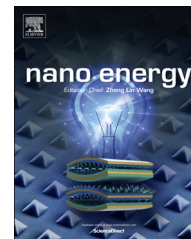Available online at www.sciencedirect.com

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Kinetically enhanced pseudocapacitance of conducting polymer doped with reduced graphene oxide through a miscible electron transfer interface

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Abstract
Herein, we report on electrochemical doping of a conducting polymer (CP) with anionically modified graphene nanosheets. The architecture built from reduced graphene oxide (rGO) skeleton skinned by polypyrrole (pPy) enhanced supercapacitor performances especially at high discharge rates superior to those of the same CP with a conventional dopant: e.g., from 141 to 280 F g^{-1} at 1000C equivalent to ∼50 A g^{-1}. At relatively low rates, the graphene-doped pPy reached the theoretical capacitance of pPy, indicating efficient use of whole electroactive mass.
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Introduction

Graphene has attracted a plethora of attention from a variety of areas of science and technology with its remarkable intrinsic properties including electronic [1-4], thermal [5] and mechanical characteristics [6,7]. However, there would be a limitation in direct incarnation of its bulk properties unless a continuous monolithic phase were used [4,8-11]. Particulated forms of graphene or its equivalents have been widely used with the intention to use its superior electronic conductivity in energy applications [12-16]. Even if performances of energy devices

have been successfully improved by the help of graphene, the fast electron movement would be limited in an isolated dimension of graphene. To fully materialize the properties of graphene in electrochemical devices, electron transfer steps (i) between graphene nanosheets as well as (ii) between the graphene phase and electroactive materials should not be a rate determining step. The main point of this work focuses on how to control or improve the second impeding step of electron transfer.

Electrochemical capacitors have been considered as an energy storage device to deliver electricity especially for high power demand applications [17]. Despite their low energy density, the electrochemical capacitors offer a complementary performance to rechargeable batteries due to their outstanding performances at high discharge rates. The distinguished difference in application sector between the two devices is based on its working principle: non-faradaic processes for electrochemical capacitors (e.g. electric double layer capacitors or EDLCs) and faradaic reactions for rechargeable batteries (e.g. lithium ion batteries or LIBs). Pseudocapacitors (capacitors based on pseudocapacitance) are situated between EDLCs and LIBs, delivering higher energy density than that of EDLCs and working more feasibly at higher power density than LIBs doing. CPs have been one of the favorite choices for pseudocapacitors, based on reduction and oxidation (redox) of charge complex sites or polarons on their backbones. While capacitance of CPs (practically, 200-300 F g^{-1}) is lower than that of metal oxides (400-500 F g^{-1}) that is another option for pseudocapacitance [18], it is still superior to that of EDLCs ($\sim$100 F g^{-1}) [19].

Various efforts have been devoted to building composites consisting of conducting polymers and graphene or its family (graphene oxide (GO) and rGO) to enhance capacitance (Table S1). The composites were made by mixing together graphenes and CPs physically [20] as well as by introducing graphenes into films or powders of CPs during polymerization [21-25]. In most of works of the latter case, small-molecular dopants such as Cl$^-$, [20,21,23] dodecylbenzene surfonic acid, [22] p-tolenesulfonate, [25] ClO$_4^-$ [21] and NO$_3^-$ [26] were used during polymerization of CPs in presence of GO or rGO. GO has anionic functional groups so that it has a potential to be used as a dopant electrostatically incorporated into CPs [21,24,26]. However, rGO would be physically and statistically entrapped in CPs when monomers are polymerized because rGO contains little amount of anionic functional groups [23,25]. Anionically modified GO obtained by sulfonation were used in presence of an anionic dopant [22]. The sulfonated GO would be more effective as a dopant due to its higher anionic charge concentration. In the work, however, dodecylbenzene sulfonate was used to support doping process during polymerization. As the case in which GO was used as a single dopant in absence of other molecular anions, GO-doped pPy film was electrochemically synthesized [24]. However, electrochemical performances would be kinetically limited due to poor conductivity of GO.

In this work, therefore, we used rGO that is more conductive version of GO for making rGO-doped pPy. Problems of rGO are its poor solubility in water and little anionic characteristics so that rGO was anionically modified with polystyrenesulfonate (pSS) before being used in polymerization. The bridged contact between pPy and rGO through pSS in pPy doped with rGO-pSS (pPy[rGO-pSS]) provided facilitated charge transfer, delivering kinetically robust capacitance.

Materials and methods

Synthesis of graphene oxide (GO)

Graphene oxide (GO) is synthesized from graphite powder (Aldrich, $<20\,\mu$m) by modified Hummers method [27]. In a pretreatment step that ensures complete oxidation, graphite powders (1 g), K$_2$S$_2$O$_8$ (0.5 g) and P$_2$O$_5$ (0.5 g) were added to 3 mL of conc. H$_2$SO$_4$ with stirring until the reactants are completely dissolved. The mixture is kept at 80 °C for 4.5 h using a hotplate, after which the heating is stopped and the mixture diluted with 1.0 L of deionized water. The mixture is filtered and washed to remove all traces of acid. The solid is transferred to a drying dish and left overnight under ambient conditions. For the oxidation step of the synthesis, the pretreated graphite is added to the 26 mL of H$_2$SO$_4$ and stirred. To this suspension, 3 g of KMnO$_4$ was added slowly in an ice bath to ensure the temperature remained below 10 °C. Then, this mixture reacts at 35 °C for 2 h after which distilled water (46 mL) is added. Since the addition of the water causes the temperature of the mixture to rise rapidly, it is carried out in an ice-bath so that the temperature does not climb above 10 °C. This mixture is stirred for 2 h at 35 °C, after which the heating is stopped and the mixture diluted with 140 mL of water and 2.5 mL of 30% H$_2$O$_2$ is added to the mixture resulting in a brilliant yellow color along with bubbling. The mixture is then allowed to settle for at least a day after which the clear supernatant is decanted. The remaining mixture is filtered and washed with a 1.0 L of 10% HCl solution. The resulting solid is dried in air and diluted in distilled water that is put through dialysis for 2 weeks to remove any remaining metal. The residual products was centrifuged and washed several times with distilled water to neutralization and removal of residual species. Finally, the dark brown GO powders were obtained through drying at 50 °C in vacuum oven for a day. The GO powder was dissolved in a known volume of water (conc. 0.50 mg mL^{-1}) and subjected to ultrasonication for 40 min to give a stable suspension and centrifuged at 4000 rpm for 10 min to recovered supernatant (typically top 90%).

Synthesis of pSS-functionalized reduced graphene oxide (rGO-pSS)

The resulting GO suspension (20.0 mL, 0.50 mg mL^{-1}) was mixed with 0.911 mL of polystyrene sulfonate (pSS, Na salt, Aldrich) solution (1:20 w/w ratio versus GO, 18 wt% dispersion in water). To this solution, 60.0 μL of hydrazine solution (35 wt% in water, Aldrich) was slowly added and the reaction mixture was heated to 100 °C for 1.5 h to afford a stable suspension of reduced graphene oxide (rGO) nanosheets functionalized with pSS (rGO-pSS). After the reaction, the suspension was filtered with poly(ether sulfone) (pES) membrane filter (pore size of 0.22 μm, Corning) and washed extensively with Millipore water to remove any residual