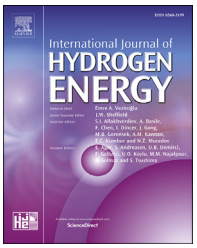
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2017) 1–14

Available online at www.sciencedirect.com

ScienceDirect

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



Supercritical fluid processing of N-doped graphene and its application in high energy symmetric supercapacitor

S. Suresh Balaji [a,b], M. Karnan [a], M. Sathish [a,b,*]

[a] Functional Materials Division, CSIR-Central Electrochemical Research Institute, Karaikudi, 630003, Tamilnadu, India

[b] Academy of Scientific and Innovative Research (AcSIR), CSIR-Central Electrochemical Research Institute, Karaikudi, 630003, Tamilnadu, India

ARTICLE INFO

Article history:
Received 29 May 2017
Received in revised form
14 August 2017
Accepted 16 August 2017
Available online xxx

Keywords:
Supercritical fluids
N-doped graphene
Glycine
Supercapacitors
Ionic liquid

ABSTRACT

A simple one-pot methodology is developed for the synthesis of nitrogen doped graphene via supercritical fluid (SCF) processing using glycine as a nitrogen precursor. The presence of various N-containing functional groups was determined by FT-IR and the amount of N-doping in the graphene was found to be 4.5 wt% using the elemental analysis and X-ray photoelectron spectroscopy. The electrochemical capacitance measurements are performed using cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopy. The nitrogen doped graphene exhibited enhanced capacitive performance with a maximum specific capacitance of 270 F/g at 0.5 A/g current density with high specific capacitance retention of 90% over 10,000 cycles at 10 A/g current density. The fabricated symmetric supercapacitor cell showed a high energy density of 4.1 and 36 Wh/kg in aqueous and ionic liquid electrolyte, respectively. The high energy density obtained in ionic liquid is promising for their potential application in electrochemical energy system.

Introduction

Nowadays considerable steps have been carried out for the development of clean and sustainable sources of energy. The most up-to-date technological developments in the market of hybrid electric vehicles and electronic devices show the way to a need for alternative energy storage devices with higher power and energy densities [1]. Supercapacitors, also known as electrochemical capacitors, which store and release energy via either electrochemical charge accumulation or faradaic reaction at the electrochemical interface between electrode and electrolyte [2]. They are capable of harmonize batteries in electrical energy storage and harvesting applications, where high power delivery is required [3]. Because of variation in nature of charge storage mechanisms and electrode materials, electrochemical supercapacitors are primarily organized into two major types namely electrical double layer capacitors (EDLCs) and redox supercapacitors [4]. Based on ragone plot, supercapacitor act as bridge between batteries and

* *Corresponding author*. Functional Materials Division, CSIR-Central Electrochemical Research Institute, Karaikudi, 630003, Tamilnadu, India.
E-mail addresses: marappan.sathish@gmail.com, msathish@cecri.res.in (M. Sathish).

http://dx.doi.org/10.1016/j.ijhydene.2017.08.101
0360-3199/

conventional capacitors, delivering more power than batteries and storing more energy than conventional capacitors [5]. As supercapacitor exhibit high power performance, long cyclability, low maintenance and fast dynamics of charge propagation, they have received substantial attention in the potential applications in load crane, forklifts, consumer electronics, portable electronics, hybrid electric vehicles etc., [6]. Due to their good electrical conductivity and enhanced surface area, carbon based materials such as carbon nanotubes, carbon nanofiber and graphene have been used as electrode materials for EDLC [7,8]. Transition-metal hydroxide/oxides including carbon-metal oxide composites [9–13] and graphene based conducting polymer composites [14–16] are reported as promising candidates for redox supercapacitor. Yet their poor cycle life and high cost would detain their dominance in further applications.

