



Graphene incorporated, N doped activated carbon as catalytic electrode in redox active electrolyte mediated supercapacitor



Zhiyong Gao^a, Xiao Liu^a, Jiuli Chang^{a,**}, Dapeng Wu^a, Fang Xu^a, Lingcui Zhang^a, Weimin Du^c, Kai Jiang^{b,*}

^a School of Chemistry and Chemical Engineering, Henan Normal University, Henan, Xinxiang, 453007, PR China

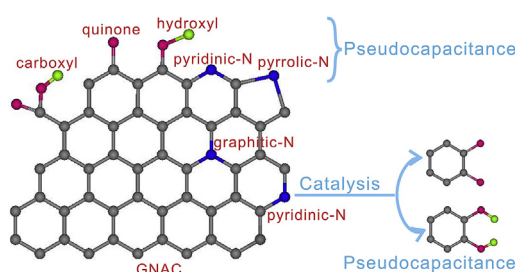
^b School of Environment, Henan Normal University, Henan, Xinxiang, 453007, PR China

^c School of Chemistry and Chemical Engineering, Anyang Normal University, Henan, Anyang, 455002, PR China

HIGHLIGHTS

- Graphene incorporated, N doped activated carbon was prepared by activation of G-PPy.
- Wettable surface area, efficient electrons and ions mobility are ensured in GNAC.
- Substantial pseudocapacitance from pyrocatechol containing electrolyte are offered.
- Pyridinic N is responsible for the catalytic redox reaction of pyrocatechol mediator.

GRAPHICAL ABSTRACT



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ABSTRACT

Graphene incorporated, N doped activated carbons (GNACs) are synthesized by alkali activation of graphene-polypyrrole composite (G-PPy) at different temperatures for application as electrode materials of supercapacitors. Under optimal activation temperature of 700 °C, the resultant samples, labeled as GNAC₇₀₀, owns hierarchically porous texture with high specific surface area and efficient ions diffusion channels, N, O functionalized surface with apparent pseudocapacitance contribution and high wettability, thus can deliver a moderate capacitance, a high rate capability and a good cycleability when used as supercapacitor electrode. Additionally, the GNAC₇₀₀ electrode demonstrates high catalytic activity for the redox reaction of pyrocatechol/o-quinone pair in H₂SO₄ electrolyte, thus enables a high pseudocapacitance from electrolyte. Under optimal pyrocatechol concentration in H₂SO₄ electrolyte, the electrode capacitance of GNAC₇₀₀ increases by over 4 folds to 512 F g⁻¹ at 1 A g⁻¹, an excellent cycleability is also achieved simultaneously. Pyridinic-N is deemed to be responsible for the high catalytic activity. This work provides a promising strategy to ameliorate the capacitive performances of supercapacitors *via* the synergistic interaction between redox-active electrolyte and catalytic electrodes.

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1. Introduction

Porous carbons are practical and durable materials in surface and conductivity dependent fields such as electrochemical devices [1], sensors [2], adsorbents [3], etc for the high conductivities, large

* Corresponding author.

** Corresponding author.

E-mail addresses: jiulichang@163.com (J. Chang), kjiang512@163.com (K. Jiang).

surface areas as well as robust chemical inertness. The versatility and potential of porous carbons can be further expanded by heteroatoms doping [4], surface modification [5] as well as guest materials compositing [6–9]. Of these approaches, the heteroatoms doping is especially intriguing, for the heteroatoms can not only modulate the surface polarity and electronic property of carbon motif, but increase the reactivity, thus dramatically enhance the performances in catalysis [10], adsorption [11] sensors [12] and electrochemical energy storage [13]. N and O are the most widely employed dopants for carbon motif, for the high electronegativities of N ($\chi = 3.04$) [14] and O ($\chi = 3.44$) [15] over C ($\chi = 2.55$) [14] enable polar surface with high hydrophilicity. Besides, the doped N into aromatic carbon framework induces the electrons donor nature and lowers the work function of carbon framework by introducing a donor level beneath the conduction band, thus enhances both conductivity and catalytic activity to some extent [16]. Concretely, the lone pair electrons of pyridinic- N delocalized from the aromatic C-N rings display Lewis alkali feature, which is acknowledged to be the main origin for high catalytic activity of C-N framework [17]. Moreover, some N, O forms, including pyridinic- and pyrrolic- N, as well as phenolic- and quinone typed O [18,19], can experience interface faradic reactions, which are beneficial for energy storage capacity. Hence N doped activated carbons (ACs) are feasible electrode materials in electrochemical energy storage systems, such as oxygen reduction reaction (ORR) [20], iodine reduction reaction (IRR) [16,17], lithium ions batteries [21] as well as supercapacitors [22] for the good electrode/electrolyte compatibility, high electronic conductivity, redox or catalytic activity as well as the intrinsic corrosion resistance.

