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High performance supercapacitor using N-doped graphene prepared via supercritical fluid processing with an oxime nitrogen source

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ABSTRACT

Heteroatom doped graphene has been proved for its promising applications in electrochemical energy storage systems. Here, nitrogen (N) doped graphene was prepared via two different techniques namely supercritical fluid assisted processing and hydrothermal heat treatment using dimethylglyoxime (DMG) as an oxime nitrogen precursor. The FT-IR and Raman spectra showed the N-containing functional group in the graphene. The XRD analysis revealed the complete reduction of graphene oxide during the supercritical fluid processing. The elemental analysis and X-ray photoelectron spectroscopy revealed the amount and nature of N-doping in the graphene, respectively. The surface morphology and physical nature of the samples were analyzed using scanning and transmission electron microscopic analysis. The electrochemical performance of prepared electrode materials was evaluated using cyclic voltammetry, galvanostatic charge-discharge analysis and electrochemical impedance spectroscopy. The N-doped graphene prepared via supercritical fluid assisted processing exhibit enhanced capacitive behaviour with a maximum specific capacitance of 286 $F g^{-1}$ at a current density of 0.5 A/g. The cycling studies showed 98% specific capacity retention with 100% coulombic efficiency over 1000 cycles at 5 A/g. The enhanced specific capacitance of N-doped graphene prepared via supercritical fluid heat treatment over the hydrothermal heat treatment is ascribed to the nature of N-doping in the graphene.

1. Introduction

Supercapacitors, also known as ultracapacitors, are a group of electrochemical energy storage devices which store and release energy via electrochemical charge accumulation or faradaic reaction at the electrochemical interface between the electrode and electrolyte [1]. Based on their charge storage mechanisms and electrode materials, electrochemical supercapacitors can be broadly classified into three major groups namely, electrical double layer capacitors (EDLCs), pseudocapacitors (redox supercapacitors) and hybrid capacitors. As supercapacitors exhibit high power performance and long cyclability, they have received substantial attention in the potential applications in portable electronics, hybrid electric vehicles, etc [2,3]. Carbon based materials such as carbon nanotubes, graphene, carbon nanofibre etc., have been scrupulously employed as electrode materials for EDLCs owing to their enhanced surface area and good electrical conductivity [4–6]. Redox-active materials such as transition-metal hydroxide/oxides including carbon-metal oxide composites [7–11], and graphene based polymer composites [12–14] are reported as promising electrode materials for pseudo-capacitors due to their high specific capacitance by means of faradaic reactions. But their poor cycle life and high cost would confine their further applications.

Graphene, the single-atom-thick sheet having two-dimensional honeycomb network of hexagonally arranged sp^2-hybridized carbon atoms, has been recently deemed as an emerging applications because of its unique morphology, high theoretical surface area of 2630 $m^2 g^{-1}$and excellent electrical conductivity [15–17]. However, the chemically derived graphene recurrently experience sheet-to-sheet restacking which occur as a result of strong interlayer van der Waals force that incorporate several consequences such as the enormous loss of high specific surface area, restriction in electrolyte penetration and ion accessibility thereby leading to the low specific capacitance [18]. Therefore both the chemical and electrochemical properties of graphene can be customized by insertion of heteroatom in graphene network. Among the different hetero atoms such as nitrogen, boron, phosphorous and fluorine, nitrogen can be readily doped into

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carbon materials by means of forming C—N bonds due to the resemblance in atomic size and valence electrons available for the formation of stable covalent bonds with adjacent carbon atoms [19]. To the best of our knowledge, there are numerous methods reported for the synthesis of nitrogen-doped graphene include thermal annealing of graphene oxide (GO) with ammonia [20], thermal annealing of GO with urea [21], 3D Nitrogen-doped graphene prepared by pyrolysis of GO with polypyrrole [22], one-pot synthesis of N-doped graphene using ammonium nitrate as a nitrogen precursor [23], synthesis of N-doped graphene hydrogel using hydroxyl amine [24], synthesis of N-doped graphene using urea as a nitrogen source using microwave route as well as supercritical technique [25,26], and ammonia assisted photoreduction in N-doping of GO [27], synthesis of N-doped graphene using EDTA as a nitrogen source [28], synthesis of N-doped graphene using three different nitrogen containing organic ligands such as ethylene diamine, melamine and hexamine [29]. It is essential to indicate here that the N-doped graphene exhibit interesting applications in various fields such as supercapacitors, lithium-ion batteries and electrocatalysts in ORR which motivated us to explore the N-doped graphene towards supercapacitor applications [30]. Herein we report the N-functionalized graphene using DMG (oxime nitrogen) as a nitrogen precursor via supercritical fluid assisted synthesis and hydrothermal technique. Since DMG is a chelating agent as well as highly basic in nature, it is expected that the N-functionalized graphene using DMG as a nitrogen source may improve the capacitive performance of graphene-based materials. Supercritical reactions in aqueous medium is essentially profitable because it encourages a simple and convenient homogeneous phase one-pot synthesis as well as environmental friendly [31]. The specific capacitance of supercritical fluid assisted DMG functionalized GO, hydrothermal heat-treated DMG functionalized GO were compared with undoped conventionally reduced graphene oxide (RGO). All the three materials were characterized using various analytical techniques such as XRD, Raman, FT-IR, CHN analysis and FE-SEM. And their electrochemical performances were examined by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge/discharge in 1 M aqueous sulphuric acid solution. The electrode materials prepared by supercritical fluid assisted DMG functionalized GO, hydrothermal heat-treated DMG functionalized GO were denoted as SCDGO and HTDGO, respectively in the subsequent discussions.

