Probing the electrical double layer by *operando* X-ray photoelectron spectroscopy through a graphene-carbon nanotube composite window

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**Abstract**

The electrical double layer is known to spontaneously form at the electrode-electrolyte interface, impacting many important chemical and physical processes as well as applications including electrocatalysis, electroorganic synthesis, nanomaterial preparation, energy storage, and even emulsion stabilization. However, it has been challenging to study this fundamental phenomenon at the molecular level because the electrical double layer is deeply “buried” by the bulk electrolyte solution. Here, we report a quantitative probing of the electrical double layer of ionic liquids from the solid side of a photoelectron-transparent graphene-carbon nanotube hybrid membrane electrode using X-ray photoelectron spectroscopy. The membrane window is ultrathin (1-1.5 nm), large (~1 cm²), and robust, enabling a tight seal of the electrolyte and quantitative measurement with excellent photoelectron signals. By *operando* monitoring the population changes of cations and anions in response to the applied electrical potentials, we experimentally resolve the chemical structure and dynamics of the electrical double layer, which corroborate results from molecular dynamics simulations.

**KEYWORDS**

carbon nanotube, electrical double layer, graphene, ionic liquid, *Operando* spectroscopy, X-ray photoelectron spectroscopy

1 | INTRODUCTION

The electrical double layer (EDL) spontaneously forms at the solid-liquid interface between a charged electrode and electrolyte.¹-³ The theory of EDL was first conceptualized by Helmholtz⁴ in 1879 and later expanded into the Guoy-Chapman-Stern model.⁵-⁷ Briefly, the ions form a compact layer (i.e., the Stern layer) and a diffusive layer of the opposite charges (i.e., the diffuse layer) at the electrode-electrolyte interface. However, this theory is formulated to explain the observations in diluted solution of electrolytes, such as inorganic ionic salts in water. For highly...
concentrated electrolytes, such as ionic liquids, which are an electrolyte family that find broad applications in electrochemistry,\textsuperscript{8,9} it is unknown whether the Guoy-Chapman-Stern model still provides the correct picture. Unlike a dilute aqueous electrolyte solution in which the cations and anions are far apart and may be considered noninteractive at the dilute limit,\textsuperscript{1,3} ionic liquids are composed of cation-anion pairs that are densely packed due to strong Coulombic interactions.\textsuperscript{2} Indeed, Landau-Ginzburg-type continuum theory\textsuperscript{10} and mean-field theory\textsuperscript{2} suggest layer-by-layer arrangements of ions in the EDL of ionic liquids. These theories have been supported by molecular dynamics (MD) simulations,\textsuperscript{11} electrochemical impedance spectroscopy (EIS) studies,\textsuperscript{12} and atomic force measurements.\textsuperscript{13} However, these experiments are largely macroscopic (i.e., EDL capacitance measured by EIS). It remains challenging to experimentally profile the ion distribution of the EDL at the molecular level.

X-ray photoelectron spectroscopy (XPS) is an elemental analysis technique that can be used to quantitatively study atom/ion concentrations, chemical composition, and bonding conditions of various materials by exciting the sample with X-rays and measuring the kinetic energy of the emitted photoelectrons.\textsuperscript{14} Since the inelastic mean free path ($\lambda_{\text{IMFP}}$) of the emitted photoelectrons is very short, XPS provides surface-sensitive detection, with the photoelectron escape depth typically ranging from a few to tens of nanometers.\textsuperscript{14} As a result, XPS should be well-suited for elucidating the EDL structures, whose thickness falls into the same scale (for aqueous solution, typically <30 nm, with the Stern layer being <5 nm; for ionic liquids, ~5 nm),\textsuperscript{1,2} allowing the observation of different ionic species and providing a better understanding of the EDL structure at the molecular level.

