Nano Energy 24 (2016) 158–164

Contents lists available at ScienceDirect

Nano Energy

journal homepage: www.elsevier.com/locate/nanoen

Continuously hierarchical nanoporous graphene film for flexible solid-state supercapacitors with excellent performance

Kaiqiang Qin [a], Jianli Kang [b,c,*], Jiajun Li [a], Enzuo Liu [a,d], Chunsheng Shi [a], Zhijia Zhang [b,c], Xingxiang Zhang [b,c], Naiqin Zhao [a,d,**]

[a] School of Materials Science and Engineering and Tianjin Key Laboratory of Composites and Functional Materials, Tianjin University, Tianjin 300072, China
[b] State Key Laboratory of Separation Membranes and Membrane Processes, Tianjin Polytechnic University, Tianjin 300387, China
[c] School of Materials Science and Engineering, Tianjin Polytechnic University, Tianjin 300387, China
[d] Collaborative Innovation Center of Chemical Science and Engineering, Tianjin 300072, China

ARTICLE INFO

Article history:
Received 28 January 2016
Accepted 13 April 2016
Available online 13 April 2016

Keywords:
Hierarchical nanoporous graphene
Hydrogenated graphite
Solid-state supercapacitor
Nanoporous copper
Chemical vapor deposition

ABSTRACT

Continuously hierarchical nanoporous graphene (hnp-G) films are synthesized by a combination of low-temperature CVD growth of hydrogenated graphite (HG) coating on nanoporous copper (NPC) and rapid catalytic pyrolysis of HG at high temperature. Low-temperature growth of HG coating on NPC can obviously delay the coarsening evolution of NPC at high temperature, providing the precondition to obtain hnp-G with small pore size (1–150 nm) by catalytic pyrolysis at high temperature. The high specific surface area (1160 m^2/g) of hnp-G are mainly originated from the external surface (954.7 m^2/g), resulting in fully accessible channels for ion transport. More importantly, the continuously 3D hierarchical nanoporous structure and fully wettability of the hnp-G with gelled electrolyte not only effectively prevent the restacking of graphene even under dramatic squeezing but also guarantee the continuous and short electron/ion diffusion pathway in the whole electrodes, resulting in ultrahigh specific capacitance (38.2 F/cm^3 based on the device) and excellent rate performance. The symmetric SC offers ultrahigh energy density (2.65 mW h/cm^3) and power density (20.8 W/cm^3) and exhibits almost identical performance at various curvatures and excellent lifetime (94% retention after 10,000 cycles), suggesting its wide application potential in powering wearable/miniaturized electronics.

1. Introduction

The fast development of soft portable electronic devices (PEDs) puts forward new challenges for the compatible energy storage devices [1–6]. Flexible solid-state supercapacitors (SCs), as a new class of energy storage devices, attracted considerable attention in recent years due to their small size, low weight, ease of handling, high power density and excellent reliability [7–12]. They can be coupled with PEDs as power sources.

As a fundamental two-dimensional (2D) materials, graphene sheets are promising to be used as basic building blocks to construct graphene-based structures for use as SC electrodes [13–16]. However, from a practical viewpoint for use in devices, it is essential to construct the 2D materials in 3D configurations with preservation of their intrinsic properties due to the parallel restacking of graphene sheets to form graphite-like powders/films and greatly reduce their active surface area [17–19]. To date, a number of synthetic methods for 3D graphene configurations, based on the strategies of either self-assembly, template-assisted preparation or direct chemical vapor deposition (CVD) [20–22], have been developed. The highly porous electrodes based on the binder-free 3D graphene can boost specific surface area and favor ion/electron diffusion for high gravimetric capacitance but usually suffer from low volumetric capacitance due to its low packing density [23–25]. For some practical applications, especially in PEDs that require small in size, it is necessary to achieve high capacitance within a limited area or volume [4,26,27]. Recently, some condensed/compressed reduced graphene oxide films with 3D meso/micro-channels for ion diffusion were developed as electrodes with high volumetric capacitance in liquid electrolyte [28–30]. However, there are few reported literatures about such condensed/compressed graphene for solid-state devices and the rate capacity or power density is not satisfactory due to the

* Corresponding author at: State Key Laboratory of Separation Membranes and Membrane Processes, Tianjin Polytechnic University, Tianjin 300387, China.
** Corresponding author at: School of Materials Science and Engineering and Tianjin Key Laboratory of Composites and Functional Materials, Tianjin University, Tianjin 300072, China.
E-mail addresses: kangjianli@tjpu.edu.cn (J. Kang), nqzhao@tju.edu.cn (N. Zhao).

http://dx.doi.org/10.1016/j.nanoen.2016.04.019
2211-2855/

uncontinuous structure and electron/ion pathway [31,32]. Although some researchers tried to prepare 3D continuous graphene with relative small pore size by chemical vapor deposition (CVD) using nanoporous metal [33–35], the average pore size of the obtained graphene film by traditional CVD is still larger than 200 nm due to the dramatic coarsening of nanoporous metal at high temperature and no works about such 3D continuous graphene with pore size less than 100 nm for solid state SCs are reported still now as far as we know. Therefore, fabricating 3D continuous graphene based solid-state flexible SCs with excellent volumetric performance is still challenging.

