellent electrical conductivity and good wettability. Theoretically, the higher specific surface area of the carbon electrode materials always signifies the higher specific capacitance. Practically, however, the specific capacitance is not linearly proportional to the surface area, but strongly depended on the pore structure. The pore size distribution is much critical for the electrochemical performances of carbon-based supercapacitors. It has been reported that micropores can guarantee the large surface area and increase the capacitance of the carbon electrode materials [24]. However, not all the micropores are effective for double layer formation; those smaller than electrolyte ions would prevent efficient electro-adsorption due to the weak wettability and then could not contribute to the total double layer capacitance. Therefore, it is highly desirable that the carbon electrode materials possess not only the high surface area, but also hierarchical porous structures combining micropores (< 2 nm), mesopores (2–50 nm) and macropores (> 50 nm). Among them, micropores provide high surface area for charge storage, mesopores offer low-resistant channels for rapid ion transportation, and macropores serve as the buffering reservoirs for short ion diffusion distance [25]. In addition, the surface functionalization of carbon materials also plays a key role in improving their electrochemical performance. The introduction of heteroatoms including nitrogen, phosphorus, sulfur and oxygen, has been suggested an effective strategy to optimize the carbon electrodes, such as improving wettability, increasing electronic conductivity and introducing pseudocapacitance [26–30]. P-doping even can broaden the potential window, enabling higher energy density [31]. It is believable that multi-heteroatom co-doping would be more powerful and advantageous compared to single heteroatom doping. Furthermore, the morphology of carbon materials is another essential factor affecting their electrochemical performance. The carbon materials with open two-dimensional (2D) morphology would have an intrinsic advantage over the particulate ones because of the significantly shortened ion transport length in the thin dimension [32].

It should be undoubted that the multiple synergistic effects of all the above merits will greatly boost the electrochemical performances of the resultant carbon materials in energy storage applications. It is therefore essential to develop 2D nanostructured carbon materials with high surface area, hierarchical porosity and multi-heteroatom co-doping. However, there are still grand challenges to prepare carbon materials satisfying all the aforementioned characteristics simultaneously by a simple and low-cost method. Recently, biomass materials have been widely used to produce advanced carbon materials for supercapacitor applications due to the significant advantages including abundance, low-cost and eco-friendliness, heteroatom containing and special microstructure [33–35]. Silkworm excrement, a type of agricultural wastes, is the largest by-product in sericulture. Millions metric tons of

silkworm excrements can be produced in China every year. Actually, silkworm excrement is composed of many constituents including crude proteins, crude fats, crude fibers, amino acids, vitamins, chlorophylls, carotenoids, luteins, flavonoids, phytols, pectins, nicotinic acids, alkaloids and so on. As a widely available and environmentally friendly biomass, silkworm excrement is mostly utilized as fertilizer; few is applied in intensive processing and comprehensive development despite its abundance, low-cost, sustainability and environmental benignity. Hence, it will be of great significance to develop green and facile strategies to transform such agricultural residue into high additional value products. To the best of our knowledge, however, there is no report on the preparation of carbonaceous materials from silkworm excrement.

In this work, the raw silkworm excrement was firstly employed as a new biomass precursor to prepare carbon nanosheets with large surface area and multi-heteroatom self-doping through a simple pyrolysis carbonization combined with chemical activation. More importantly, the obtained carbon-based electrode exhibits excellent supercapacitive performances such as high specific capacitance, good rate capability, and outstanding cycling stability. Moreover, the constructed symmetric supercapacitor device can deliver both high energy density and high power density.

2. Experimental section

2.1. Preparation of carbon nanosheets from silkworm excrement

The raw silkworm excrement was directly obtained from sericulturists of Sichuan, China. In a typical process, silkworm excrement was ground into powder and soaked in 1 M diluted hydrochloric acid under ultrasound. The biomass was filtered out, washed thoroughly with distilled water, and freeze-dried. Subsequently, the above precursor was loaded in a horizontal tubular furnace and carbonized at 900 °C for 3 h with a heating rate of 10 °C min⁻¹ under N₂ flow. Afterwards, the resulting carbon powder was impregnated in KOH aqueous solution at a mass ratio of C:KOH = 1:4 and dehydrated at 80 °C to form a slurry. The mixture was then transferred into a nickel crucible and pyrolyzed in a tubular furnace at 600 °C for 2 h with a heating rate of 10 °C min⁻¹ under N₂ flow. After cooling down to room temperature, the resulting product was added into appropriate content of 1 M HCl to neutral pH under magnetic stirring for several hours. Finally, the activated carbon sample was centrifuged and abundantly washed by deionized water until no detection of Cl⁻ anions in supernatant by AgNO₃ titration method, and dried at 80 °C overnight.

2.2. Material characterization

X-ray powder diffraction (XRD) patterns were recorded on a PANalytical Empyrean diffractometer with Cu K α_1 radiation ($\lambda = 1.5406 \text{ \AA}$, operating at 40 kV and 40 mA). The room temperature Raman measurement was performed by a LABRAM-HR confocal laser micro-Raman spectrometer (Jobin-Yvon, France) in the backscattering configuration excited with the 514.5 nm line of an Ar⁺ ion laser. The X-ray photoelectron spectroscopy (XPS) analyses were carried out using an ESCALAB 250Xi X-ray photoelectron spectrometer with Al K α monochromatic radiation at a constant pass energy of 1486.6 eV (ThermoFisher Scientific, USA). Scanning electron microscopy (SEM) measurements were conducted on a JSM-6701F (JEOL, Japan) field emission scanning electron microscope. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) images together with parallel electron energy loss spectroscopy (EELS) were taken from a JEM-2100F (field emission) scanning transmission electron microscope (JEOL, Japan) with an acceleration voltage of 200 kV. The nitrogen adsorption-desorption isotherms were measured by nitrogen physisorption at 77 K on an automatic Micromeritics ASAP-2020 nitrogen adsorption analyzer. The

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