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Rational functionalization of reduced graphene oxide with imidazolium-based ionic liquid for supercapacitor application

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ABSTRACT

Graphene-based materials are very promising for the development of energy storage devices like supercapacitor. Herein, we describe the rational covalent functionalization of reduced graphene oxide (rGO) with hydrophilic imidazolium-based ionic liquid (Im-IL) and the development of aqueous and all-solid supercapacitor devices. The rational functionalization of rGO significantly alters the wettability and increases the interlayer distance of the honeycomb carbon network. It effectively prevents the restacking of individual honeycomb carbon sheets. Im-IL functionalization on rGO surface significantly decreases the water contact angle (94° – 37°). Aqueous symmetric electrical double layer supercapacitor based on functionalized rGO sheet (rGO-Im-IL) has been developed and it shows excellent performance with a wide potential window of 0–2 V. The device could provide an energy density of 36.67 Wh kg^{-1} at a power density of 2 kW kg^{-1} . It has very good cycling stability and it retains 97% of its initial specific capacitance even after 5000 continuous charge–discharge cycles. The enhanced wettability, increased interlayer distance, large surface area and high electronic conductivity contributes to the excellent performance of the supercapacitor. The potential application of rGO-Im-IL is demonstrated by fabricating an all-solid-state supercapacitor device with gel electrolyte.

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Introduction

The development of next generation electrical double layer (EDL) capacitor, also called supercapacitor, for automobile applications and portable electronic devices has received considerable attention in the recent years as they can deliver high power density and have fast charge–discharge capability and long life cycle. The EDL capacitor stores charge at the electrode-solution interface via adsorption of ionic charge on

the electrode surface. The large surface area porous materials having high conductivity are ideal for the development of such EDL capacitors. Traditionally, carbon-based materials are preferred due to their high conductivity and chemical inertness. Conventional carbon-based materials deliver poor energy density though they are chemically very stable [1,2]. Several attempts have been made in the past to improve the energy density of EDL-based capacitors [1,3,4]. The as-synthesized and functionalized carbon nanostructures such as carbon nanotubes (CNT) and graphene are ideal for the

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development of next generation supercapacitors as they can deliver high specific capacitance. Graphene, the one-atom thick 2-dimensional layered material, has very large surface area ($2600 \text{ m}^2 \text{ g}^{-1}$), high electronic conductivity and mechanical strength. It is a promising wonder material for the fabrication of energy storage devices such as supercapacitors and batteries [5]. In the recent years, the as-synthesized graphene or reduced graphene oxide (rGO) and their hybrid/composite materials are being used for supercapacitor and other energy storage device applications [5–12]. The hybrid/composite materials derived from rGO and pseudocapacitive polymers, metal oxide, etc. are known to show excellent supercapacitive performance [8–12]. The restacking of individual graphene/rGO sheets due to non-covalent interactions is a serious concern in the development of EDL capacitors based on as-synthesized graphene or rGO. The pristine graphene and chemically synthesized rGO samples are rather hydrophobic and have very poor wettability. The hydrophobic interaction is one of the main driving forces behind restacking of graphene/rGO layers. The restacking of neighbouring layers has negative impact on the capacitive performance owing to the decreased accessible specific surface area for the electrolyte and increased diffusion resistant to the ions. Efforts have been taken in the past to prevent the re-stacking of neighbouring sheets and to improve the capacitive performance of EDL based capacitors [13–16]. The rational functionalization of graphene/rGO with suitable hydrophilic functional moiety would prevent the restacking and increase the wettability of the surface. Such functionalization can significantly enhance the capacitive performance. Although the non-covalent functionalization of rGO with polymers, surfactants, ionic liquids, etc. for supercapacitor applications have been documented in the literature [17–20], the studies on the supercapacitive performance of covalently functionalized rGO is very limited [21,22]. The covalent functionalization of rGO with hydrophilic functionalities without compromising the integrity of the honeycomb carbon network is a promising approach to prevent restacking of the rGO layers and to increase the surface wettability. However, the extensive covalent attachment of hydrophilic functional moiety on the basal plane is known to convert the conducting rGO into an insulator, though it significantly enhances the wettability of the surface [23]. The controlled and rational functionalization is critically required to increase the wettability of the rGO surface and to prevent restacking without compromising the electronic property.