In principle, there are two ways to use XPS to investigate the EDL: either applying the X-rays and collecting the resulting signal from the electrolyte (liquid) side of the device (Figure 1A), or doing the same except from the electrode (solid) side (Figure 1B). With the former experimental configuration, the emitted photoelectrons must penetrate through a bulk electrolyte solution to reach the detector, and as a result, a significant amount of the signal with valuable information about the “buried” EDL structure is lost. Sophisticated experimental setups and ultrabright light sources are needed to mitigate the severe inelastic scattering of emitted photoelectrons in bulk electrolytes, and therefore only a limited number of successful cases have been demonstrated (e.g., the “dip-and-pull” method involving a synchrotron light source).\textsuperscript{15,16}

Alternatively, the emergence of two-dimensional materials, such as graphene,\textsuperscript{17,18} has made the latter (solid-side) experimental configuration possible (Figure 1B). Photoelectrons emitted from the EDL can easily penetrate a graphene sheet without much inelastic scattering due to its ultrathin thickness and the low-atomic-number of carbon atoms. Towards this end, photoelectron spectroscopic studies on aqueous electrolyte\textsuperscript{19-21} and solid nanoparticles\textsuperscript{21-23} capped

![FIGURE 1](https://example.com/image1.png)

**FIGURE 1** Schematics of operando X-ray photoelectron spectroscopy (XPS) that directly measures the electrical double layer (EDL) at the solid-liquid interface. Two ways of detecting the solid-liquid interface: from the (A) liquid and (B) solid sides of the electrode. The dimmer purple color of the photoelectron beam in (A) indicates the decay of the photoelectron flux travelling through the bulk liquid. C, Schematic illustration of operando XPS visualization of the EDL behind an atomically thin G + T window (single-walled carbon nanotubes are not shown for image clarity). We apply a negative voltage to the graphene to produce an EDL behind the XPS-transparent electrode.
by graphene or graphene oxide layers have been conducted and provided deeper understanding of fundamental electrochemical oxidation/reduction processes. It is expected operando experiments could further decipher the molecular structures of the EDL formed by ionic liquids at the solid/liquid interface; however, until now, no such experiments have been conducted, presumably because the high viscosity of the ionic liquids makes it difficult for a bare graphene membrane to hold the liquid without leaking.

In this work, we synthesized a hybrid graphene/carbon nanotube (G + T) transparent working electrode that enables us to measure the EDL configuration formed on the solid-liquid interface (Figure 1C). In our design, an ionic liquid electrolyte (1-butyl-1-methylpyrrolidinium bis[(trifluoromethane)sulfonyl] imide [Bpy1,4][TFSI] containing 1 M of lithium TFSI) is sandwiched between a counter electrode and the electrically biased G + T working electrode, which also serves as a photoelectron-transparent “watching window” that allows us to directly “observe” the EDL formed behind it responding to the applied voltage. Our G + T hybrid membrane features multiple advantages compared with other graphene-based thin films:21,24-26: (a) the mechanical strength of the hybrid film is reinforced by long, single-walled carbon nanotubes (SWCNTs) with little sacrifice of the photoelectron transparency; (b) the hybrid membrane is electrochemically stable due to the inertness of both the graphene and SWCNTs; (c) the superior electrical conductivity makes the G + T membrane an excellent working electrode; (d) the hybrid film can easily cover a large area (~1 cm²), well accommodating the analysis spot size of XPS (for high sensitivity XPS on lab-based instruments, the spot sizes are generally ~1 mm in diameter or greater) and allowing for more photoelectron signal detection and therefore higher sensitivity; (e) no assistive polymers are needed during the membrane transfer process, ensuring a clean membrane and therefore preventing contamination signals in subsequent XPS measurements. Due to these advantages, our integrated liquid cell featuring the G + T hybrid membrane as a transparent working electrode enables the sensitive detection of elements with small photoionization cross-sections, such as nitrogen and sulfur. With this liquid cell device, we quantitatively monitored the concentration distribution profile of cations and anions in the resulting EDL and successfully observed the “charge flipping” phenomenon when the G + T working electrode was biased with the reverse electrical potential.