2. Experimental

2.1. Materials

Graphite flakes powder (≤20 μm, 99%), Polytetrafluoroethylene (PTFE) $(-CF_2-CF_2-)_n$ were 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%) were purchased from E-Merck, India. Sulphuric acid (H_2SO_4, 98 wt%) was purchased from Ranbaxy laboratories., Ltd. Dimethyl glyoxime ($C_4O_2N_2H_8$, 99 wt%) was procured from Merck. All the chemicals and reagents were used as received without any further purification. Deionized (DI) water was obtained from MILLIPORE water system.

2.2. Preparation of supercritical fluids assisted dimethyl glyoxime doped GO (SCDGO)

GO was synthesized from synthetic graphite flakes using modified Hummer's method [26,32]. The above prepared GO solution (20 mL) and dimethyl glyoxime (DMG) were mixed together at 1:1 weight ratio and loaded into stainless steel reactors of total 35 mL capacity and the reactors were placed into a furnace at 400 °C for 2 h. The resulting precipitate was filtered and washed with water for several times and finally with ethanol and then dried in an oven at 90 °C for overnight.

2.3. Preparation of hydrothermal assisted dimethyl glyoxime doped GO (HTDGO)

GO solution (70 mL) and dimethyl glyoxime (DMG) were mixed together at 1:1 weight ratio and loaded into Teflon autoclave of total 100 mL capacity and then autoclave was placed into a hot-air oven 200 °C for 12 h. The resulting precipitate was filtered and washed with water for several times and finally with ethanol and then dried in an oven at 90 °C for overnight.

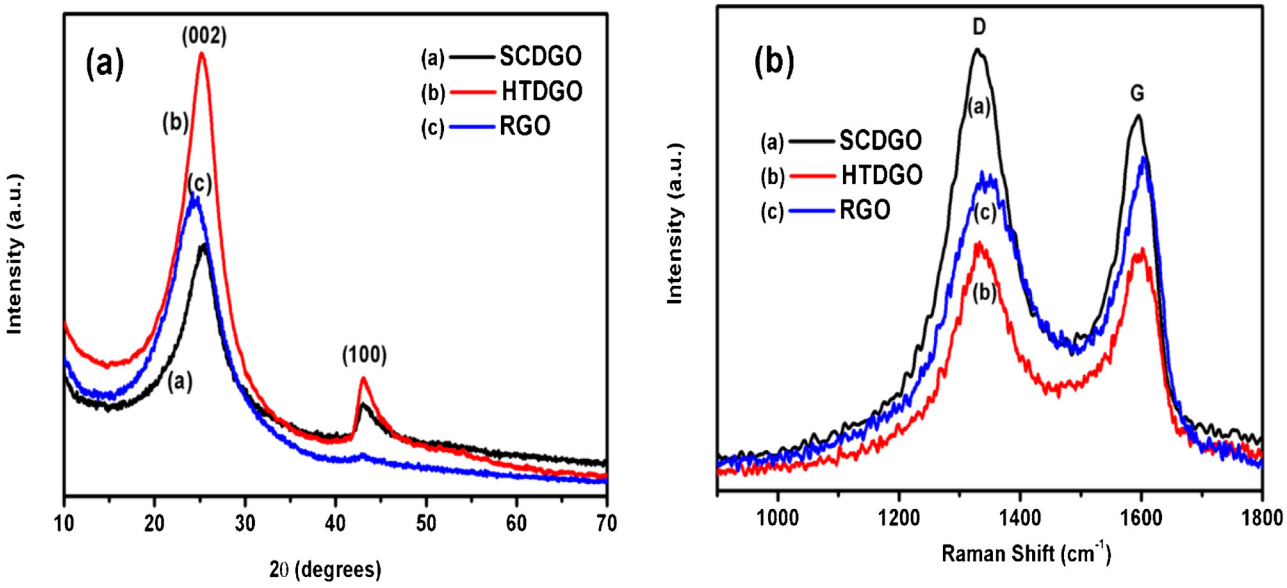

Fig. 1. (a) XRD pattern and (b) Raman spectra of (a) SCDGO, (b) HTDGO and (c) RGO.