Graphene, a single-atom-thick sheet which consists of two-dimensional honeycomb hexagonal array sp^2-hybridized carbon network, has been believed as emerging applications owing to its unique morphology, high theoretical surface area of 2630 $m^2 g^{-1}$ and excellent electrical conductivity [17,18]. Still the chemically obtained graphene experience sheet-to-sheet restacking which happen due to strong interlayer van der Waals force that may lead to several consequences such as failure in specific surface area, constraint in electrolyte penetration and ease of access by ion thereby leading to the low specific capacitance [19]. Heteroatom doping is one of the efficient approach for tailoring the chemical and electrochemical properties of graphene [20]. Among the various hetero atoms (N,S,B,P and F), nitrogen can be easily doped into graphene network by means of forming stable covalent C–N bonds due to the similitude in atomic size and valence electrons available for the formation of stable covalent bonds with adjacent carbon atoms [21]. Particularly N-doping over graphene network is the most efficient approach of doping because of higher electronegativity of nitrogen relative to that of carbon and conjugation between lone pair of electrons over nitrogen and π-electrons of graphene [22]. There are many methods involving different nitrogen precursors reported for the synthesis of nitrogen-doped graphene namely hydrothermal synthesis using 2, 4, 6-Triaminopyrimidine as a nitrogen precursor [23], one-pot preparation of N-doped graphene by urea via hydrothermal [24], synthesis of N-doped carbon by thermal annealing using melamine [25], one-pot synthesis of N-doped graphene by ammonium nitrate [26], synthesis of N-doped graphene hydrogel using hydroxyl amine etc., [27]. In our earlier studies, we prepared the N-doped graphene using three different nitrogen containing organic compounds such as ethylene diamine, melamine and hexamine and reported the maximum capacitance of 280 F/g by ethylene diamine derived N-doped graphene [28]. Synthesis of N-doped graphene using other organic nitrogen sources such as nitric acid treated urea, EDTA and DMG are also reported for the application as an electrode material for supercapacitor in acidic medium [29–31]. Recently Wang et al. reported that N-doped activated carbon as a symmetric supercapacitor electrode using pyrrole as a nitrogen precursor [32]. The reported specific capacitance of N-doped graphene synthesized by various methods using different nitrogen precursors in the literature are compared in Table S1.

Herein we report the synthesis of N-doped graphene using glycine as a nitrogen precursor via supercritical fluid technique using water as a solvent and its application in supercapacitor. Supercritical reactions in aqueous medium are basically advantageous since it promotes a simple and convenient homogeneous phase one-pot synthesis as well as environmental friendly [33]. The specific capacitance of supercritical fluid assisted glycine/graphene oxide composites of three different ratios are compared with RGO in alkaline medium (20% KOH solution). In general, the energy density of the supercapacitor depends on the specific capacitance and cell voltage. In aqueous based electrolytes, the cell voltage is restricted due to the thermodynamic decomposition of water at 1.23 V, whereas in case of organic and ionic liquid based electrolytes, higher operating potential window is feasible which will enhance the energy density of the supercapacitor appreciably [34,35]. For this reason, ionic liquids are presumed as useful candidates for electrolytes in supercapacitors. Recently, we reported a high energy density of 17.4 and 25 Wh/kg for bio derived carbon from rice straw and corn cob in 1-ethyl-3-methyl imidazolium tetrafluoroborate ionic liquid electrolyte [36,37]. Here, we demonstrated that the N-doped graphene prepared with 4.5 wt% of nitrogen as a symmetric supercapacitor in ionic liquid electrolyte. All the materials are characterized using various analytical techniques such as XRD, Raman, FT-IR, CHNS analysis and FE-SEM. Their electrochemical performances are examined by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge/discharge. The electrode materials prepared by supercritical fluid assisted glycine/graphene oxide composite in different ratios at 1:2, 1:1, 2:1 in 1 h and conventionally reduced graphene oxide are designated as GGO-(1:2), GGO-(1:1), GGO-(2:1) & RGO respectively in the subsequent experimental as well as results and discussion part.

Experimental section

Materials

Graphite flakes powder (≤20 μm, 99%), Polytetrafluoroethylene (PTFE) $(-CF_2-CF_2-)_n$ are purchased from Sigma-Aldrich, India. Sodium Nitrate ($NaNO_3$, 99 wt%), potassium permanganate ($KMnO_4$, 99.5 wt%), hydrogen peroxide (H_2O_2, 30 wt%), hydrazine hydrate (H_6N_2O, 99 wt%) are purchased from E-Merck, India. Sulfuric acid (H_2SO_4, 98 wt%) is purchased from Ranbaxy laboratories., Ltd. Glycine ($C_2O_2NH_5$ 99 wt%) is procured from Merck. All the chemicals and reagents are used as received without any further purification. Deionized (DI) water is obtained from MILLIPORE water system.

Preparation of graphene oxide (GO)

GO was synthesized from synthetic graphite flakes using modified Hummer's method [38]. In a typical synthesis, 2 g of graphite and 2 g of $NaNO_3$ were mixed with 100 mL of concentrated H_2SO_4 in a 1000 mL round-bottom flask and stirred for 30 min using magnetic stirrer. Then, $KMnO_4$ (12 g) was gradually added with constant stirring and the reaction temperature was maintained at below 5 °C using ice bath. Then, the ice bath was removed and 160 mL DI water was

Please cite this article in press as: Suresh Balaji S, et al., Supercritical fluid processing of N-doped graphene and its application in high energy symmetric supercapacitor, International Journal of Hydrogen Energy (2017), http://dx.doi.org/10.1016/j.ijhydene.2017.08.101