Supercapacitor is a sustainable electrochemical energy storage system featured by high power density, short charging duration, long cycling lifetime and high safety, which can be potentially applied in uninterrupted power system, auxiliary motive power and other pulse electric facilities. In principle, supercapacitor mainly operates *via* electrostatic sorption of electrolyte ions onto porous electrodes, namely electric double-layer (EDL-) capacitance, as well as the surface reversible redox reactions of active electrodes or the redox intercalation of metal ions into layer electrode, *viz* pseudocapacitance. The structural and surface feature of electrode material directly determines the capacitance and therefore energy density of supercapacitor. ACs are common EDL-electrode materials for the large surface areas, good conductivities and low costs. As mentioned above, N doping and O functionalization can not only raise the surface wettability, but increase the redox reactivity of carbon surface [23], therefore provide dramatic pseudocapacitance. Different N-rich polymers such as polyaniline [24,25], polypyrrole [26,27], methylated melamine resin [28,29] are popular precursors for preparation of N doped ACs. Graphene is a monolayer sp^2 hybrid carbon material with extraordinary conductivity and huge theoretical surface area, thus can serve as good mat for coating of guest materials to afford porous composites with enhanced electrons/ions mobilities, so the incorporation of graphene into N, O containing ACs is a promising way to enhanced capacitive performances of supercapacitors from electrode material aspect.

The introduction of redox-active mediators to electrolyte is another alternative approach to improve the overall capacitance through the faradic capacitance contribution of electrolyte. A variety of redox-active mediators including iodide [30,31], hydroquinone [32–34], *p*-phenylene diamine [35], mercaptopyridine [36], potassium ferricyanide [37,38], methylene blue [33,39] as well as Cu^{2+} [40,41], have proven to be feasible mediators that can substantially enhance the capacitive performances. In essence, similar to the electrochemical sensing of redox active species, the reversible conversion between different forms of redox mediators relies to some extent on the catalytic activity of electrode. The

higher catalytic activity of electrode will stimulate the efficient redox reaction of mediators, hence prominent faradic capacitance from electrolyte can be ensured, which is highly desired in supercapacitor design. However, in the previous works [30–41], the catalytic effect of electrode on the capacitive performance of redox electrolyte mediated supercapacitor has not been discussed yet, so the investigation on catalytic activity of electrode on capacitive performances of supercapacitor is meaningful.

Herein, GNACs were prepared as electrode materials of supercapacitors. The N, O functionalities offered apparent pseudocapacitance contribution to the carbonaceous materials. Additionally, the GNACs demonstrated high catalytic activity for the redox reactions of pyrocatechol in acid electrolyte, which evoked dramatic pseudocapacitance from electrolyte, so the electrode capacitance elevated by over 4 folds relative to that based on mere acidic electrolyte. The present work provides a new concept to improve the capacitance of supercapacitor aided by catalytic electrode.

2. Experimental

2.1. Synthesis of GNACs

All reagents used were of analytical grade, graphite oxide (GO) was prepared by modified Hummer's method [42]. In the synthesis of graphene-polypyrrole composite (G-PPy), 40 mg of GO was ultrasonically dispersed in 40 mL deionized water and centrifuged to afforded suspension with concentration of *ca.* 1 mg mL⁻¹, 2.4 g CTAB was dispersed in the GO suspension under vigorous stirring and ice bath for 12 h. Subsequently, 4.0 g persulfate ammonium, used as oxidant, was dissolved in the mixture under continuous stirring for another 1 h. Thereafter, 4 mL pyrrole monomer was added to undergo oxidative polymerization for 24 h. The yielded black precipitate was added to 10 mL fresh NaBH₄ (1 M) at 80 °C for reducing treatment for 1 h, then washed copiously with deionized water and dried naturally to afford G-PPy.

GNACs were prepared by alkali activation of G-PPy precursor at different temperatures. In brief, G-PPy was mixed with KOH at mass ratio of 1:3, the mixture was transferred to a nickel crucible placed in N₂ filled horizontal tube furnace and subjected to pyrolysis at target temperature (600, 700 or 800 °C) with ramping rate of 5 °C min⁻¹ and maintained for 1 h. After being cooled naturally, the black product was washed with 1 M HCl to neutral pH followed by rinsing with deionized water, the GNACs were denoted as GNAC₆₀₀, GNAC₇₀₀ and GNAC₈₀₀, respectively according to activation temperature.

2.2. Characterizations

The morphologies, microstructures, phases and chemical compositions of the samples were characterized by scanning electron microscopy (SEM, JEOL JSM-6390), high resolution transmission electronic microscopy (HRTEM, JEOL JEM-2100 at accelerating voltage of 200 kV), X-ray powder diffraction (XRD, Bruker D8 diffractometer with Cu K α radiation), Raman spectroscopy (JOBIN YVON HR800 confocal Raman spectrometer with 632.8 nm laser excitation) and X-ray photoelectron spectroscopy (XPS, Kratos Amicus X-ray photoelectron spectrometer with Mg K α radiation under 2×10^{-6} Pa). Hypothermal N₂ sorptions were measured on a Micromeritics ASAP 2020 surface analyzer at 77 K. The specific surface areas were calculated by multiple points Brunauer-Emmett-Teller (BET) method, and the pore size distributions were estimated according to nonlocal density function theory (NLDFT) model on the basis of slit-like pore geometry. Surface wettabilities of GNACs were reflected by water contact angles of the work electrodes, 6 μ L of water was slowly touched onto electrode surface,

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