



Nanocellulose-assisted low-temperature synthesis and supercapacitor performance of reduced graphene oxide aerogels



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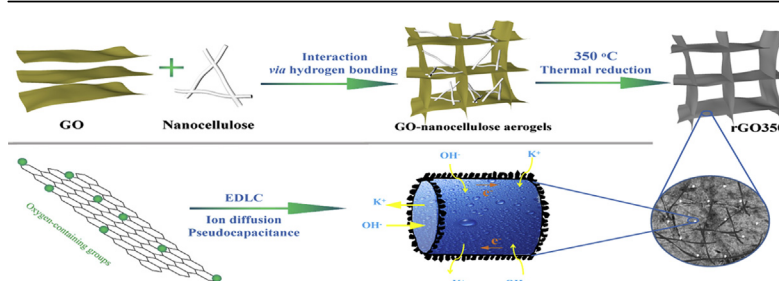
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HIGHLIGHTS

- Nanocellulose was an efficient promoter for the gelation of graphene oxide solution.
- rGO aerogels were prepared via a thermal treatment at 350 °C.
- The pseudocapacitance for rGO350 electrode accounted for 40.7% of the total capacity.
- rGO350 electrodes also showed relatively good rate capability.

GRAPHICAL ABSTRACT



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ABSTRACT

Here, we have synthesized reduced graphene oxide (rGO) aerogels using a nanocellulose-assisted low temperature (less than 500 °C) thermal treatment route where nanocelluloses promote the gelation of graphene oxide (GO) solution that benefits the fabrication of GO aerogels from low concentration dispersion (2.85 mg mL⁻¹), and after their thermal decomposition the residual nanofibers act as spacer both prevent the re-stacking of graphene sheets and integrate with rGO sheets to give a particular kind of carbon-based aerogel along with numerous defects (holes). Thermal decomposition of nanocellulose appears to be complete beyond 350 °C thus its presence in form of amorphous carbon nanofibers in rGO sheets. The rGO aerogels synthesized at 350 °C provide the best balance in terms of wide interlayer spacing, high content of CO-type functional groups, and high defects content. This translates into a high discharge capacitance of 270 F g⁻¹ at a current rate of 1 A g⁻¹ for compressed rGO aerogels without any binder or conductive additive. Detailed electrochemical tests using 6 M KOH electrolyte establish the fact that pseudocapacitance component has substantial contribution towards the overall capacitance; closely approaching the contribution of the double layer capacitance that is the most dominant capacitance component.

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1. Introduction

Supercapacitors or electrochemical capacitors (ECs) have received considerable attention for energy storage application given their high power density, high rate capability, and long life [1]. Based upon their distinct charge mechanisms, two types of ECs

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can be distinguished, electrical double-layer capacitors (EDLCs) and pseudocapacitors. EDLCs rely on the separation of (positive and negative) charges in double layer at the interface between the surface of the electrode and the electrolytic layer of the electrolyte solution to store electrostatic energy [2]. Given their high surface areas, upon contact with suitable electrolyte, carbon materials such as activated carbon, carbon nanotubes, carbon aerogels, and graphene oxide can provide efficient charge separation according to this principle and therefore, are classified as EDLCs electrode materials [3,4].

Graphene oxide (GO), in particular, has become an attractive component within batteries and ECs, due to its 2-dimensional, atom-thick planar structure and its excellent mechanical and electrical properties [5]. To obtain low cost graphene in large quantities, chemical exfoliation route is normally utilized. Relative to the oxidized graphene oxide, the reduced graphene oxide (rGO) has superior electrical conductivity [6]. Moreover, the oxygen-containing groups on the surface of the rGO sheets have been reported to provide pseudocapacitive charge storage (*via* Faradaic reaction mechanism) in addition to its main double layer storage [7–11]. Most of the studies that confirm the pseudocapacitance contribution from such groups nonetheless have mostly been performed using (H-rich) H_2SO_4 electrolyte solution [9–11]. CO-type oxygen containing groups such as phenol, ethers, and carbonyls are perhaps the most attractive oxygen containing groups since they offer enhanced electrolyte wettability besides the pseudocapacitive contribution. Such property can provide better electrolyte ions accessibility to the rGO channels and surfaces [10]. Despite the observation that rGO also shows pseudocapacitance effect in KOH electrolyte solution, its detailed electrochemical kinetics and redox reactions in such solution have so far received less attention [7–9]. Conceptually, higher amount of CO-type oxygen containing groups within rGO is envisioned to give higher pseudocapacitance contribution and thus, higher overall capacitance. Still, the overall performance of rGO also depends upon the re-stacking degree of graphene sheets, electrical conductivity, and the surface functional groups, analogous to the other porous carbons.

