



Efficiently dense hierarchical graphene based aerogel electrode for supercapacitors



Xin Wang^{a, c}, Chengxing Lu^{a, c}, Huifen Peng^{a, b, c}, Xin Zhang^{a, b}, Zhenkun Wang^{a, c}, Gongkai Wang^{a, b, *}

^a Research Institute for Energy Equipment Materials, Hebei University of Technology, Tianjin, 300130, China

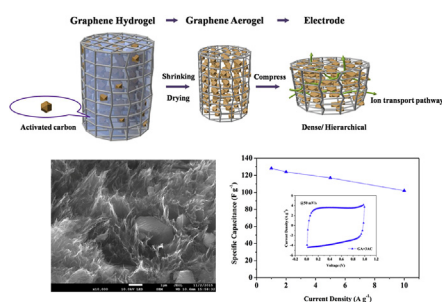
^b Tianjin Key Laboratory of Laminating Fabrication & Interface Control Technology for Advanced Materials, Tianjin, 300130, China

^c School of Material Science & Engineering, Hebei University of Technology, Tianjin, 300130, China

HIGHLIGHTS

- Dense hierarchical graphene/activated carbon composite aerogels are prepared.
- The compact and porous structures of composite aerogels could be maintained.
- The aerogels boost gravimetric and volumetric capacitances simultaneously.
- Superior cyclic stability in 6 M KOH aqueous electrolyte is achieved.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 25 January 2016

Received in revised form

20 April 2016

Accepted 19 May 2016

Keywords:

Dense
Hierarchical
Graphene
Aerogel
Supercapacitor

ABSTRACT

Boosting gravimetric and volumetric capacitances simultaneously at a high rate is still a discrepancy in development of graphene based supercapacitors. We report the preparation of dense hierarchical graphene/activated carbon composite aerogels via a reduction induced self-assembly process coupled with a drying post treatment. The compact and porous structures of composite aerogels could be maintained. The drying post treatment has significant effects on increasing the packing density of aerogels. The introduced activated carbons play the key roles of spacers and bridges, mitigating the restacking of adjacent graphene nanosheets and connecting lateral and vertical graphene nanosheets, respectively. The optimized aerogel with a packing density of 0.67 g cm^{-3} could deliver maximum gravimetric and volumetric capacitances of 128.2 F g^{-1} and 85.9 F cm^{-3} , respectively, at a current density of 1 A g^{-1} in aqueous electrolyte, showing no apparent degradation to the specific capacitance at a current density of 10 A g^{-1} after 20000 cycles. The corresponding gravimetric and volumetric capacitances of 116.6 F g^{-1} and 78.1 cm^{-3} with an acceptable cyclic stability are also achieved in ionic liquid electrolyte. The results show a feasible strategy of designing dense hierarchical graphene based aerogels for supercapacitors.

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1. Introduction

Supercapacitors with features of extraordinary power density, long cyclic lifetime and low maintenance cost offer a leap forward in the field of green energy storage applications, whereupon, have

* Corresponding author. Research Institute for Energy Equipment Materials, Hebei University of Technology, Tianjin, 300130, China.

E-mail address: wang.gongkai@hebut.edu.cn (G. Wang).

attracted great attention in recent years. Considerable efforts have been devoted to improving the performances of supercapacitors by developing novel electrode materials, however, it is still plagued with the limited energy density derived from the mechanism of physical ion adsorption/desorption at the interface between electrode and electrolyte [1,2]. Graphene gives rise to the colossal upsurge of interests in the widespread research fields. It could be a judicious option as of primary importance electrode materials for advanced and even flexible supercapacitors owing to its intrinsically high surface area, superior electrical conductivity, flexibly mechanical robustness and chemical stability [3–5]. The mass production of graphene nanosheets under the industrial standard has been achieved basically, however, the dispersion and re-aggregation issues due to the inherent hydrophobicity and the van der Waals and π - π interaction between graphene nanosheets decrease the efficient surface area and deteriorate the specific capacitance, which penalize the downstream application and mitigate against the further progress [6,7].

Macroscopic assembled graphene is a three-dimensional (3D) architecture made from individual graphene nanosheet. It has a preponderance of structure that greatly avoids the self-restacking and maintains the porous structure in the entire one as compared with raw graphene nanosheets [8–10]. Various types of macroscopic assembled graphene with homogeneous structure or heterostructure have been proposed including graphene film or paper [11,12], graphene fiber [13,14], graphene hydrogel and graphene aerogel by versatile routes for supercapacitors [15,16]. For example, Yang et al. reported a compact graphene film mediated by liquids using vacuum filtration and capillary compression, which showed a gravimetric capacitance of 167 F g^{-1} [11]. Xu et al. reported a graphene hydrogel with a gravimetric capacitance of 160 F g^{-1} by a one-step hydrothermal method [15]. Hao et al. synthesized graphene based aerogel with a gravimetric capacitance of 197 F g^{-1} derived from chitosan [17]. Although the gravimetric capacitance was deemed as the primary performance metric to evaluate an electrode material of supercapacitors traditionally, the volumetric capacitance intended for device-level energy density was urgently expected for the rising graphene based materials. If an electrode material with microstructures of more accessible surface area and ion diffusion channels could offer a high gravimetric capacitance, usually, it also results in a low volumetric capacitance owing to the derived low packing density. It seemingly has a trade-off relationship between gravimetric and volumetric capacitances, corresponding to a porous microstructure and a high packing density, respectively. Therefore, it quests for proper methods that could boost gravimetric and volumetric capacitances simultaneously, and this is where research projects run [11,18–22].