We fabricated the G + T hybrid membrane by spin coating a thin layer of SWCNTs on the surface of a graphene sheet. To guarantee enough mechanical support for the graphene layer without building up the film thickness, a uniform SWCNT network mainly comprised of long SWCNTs24,27-29 is favorable. Furthermore, the solvent dissolving the SWCNTs should be able to wet the graphene, which is hydrophobic, so that the SWCNTs can be homogenously distributed on the graphene surface during spin coating. Towards this end, we chose chlorosulfonic acid to disperse the SWCNTs because it can nondestructively dissolve SWCNTs through protonation as well as wet the graphitic surface.28,30-32 The SWCNT-chlorosulfonic acid solution was spin coated onto a few-layered (2-3 layers) piece of graphene that was grown on copper foil by chemical vapor deposition33 (Figure 2A; see Appendix S1 for details). The resulting G + T hybrid membrane is mechanically robust, as clearly evidenced by the large and uniform free-standing film floating on water after the copper substrate is etched away (Figure 2B). In contrast, graphene without SWCNTs cracks into small pieces due to the strong surface tension of water (Figure S1). Transmission electron microscopy (TEM) imaging (Figure 2C) of the G + T membrane clearly demonstrates that the SWCNTs are uniformly distributed across the graphene surface, which may act as rebar-like supporting structures. Due to the strengthening effect of the SWCNT network, the G + T membrane can be easily fabricated into centimeter-sized pieces (Figures 2B,S1). The electron diffraction also indicates its high crystallinity, which is consistent with the resonant Raman spectroscopy measurement, which shows no obvious D peak (~1350 cm⁻¹) (Figure S2). Compared to graphene without the SWCNT supports, the G + T membrane also features ~4-fold improvement in electrical conductivity, a cleaner surface from the transfer, and only ~3% sacrifice in the optical transmittance (Figures S3-S5). We also determined the thickness of the hybrid film was 1-1.5 nm based on the ~92% optical transmittance (Figure S5).34,35

Apart from the large size, mechanical robustness, high electrical conductivity, clean surface, and ultrathin thickness, the G + T hybrid membrane must also be pinhole free if it is to contain a liquid electrolyte. In order to statistically evaluate the intactness of the film, we transferred the G + T membrane onto a perforated Si₃N₄ microsieve membrane with different hole sizes and then used high-resolution scanning electron microscopy (SEM) to examine the quality of the suspended film. Figure 2D displays a typical SEM image of the suspended G + T film on the Si₃N₄ membrane with circular hole diameters of 1.2 μm. Higher magnification demonstrates the high quality of the suspended graphene film on a 5 μm circular hole supported by long SWCNTs with no observable pinholes (Figure 2E). We further analyzed the intactness of the film by examining a suspended area over 10 000 μm² across hole sizes of 5 μm, 3 μm and 1.2 μm, respectively, finding that the G + T membrane...
achieved intactness rates of 98.2%, 99.6% and 99.7%, respectively (Figure S6, and see the Appendix S1 for details about our statistical analysis). We note that the intactness of our hybrid membrane is among the best of suspended graphene on perforated substrates reported in the literature (Figure 2F).25,26

