

Porous carbon nanosheets as electrode materials for supercapacitors

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Abstract

With single to many atom layers thickness and infinite planar lengths, two-dimensional porous carbon nanosheets have achieved great development because of their advanced physicochemical properties. Many encouraging characteristics such as high electron mobility and fast ion diffusion have been discovered, leading their ideal utilization in electrode material for supercapacitors. This review provides a brief summary of recent research progress on the design and synthesis of two-dimensional porous carbon nanosheets, as well as their capacitive performance as electrode materials for supercapacitors. In addition to two-dimensional graphene and graphene derived nanosheets, porous carbon nanosheets obtained by wet-chemistry synthesis, hard templating method, molten salt route and direct carbonization of precursors have thus increasingly attracted fundamental research interest because they have the potential to be produced in large scale. Such fundamental understanding of porous carbon nanosheets might offer an important guideline for future design of advanced electrode materials for supercapacitors.

Keywords: Porous materials; Carbon nanosheet; Supercapacitors

1. Introduction

With the development of renewable and sustainable energy, a fast-growing market for portable energy storage devices, such as batteries, supercapacitors and fuel cells has been rapidly increasing [1, 2]. Among current devices, supercapacitors, also known as electrochemical capacitors or ultracapacitors, have attracted lots of attentions due to their long cycle life, high power density, greater stability and good reversibility [3, 4]. In general, supercapacitors can be classified into two categories based on the specific energy storage mechanism: electrical double layer capacitors [5, 6], (EDLCs) and pseudo-capacitors [7-9]. Thereinto, EDLCs represent today more than 80% of the commercially manufactured supercapacitors using carbon as the active material, which strongly depend on the accessible specific surface area (SSA) and porous structure of the electroactive carbon materials to the electrolytes as well as the electronic conductivity themselves [10-13].

Therefore, carbon materials with a high surface area, well-developed porosity and good electrical conductivity have been extensively considered as superior electrode materials for supercapacitors, including quasi-zero-dimensional (0D) onion-like carbon (OLC), one-dimensional (1D) carbon nanotubes (CNTs), two-dimensional (2D) graphene and three-dimensional (3D) porous carbon monoliths [14-16], etc. Among them, porous carbon nanosheets (PCSs), stacked assembly or hybrid composite formed from single to many layers of two-dimensional carbon materials, have recently become a new class of promising electrode material for EDLCs [17]. PCSs can show outstanding capacitive performance, because they have higher electroactive surface area than 0D and 1D material. On the other hand, compared to 3D material, mesoscopic structure of PCSs provides better conductivity and shorter pathways for ion transferring in its pores, resulting in fast charge/ion transfer kinetics [18]. It has

been demonstrated that unique nanosheet structure favors a fast ion diffusion and charge transfer rate, which lead to an effective utilization of porosity and ideal capacitive performance [19].

PCSs were initially synthesized by chemical vapor deposition that relies on a metallic substructure and the yield of this method is very limited [20-22]. Unambiguously, carbon nanosheets obtained by carbonization of various carbonaceous precursors at fairly good yields would be much suitable for large scale production and practical applications in the future. Thus, this review focuses on the typical syntheses of PCSs and their applications for supercapacitors, including (i) reduction of graphene oxide to graphene nanosheet; (ii) graphene directed synthesis; (iii) hard templating method; (iv) molten salt route; (v) direct carbonization of carbonaceous precursors and others. To keep the review down to a manageable level, the porous sheets fabricated from assembly of fibers/tubes [23] or graphene films/membrane [24], or vacuum filtration method are not considered in this review.

2. Graphene-based nanosheets

Graphene, a 2D carbon nanosheet composed of sp^2 bonded single-layer carbon atoms, has recently gained significant interest in major areas of scientific research. Due to its special structure, graphene nanosheet possesses unique properties, such as strong mechanical strength (~ 1 TPa), extraordinarily high electrical and thermal conductivity, and large specific surface area (SSA) ($2675 \text{ m}^2 \text{ g}^{-1}$) [25-27]. Consequently, utilizing supercapacitor electrode materials based on graphene nanosheets have attracted great attentions due to the beneficial combination of the excellent mechanical, electrical properties as well as large surface area [28, 29].

The most promising approach for the large-scale production of graphene is the chemical oxidation of graphite, conversion of the resulting graphite oxide to graphene oxide

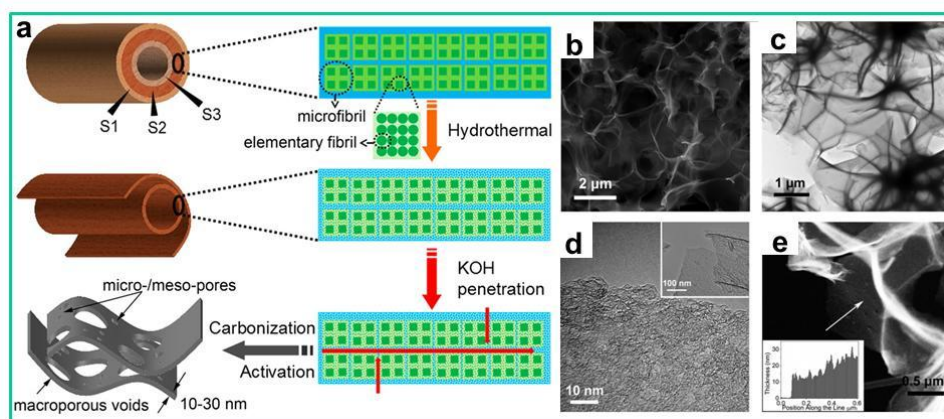


Figure 12. (a) Schematic of the synthesis process for the hemp-derived carbon nanosheets, with the three different structural layers S1, S2, S3. (b) SEM micrograph highlighting the interconnected 2D structure of sample CNS-800. (c) TEM micrograph highlighting the structure of CNS-800. (d) High resolution TEM micrograph highlighting the porous, partially ordered structure of CNS-800. (e) ADF TEM micrograph, EELS thickness profile (inset) of CNS-800. Reprinted with permission from Ref. [86]. Copyright 2013, American Chemical Society.

The carbons are highly interconnected and partially graphitic, yielding excellent electrically conductive electrode. The macroporous voids with diameters of 1–2 μm serve as ion buffering reservoirs. The low thickness of the carbon nanosheets (10–30 nm) ensures nanoscale distances (5–15 nm) for ion diffusion (Figure 12b-e). The high total content of mesopores facilitates the accessibility of the electrolyte ions to the electrode surface and allows for fast ion transport.

8. Conclusions

To summarize up, various kinds of carbon sheets have been so far synthesized using the methods, such as wet-chemistry synthesis, hard templating method, molten salt route and direct carbonization of precursors, etc. This provides a material platform for fundamentally understanding the physical and chemical properties of porous carbon nanosheets at molecular level. This novel sheeting-like structure reduces the path length of reactant inside reaction medium and enhances mass/ion transfer rate in carbon pores. The carbon nanosheets have demonstrated their grand capability in the application of electrode materials for supercapacitors. Although porous carbon nanosheets with short diffusion paths and enhanced electrical conductivity have achieved great improvement to the performance of current supercapacitors, considering the ever-increasing demands for electrical energy storage, adsorption and separation, researchers will continue to develop simple and efficient techniques to create well-defined porous carbon sheets with controlled porosity and fine structure, thus to improve the performance in according applications. With current research interests in graphene and graphene-derived nanomaterials, we therefore believe that the development of carbon sheets with new nanostructure and composition and investigation of their properties are still ongoing hot research topics.

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