Herein, a continuously hierarchical nanoporous graphene (hnp-G) film with high specific surface area was prepared by rapid catalytic pyrolysis of hydrogenated graphite (HG) using nanoporous copper (NPC) as catalyst. It is known that nanoporous metal is inclined to coarsen at high temperature [36] and thus the resulted 3D graphene by traditional CVD have large pores and low density [33–35]. To control the pore size of the grown nanoporous graphene (np-G) with higher density, we propose a two-step method to prepare 3D continuous graphene with hierarchical nanopores, which combines coating a thin layer of HG by CVD on NPC at low temperature (200 °C) and then rapid catalytic pyrolysis of HG at high temperature (Fig. 1A). Low temperature uniform coating of HG on NPC can obviously delay the coarsening evolution of NPC at high temperature, providing the precondition to obtain np-G with small pores by catalytic pyrolysis at high temperature. Furthermore, the obtained hnp-G films are continuous and flexible, which can be directly used as binder-free electrodes for flexible solid state SCs. As shown in Fig. 1B, the two pieces of hnp-G films are dipped into sulfuric acid/polyvinyl alcohol (H_2SO_4/PVA) solution and then partially extracted and dried. The as-obtained electrodes with thin electrolyte coating layers are squeezed to form a micrometer-thin solid state device, sandwiched by gelled electrolyte between. Brunauer–Emmett–Teller (BET) analysis reveals that the high specific surface area (1160 m^2/g) of hnp-G are mainly originated from the external surface (954.7 m^2/g), resulting in fully accessible channels for electrolyte/ion transport. Furthermore, the continuously 3D hierarchical nanoporous structure and good wettability of the hnp-G with gelled electrolyte not only effectively prevent the restacking of graphene even under dramatic compression but also guarantee the continuous and short electron/ion diffusion pathway in the whole device, resulting in ultrahigh device capacitance (38.2 F/cm^3) and excellent rate performance.

2. Experimental section

2.1. Preparation of nanoporous copper catalyst

$Cu_{40}Mn_{60}$ ingots were prepared by melting pure Cu and Mn (> 99.9 at%) using an Ar-protected arc melting furnace. After

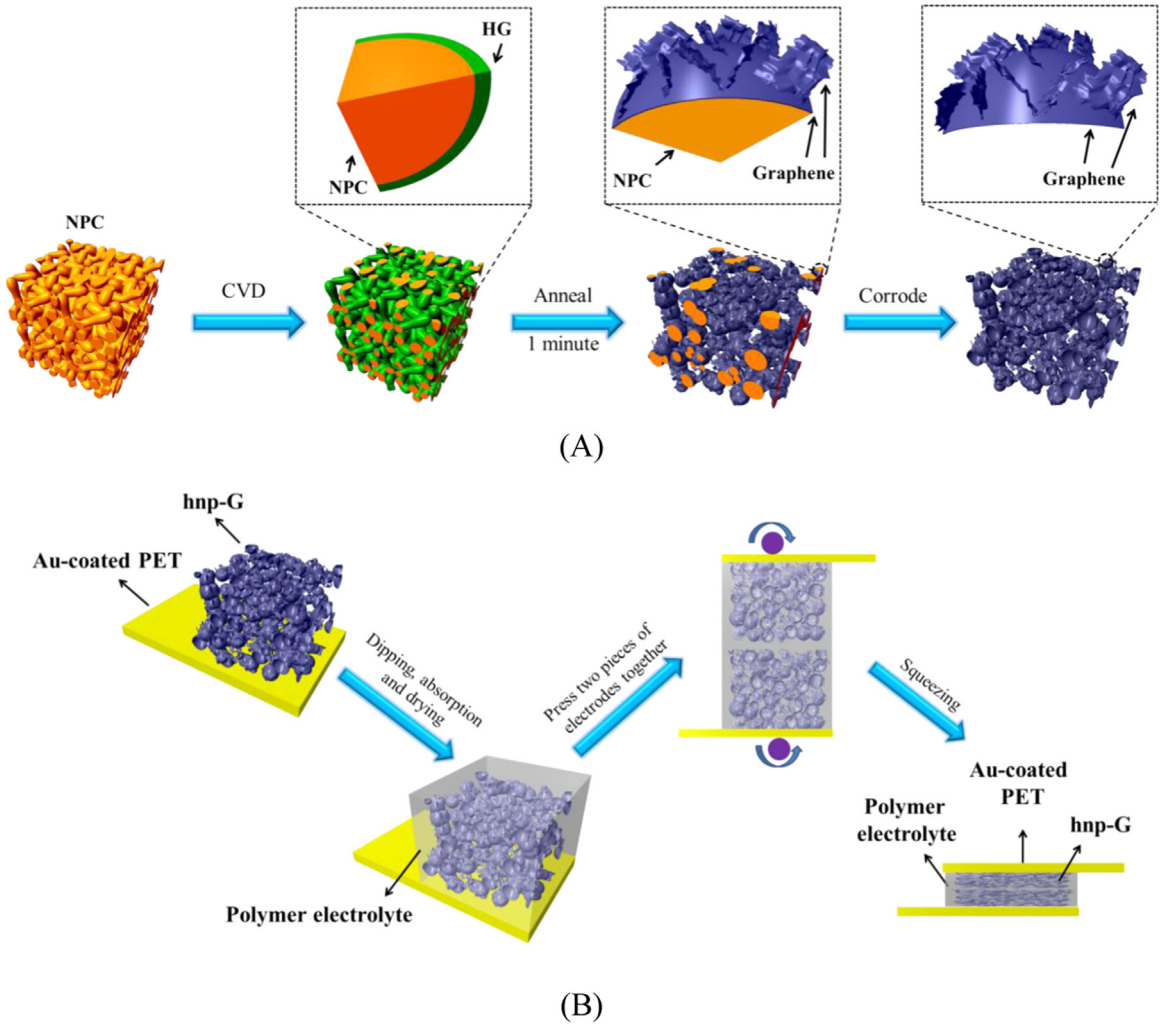

Fig. 1. (A), (B) Schematic diagram of the fabrication process of the hnp-G and flexible solid state supercapacitors.