We then assembled a liquid cell by transferring the G + T hybrid membrane (as the transparent working electrode) onto a piece of insulating anodic aluminum oxide (AAO) film to produce a parallel electrical capacitor (Figure 3A and see Appendix S1 for the detailed fabrication procedure). A piece of gold sheet was used as the counter electrode in our liquid cell (Figure 3A). We note that the gold electrode is grounded. Figure S7 shows the SEM image of the surface morphology of the liquid cell after infusing the AAO with the ionic liquid. Compared with the filled pores, the cracked film/empty pores/membrane pinholes (red arrow in Figure S7) appear darker under SEM, and correspondingly, the energy dispersive X-ray spectroscopy (EDS) shows significantly lower C and F signal at the darker pores (Figure S8). These results confirm that after the infusion of ionic liquid, the AAO pores are filled and the G + T membrane remains mostly intact. Note that the contact angle between the ionic liquid and the sp2 graphitic materials is only ~27°, guaranteeing good wettability of the electrolyte to the G + T working electrode (Figure S9). We then measured the signal attenuation by comparing the XPS signal from the pure ionic liquid and that from the ionic liquid beneath the G + T film (Figure 3B). Although we observed a significant increase of the sp2 C 1s signal (~284.4 eV) in the presence of the G + T film, photoelectrons generated from the film-capped ionic liquid were clearly resolved (see F 1s, N 1s, and S 2p in Figure 3B). Additionally, we can deconvolute and unambiguously assign the C 1s signals to different carbon species of the ionic liquid molecule (Figure 3C,D).

Having observed clean XPS signals though the G + T window, we further show it is possible to directly observe the EDL formation at the electrified G + T membrane.

**FIGURE 2** Fabrication and characterization of the G + T hybrid membrane. A, Schematic illustration of the G + T hybrid membrane fabrication process. B, An optical photo showing a centimeter-sized G + T membrane floating on water without cracking. C, A transmission electron microscopy image of a G + T membrane. The edge of the membrane can be clearly resolved. D, Scanning electron microscopy image of the G + T membrane suspended on a perforated Si3N4 microsieve with 1.2 μm holes. The G + T film maintains excellent intactness with only a few pinholes observed (red arrows). E, High-resolution SEM image of the suspended G + T film on a 5 μm diameter hole. This image shows the single-walled carbon nanotube “supports” for the graphene membrane. F, Comparison of the intactness between the G + T membrane in this work (red triangles) with other suspended graphene films from the literature.25,26
under applied potential while *operando* monitoring the XPS signal changes from different elements. Cyclic voltammetry (CV) reveals the double layer capacitive behavior of the liquid cell, as shown by the near rectangular-shape of the CV curve (Figure S10). We then applied chronoamperometry to the G + T membrane to charge/discharge the liquid cell and *operando* measure the XPS signal. The XPS results were acquired when the equilibrium state of the EDL charging/discharging was reached, as evidenced by a negligible constant residue current of close to zero (Figure S11). We note that ohmic resistance in the circuit (e.g., contact resistance to electrodes) can cause potential drop on the G + T membrane, making it smaller than the potential applied by the potentiostat. We determined the local electrical potentials on the G + T membrane from the binding energy shifts of sp² carbon relative to its peak position in the absence of an applied potential. These binding energy shifts originate from the changes in the Fermi level of the elements, and therefore directly measure the local potentials.36,37 Figure 4A shows the N 1s signal at different local potentials of the G + T membrane (other elements can be found in Figure S12). The signal can be deconvoluted into two distinct peaks, which can be attributed to the Bpy1,4 cations (higher binding energy, N⁺ 1s, red) and the TFSI anions (lower binding energy, N⁻ 1s, blue) of the ionic liquid, respectively. Since the escape depth of the emitted photoelectrons is only a few nanometers, as we varied the local potentials, changes in the peak areas of the N⁺ 1s and N⁻ 1s signals reflect the ion population changes adjacent to the G + T. The intensity of the N⁺ 1s signal increases at more negative voltages, indicating that Bpy1,4 cations preferentially accumulate beneath the G + T membrane. Switching to a positive voltage range, we observed an increase of the N⁻ 1s signal as a result of more accumulated TFSI anions.

We further plotted the ratio of the integrated area for N⁺/N⁻ as a function of the local potential in Figure 4B to better illustrate the change of the cation/anion concentrations. Specifically, the N⁺/N⁻ ratio changed from ~1.10 at −2.5 V to ~0.55 at +2.2 V. Figure 4C shows the reversible, switching behavior of the N⁺/N⁻ ratio, as...
unambiguously demonstrating the dynamic spectral changes that originate from the charging-discharging capacitive behavior of the EDL formed at the electrode/electrolyte interface. We also note that, although more cracks can be observed on the G + T membrane after the electrochemistry and XPS test, the intactness is still higher than 90% (Figure S13), demonstrating the superior robustness of the membrane.