Additionally, a method of solvent-exchange was proposed during the assembly of graphene hydrogel based supercapacitor cells. It aims to replace solvents by electrolytes directly upon the different volatilities of various liquids [11,23]. Although the microstructure of graphene hydrogel was well maintained and a high gravimetric capacitance and rate capability performance could be obtained, the rigorous exchange conditions such as temperature, period, moisture and oxygen content were required during the solvent-exchange process. Accordingly, it is speculated to increase the industrial expense and reduce the feasibility inevitably for scale up in the future.

Together, it remains a formidable challenge to achieve high gravimetric and volumetric capacitances while maintaining a superior rate capability simultaneously by using a facile supercapacitor assembly process. Whereupon, the strategy employed in this study was incorporating graphene aerogels with activated carbons all-in-one as supercapacitor electrodes. Even though graphene/activated carbon materials applied in supercapacitors were

published in some previous reports, our motivation with respect to the improvement of packing density of graphene materials is intrinsically different by contrast [24]. The schematic and features of this study are shown in Fig. 1. The graphene aerogel serving as a matrix was formed through a facile reduction induced self-assembly process as shown in Fig. 1(a) [25]. The activated carbons were introduced into the graphene aerogel uniformly during the self-assembly process. The composite was used as electrodes directly for supercapacitor assembly after a drying post treatment. The volume of the composite aerogel shrank greatly due to the capillary compression driven by the drying process, which increased the packing density accordingly. The incorporated porous activated carbons mitigated the restacking of graphene nanosheets and facilitated effective ionic and electronic transport, resulting in a good rate capability. Meanwhile, the activated carbons also increased the pore volume that provides more accessible surface area for gravimetric capacitance of the entire composite aerogel as shown in Fig. 1(b). Therefore, the gravimetric capacitance and the packing density of the optimized composite aerogel is 128.2 F g^{-1} at a current density of 1 A g^{-1} in aqueous electrolyte and 0.67 g cm^{-3} , respectively, with no apparent degradation to the specific capacitance at a current density of 10 A g^{-1} even after 20000 cycles. The composite aerogels with the solvent-exchange treatment were also evaluated for comparison. The morphology and microstructures were analyzed using various characterization approaches. The results demonstrate that the dense hierarchical graphene based aerogel using a facile synthesis and assembly process holds a promise for advanced supercapacitor applications.

2. Experimental

2.1. Material preparation

Graphite oxide (GO) was synthesized using the Hummers method, as reported in our previous work [26]. GO was dispersed in DI water by sonication for 1 h to form a GO aqueous solution. The resulting solution was centrifuged at 3000 rpm for 30 min to remove any aggregates. The final GO dispersion (2 mg ml^{-1}) was obtained for the following experiments. The incorporated activated carbon (Kuraray Chemical Co., Ltd., YP-50F, specific surface area of $1600 \text{ m}^2 \text{ g}^{-1}$) was modified first by strong oxidizing agents. In a typical procedure, the activated carbons (150 mg) were suspended in the mixture of concentrated $\text{H}_2\text{SO}_4/\text{HNO}_3$ (3:1) (30 ml) and sonicated in a bath cleaner for 4 h. The resultant solution was diluted with DI water (400 ml) followed by vacuum filtration through a polyvinylidene fluoride (PVDF) membrane. The solid was washed by excess 80°C DI water and dried under vacuum at 60°C for 12 h. The graphene/activated carbon aerogel was prepared according the following procedure: 10 ml GO dispersions mixed with series of weight percentage of modified activated carbons to GO were sonicated first for 30 min. 0.5 ml 1 M sodium ascorbate aqueous solution was added into the above solution followed by heating in an oil bath at 100°C for 2 h without stirring. The resulting graphene/activated carbon hydrogel was taken out and washed with excess DI water three times to remove any impurities. Slices with a thickness of $\sim 2 \text{ mm}$ were cut from the above purified composite hydrogels and then dried under vacuum at 80°C for 12 h. The monolithic graphene hydrogel was synthesized without introduction of activated carbons. Namely, 0.5 ml 1 M sodium ascorbate aqueous solution was added into the as-prepared 10 ml GO dispersion, which was heated in an oil bath at 100°C for 2 h without stirring. The resulting graphene hydrogel was followed the same washing and drying processes as those of graphene/activated carbon hydrogel. The samples were denoted as GA, GA+1AC, GA+3AC and GA+4AC according to the weight percentage of added

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