nano energy

RAPID COMMUNICATION

Elucidating graphene-ionic liquid interfacial region: A combined experimental and computational study

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Abstract
Graphene and ionic liquids are promising candidates for electrode materials and electrolytes, respectively, for modern energy storage devices such as supercapacitors. Understanding the interactions at the interfacial region between these materials is crucial for optimizing the overall performance and efficiency of supercapacitors. The interfacial region between graphene and an imidazolium-based ionic liquid is analyzed in a combined experimental and computational study. This dual approach reveals that the imidazolium-based cations mostly orient themselves parallel to the graphene surface due to π-π stacking interaction and form a primary interfacial layer, which is subsequently capped by a layer of anions from the ionic liquid. However, it also becomes apparent that the molecular interplay at the interfacial region is highly influenced by functional group defects on the graphene surface, in particular by hydroxyl groups.
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Introduction

The interactions between electrode surfaces and an electrolyte are the crucial phenomena behind most modern energy storage devices, such as lithium ion batteries and ultracapacitors. In recent years, graphene (G) has been recognized as a desirable electrode material owing to its large surface area and high electronic conductivity [1,2]. Similarly, room temperature ionic liquids (IL) are outstanding candidates for electrolytes due to their higher electrochemical and thermal stability combined with low toxicity [3]. Consequently, G-IL based composite materials are reported as base materials for a variety of applications including ultracapacitors, solar cells and chemical sensors [4-8]. This spurred considerable interest in understanding the G-IL interfacial region. However, the unique properties of ILs, such as highly

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concentrated ionic charges and the asymmetric nature of the ions, combined with lesser-known properties of graphene surfaces result in a complex interfacial region. Recently, some attempts have been made to understand the interaction between G and ILs using computational modelling [9-11]. Despite these efforts, the molecular level structure of G-IL interfacial regions is still unclear due to limitations in computational methods and lack of experimental studies of these materials. Most of the experimental work so far is aimed at demonstrating the respective application, not at studying the interfacial region of the composite material. In addition, theoretical studies reported about G-IL interfacial regions were carried out assuming a perfect defect-free graphene surface, which is far from practical reality. For example, cost effective chemical synthesis methods often lead to the formation of oxygen-containing functional defect groups such as epoxy (C-O-C), carboxyl (O=C-OH) and hydroxyl groups (C-OH) on graphene surfaces [12-14]. Hence it is necessary to study realistic graphene surfaces that include these functional groups, using theoretical and experimental analysis to explore the graphene-ionic liquid interfacial region.

To understand the molecular interaction between the G and IL, a monolayer of 1-butyl-3-methyl-imidazolium (BMIM$^+$) trifluoromethanesulfonate (TfO$^-$) on graphene surfaces was synthesized (hereafter called as G-IL). This IL monolayer formation enables us to study the molecular level interaction at the interfacial region between graphene and ionic liquid. Subsequently, Nuclear Magnetic Resonance (NMR), X-ray Photoelectron (XPS) and Infrared (FTIR) spectroscopy analyses on this G-IL material were carried out. These analytical results are then correlated with molecular models, which were derived using Density Functional Theory with empirical dispersion correction (DFT-D3) based methods [15]. This combined approach yields a clear view about the G-IL interactions at the interfacial region.

Experimental methods

Materials synthesis

To prepare the G-IL material, 1-butyl-3-methyl-imidazolium (BMIM$^+$) trifluoromethanesulfonate (TfO$^-$) (99.9% purity; Sigma-Aldrich) and high purity graphene (the oxygen impurity is about 1% *i.e.* C/O ratio of 100; Vorbeck Materials) were used without any further purification. For the synthesis of the G-IL composite material, 2.23 ml of ionic liquid, *i.e.* [BMIM$^+$] (TfO$^-$), is added into 97.77 ml deionized water and stirred for 4 h at room temperature, then 100 mg of graphene powder (C/O=100) is added to the solution and stirred for 15 min. The resulting molar ratio of graphene to IL is 1:1.2. The solution is then sonicated for 1 h in 1 s pulse increments using a horn sonicator with a 13 mm tip (Branson Sonifier 450D, 450 W, 55% amplitude). After sonication, the black solution is transferred into test tubes and centrifuged for 10 min at 10,000 rpm. The resulting clear, colorless supernatant is carefully pipetted off, and the black precipitate is dried at 60 °C. Any IL molecule not bound or coordinated to a graphene surface will have been removed with the supernatant because of the very high solubility of the IL in water. Overall, the low molar ratio of *G* to IL

(1:1.2) used in this synthesis and the extreme solubility of IL in water ensures the formation of an IL monolayer on the graphene surface. The formation a monolayer coverage of the few-layer graphene surface with IL is analytically confirmed by the absence of sharp peaks in ^{1}H and ^{19}F NMR (which would represents a liquid component with high rotational freedom, such as residual neat IL; see supplemental information). As control experiments, the same analytical characterization (data not shown) was carried out on as-received graphene and graphene that had been sonicated in pure deionized water for 1 h and then worked up in the same way as the G-IL hybrid material. The absence of any signals attributable to water in the ^{1}H NMR spectra of the control samples as well as the spectra of the G-IL composite material confirm that the samples were completely dried, and that the presence of water during the synthesis did not affect the surface of the few-layer graphene or the interaction between graphene and the ionic liquid. Furthermore, we can conclude that the water-based synthesis method will not pose a problem when the material will be tested in the water-free environment of a supercapacitor.

Spectroscopic measurements

The ^{1}H and ^{19}F MAS NMR measurements were performed on a Varian 500 spectrometer (B_0=11.7 T and ^{1}H and ^{19}F Larmor frequency of 500.1 and 470.5 MHz, respectively) with MAS at 12 kHz using 4 mm rotors. The ^{1}H and ^{19}F chemical shifts are referenced with secondary reference of adamantine (δ=1.63 ppm) and aqueous solution sodium trifluoroacetate (δ=−76.5 ppm), respectively. The X-ray Photoelectron Spectroscopy (XPS) measurements were performed with a Phi 5000 Versa Probe. This system consists of a monochromatic focused Al Kα X-ray (1486.7 eV) source and a hemispherical analyzer. The aliphatic carbon (*i.e.* C-C bond) C1s peak position is used as reference at 284.5 eV for charge neutralizer correction in XPS spectra. FTIR spectra of pure Ionic liquid, graphene and G-IL hybrid material were recorded with a Nicolet iS10 (Thermo Scientific). The spectra shown were recorded at a resolution of 1 cm^{-1} or higher employing a diamond Smart ITR accessory.

Computational methods

Density functional theory (DFT) based calculations were carried out using the *Amsterdam Density Functional* (ADF-2010) package. The Becke (exchange)+LYP (correlation) based function with recent dispersion correction (DFT-D3) is employed for both geometry and NMR chemical shift calculations [15-18]. All the calculations were carried out using the TZP (triple *Z*, single polarization function, all electron) basis set with the Slater type functional implemented in the ADF program [19]. The organic polyaromatic compound circumcircumcoronene ($C_{96}H_{24}$), which is a polycyclic arene compound with hydrogen termination, is used as starting geometry for the graphene layer [9]. The fully optimized structure of $C_{96}H_{24}$ yields C-C and C-H bond length of 1.42 Å and 1.08 Å, respectively which are in good agreement with literature reported values. For the G-IL molecular structure, a single ion pair of the fully optimized