The main challenge pertaining to CO-type oxygen containing groups is the simultaneous attainment of high content and homogeneous distribution of such groups within the rGO sheets. Increasing the amount of surface oxygen groups can be simply attained *via* chemical treatment route such as chemical activation using potassium hydroxide (KOH) [12] or carbon dioxide (CO_2) [13], hydroquinone modification [11], and acid oxidation [8,14]. Obtaining homogeneous distribution of such surface oxygen groups is perhaps the more difficult task. Subsequent chemical or thermal reduction of the oxidized graphene oxide (after chemical treatment) can be performed to substantially eliminate the oxygen containing functional groups and restore the π -conjugated structure which allows some CO-type oxygen containing groups to be left behind. Thermal reduction serves as a more attractive route compared to chemical reduction, to obtain fine control over the content of CO-type oxygen containing groups, particularly given the possibility to adjust the temperature [7]. Another concern lies in the Van der Waals and hydrophobic forces interactions between the rGO sheets that may manifest into their tendency to form stacks [1,5]. This stacking issue nevertheless can be solved by applying a spacer in the form of carbon materials [15], metal oxide [16], and conducting polymers [17] between rGO sheets to maximize the specific surface area and concomitantly obtain three-dimensional (3D) architectures [18]. Accordingly, thermal reduction and spacer application can be combined to obtain rGO aerogels in its dry form.

In the present work, oxygen-enriched 3D porous carbon aerogels containing rGO sheets with large amount of channels were successfully synthesized *via* nanocellulose-assisted low

temperature thermal reduction route as schematized in Fig. 1. The cotton-derived nanocellulose has an important role in the gelation of the dilute GO solution, a pre-requisite to obtain GO aerogels. The decomposition of the nanocellulose, obtained during the low temperature thermal treatment, strongly affected the re-stacking degree of rGO sheets as well as the surface functional groups of the resultant porous carbon. By adjusting the temperature, the content (or amount) of CO-type oxygen containing groups can be controlled. The structural integrity of the rGO films, in turn, enabled the resultant films from the compressed aerogels to be used directly as an electrode component for ECs without the presence of any binder or conductive additive. The electrochemical kinetics of the rGO film electrode was then evaluated, the results of which highlight the dominant contribution of the EDLC mechanism. Notably, the synthesized rGO electrode had high content of CO-type oxygen containing groups that led to high pseudocapacitance, low electrical conductivity as well as ionic diffusion process. The last feature particularly became visible upon inspecting the voltammogram at low scan rate. This work provides a better understanding of the correlation between the electrochemical performance and graphene structure and physical properties, and the other carbon materials grafting with these stable CO-type oxygen containing functional groups also hold a promise for future design of low-cost electrodes for high energy supercapacitors. The ionic and electronic transport mechanisms of the rGO capacitor electrode within the KOH electrolyte is also displayed in Fig. 1.

2. Experimental

2.1. Synthesis

GO was prepared using the previously described method [19]. The final GO dispersion has a concentration of 5.7 mg mL^{-1} . About 3 g of cotton-derived celluloses (99%) with the size in micrometers was dispersed into 500 mL of deionized water by ultrasonication for 30 min and further milled by a grinder for 20 times at 1800 rpm to obtain a stable suspension containing tailored celluloses. Moreover, the concentration of the cellulose (0.3 g within 50 mL of aqueous suspension, approximately 6 mg mL^{-1}) was further diluted to 5.6 mg mL^{-1} by adding a little bit extra deionized water. Subsequently, this 5.6 mg mL^{-1} cellulose suspension was subjected to ultrasonic cell disruptor for 20 min to get a clear, transparent nanocellulose aqueous solution. In a typical procedure, 2 mL of the aqueous dispersion of GO (5.7 mg mL^{-1}) was mixed thoroughly with 1 mL of the deionized water and 1 mL of the nanocellulose solution (5.6 mg mL^{-1}) within a plastic measuring cylinder. After subjected to freeze-drying, GO-nanocellulose aerogels were obtained. These aerogels were then annealed within reducing atmosphere, i.e., 5 vol % H_2 -containing Ar atmosphere for 5 h at several different temperatures, i.e., 300, 350, 400, and 450°C ; the products of which are denoted as rGO300, rGO350, rGO400, and rGO450, respectively.

2.2. Characterization

The crystal structure of the samples was characterized by powder X ray diffraction (XRD) using a Bruker D8 Advance diffractometer with filtered Cu-K α radiation. The diffraction patterns were collected at room temperature by step scanning in the $10^\circ \leq 2\theta \leq 90^\circ$ range. The morphologies and microstructures of the samples were obtained using field emission scanning electron microscopy (FE-SEM, Hitachi S-4800) and transmission electron microscopy (TEM, JEOL JEM-200CX). Raman spectra were recorded using a Horiba HR800 with an argon ion laser operating at 514 nm for excitation. X-ray photoelectron spectroscopy (XPS)

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