We note that synchrotron beamlines with variable beam energies, which allow depth profiling, may provide further details on the EDL structure. In a synchrotron light source, since the kinetic energy of the emitted photoelectrons can be adjusted by changing the beam energy, the escape depth of the photoelectrons can be tuned within tens of nanometers (estimated from beam energy range and the corresponding $\lambda_{\text{IMFP}}$). However, due to the ultrahigh beam intensity (more than two orders of magnitude higher than that of the X-ray from the lab-based XPS instrument), we found beam damage occurred almost instantly (less than 1 minute) and the ionic liquid decomposed. This beam damage makes it difficult to deconvolute the XPS spectra obtained at different kinetic energies, warranting further study to address this problem.

To provide further insight into the EDL formation on the G + T hybrid film, we used MD simulations to model the EDL structures and calculate the theoretical $N^+/N^-$ ratio changes at different local potentials. We confined 2645 [Bpy1,4][TFSI] and 805 [Li][TFSI] ion pairs between two parallel $10 \times 10$ nm graphene monolayers separated by a distance of 20 nm as the working and counter electrodes (Figure 5A), which were kept mechanically rigid during MD simulations. Constant voltages were then applied to the two electrodes corresponding to experimental conditions, and the dielectric constant was adjusted to that of the studied ionic liquid.38 Figure 5A,B present the snapshots of the MD trajectory for the EDL structure at the equilibrium state for $-3$ V and $+3$ V after the total energy was converged at 298 K after 6 ns time propagation of the MD trajectory. The accumulation of Bpy1,4 cations and TFSI anions was observed at the negative and positive electrodes, respectively. Moreover, we observed multilayered structures extending for more than ~20 Å from the graphene electrodes, which agrees with the previous theoretical simulations11 and experimental results.13 Figure 5C,D plot the horizontal ion density distribution profiles of the Bpy1,4 cations, TFSI anions, and Li cations as a function of their position relative to the graphene electrode surface at $+3$ V and $-3$ V, respectively. Based on the MD simulation results, we calculated the theoretical change in the XPS $N^+/N^-$ ratio with respect to different voltages and compared these findings with our experimental data (Figure 5E, see Figures S14 to S15 and Appendix S1 for calculation details). We found
our experimental data are highly consistent with the theoretical modeling results.

In conclusion, we have successfully observed the formation and dynamics of the EDL of an ionic liquid electrolyte using operando XPS and a robust graphene-nanotube hybrid membrane as the transparent working electrode in a liquid cell capacitor. Due to the mechanical support provided by long SWCNTs, the membrane can be synthesized in centimeter size while also being ultrathin to provide outstanding photoelectron transparency. With this setup, we show it is possible to obtain high resolution XPS spectra of the resulting EDL structure when an electrical field is applied, even from elements that feature a small photoionization cross-section, such as nitrogen. Cation and anion concentration changes calculated from their peak areas at different local potentials were correlated and found to be consistent with MD modeling. Our results suggest that the Guoy-Chapman-Stern theory breaks down at high concentrations, forming layered structures at the limit of ionic liquids where ion pairs dominate. The experimental configuration introduced here also opens up opportunities for exploration of many other chemical and physical phenomena at the solid-liquid interface such as oxidation/reduction of chemical compounds, selective adsorption/insertion of ions, and solvation/desolvation of ions and reorganization of solvent molecules, and may spur future development in chemical synthesis, catalysis, and energy storage research.

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CONFLICT OF INTEREST
The authors declare no potential conflict of interest.

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REFERENCES


**SUPPORTING INFORMATION**

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