The room temperature ionic liquids (IL) are very attractive for supercapacitor applications due to their unique properties. The high thermal and electrochemical stability, acceptable ionic conductivity, and low toxicity of IL are ideal for supercapacitor applications. They have been widely used as electrolytes for electrochemical applications as they exhibit wide potential window [20]. Moreover, IL and poly ILs have been used in combination with carbon-based materials such as CNT, graphene, etc. as an electrode material in the development of supercapacitor devices [20,24–27]. Ruoff's group demonstrated the interesting properties of IL in the development of supercapacitor; the poly(IL) modified graphene-based supercapacitor with IL electrolyte could deliver energy density of 6.5 Wh kg^{-1} with a power density of 2.4 kW kg^{-1} [20]. Very

recently, Wu's group reported the use of conjugated polyfluorene imidazolium IL intercalated rGO in the development of aqueous and non-aqueous supercapacitor devices [28]. Although the non-covalent attachment of IL onto rGO is known for supercapacitor applications, to the best of our knowledge, the IL covalently attached to rGO has not been explored for EDL supercapacitor. We are interested in the synthesis of new electrode materials for the development of symmetric and asymmetric supercapacitor devices of high energy density [12]. In continuation of our earlier efforts, herein we describe the covalent functionalization of rGO sheets with hydrophilic Im-IL and the fabrication of symmetric aqueous and all-solid supercapacitor devices capable of delivering high energy density and excellent recyclability and rate capability. The covalent functionalization of rGO with Im-IL significantly enhances the wettability and improves the supercapacitive performance. Interestingly, significant increase in the potential window was observed.

Experimental section

Materials and methods

Graphite powder and polyvinylidene fluoride (PVF) were obtained from Sigma–Aldrich. All the other chemicals used in this investigation were of analytical grade and obtained from Merck, India. All the solutions were prepared with Millipore water (Milli-Q system).

Covalent functionalization of rGO with Im-IL

The synthesis of amine-terminated ionic liquid (IL-NH₂) and the covalent functionalization of rGO with Im-IL was achieved using the modified literature procedure [29]. In a typical synthesis of IL-NH₃⁺Br[−], 3-bromopropylamine hydrobromide and 1-methylimidazole were added to ethanol to form a colourless solution. The solution was subjected to reflux under inert condition for 24 h. The product was collected and purified by recrystallization. Then IL-NH₃⁺Br[−] was treated with methanol and sodium methoxide to yield free amine group (IL-NH₂). A solution of purified IL-NH₂ (100 mg) in N-methyl-2-pyrrolidone (NMP) (5 mL) was added drop-wise to NMP containing GO (1 mg mL^{−1}) in an inert atmosphere under constant stirring. The reaction mixture was then refluxed at 170 °C for 3 h. Then the reaction vessel was cooled at room temperature and the unreacted IL-NH₂ was removed by centrifuging the reaction mixture at 7000 rpm. The supernatant was discarded and the residue was washed repeatedly with copious amount of NMP, water and then with ethanol. The solid product was dried in vacuum for 24 h to obtain rGO-Im-IL. The unfunctionalized rGO was obtained at an identical procedure without IL-NH₂.

Instrumentation

TEM measurements were carried out with JEOL JEM 2010 electron microscope at an operating voltage of 200 kV. XRD profiles were acquired with BRUKER D8 advance unit using Cu-K α ($\lambda = 1.54 \text{ \AA}$) radiation. FTIR spectroscopic measurements were performed with Perkin Elmer spectrophotometer

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