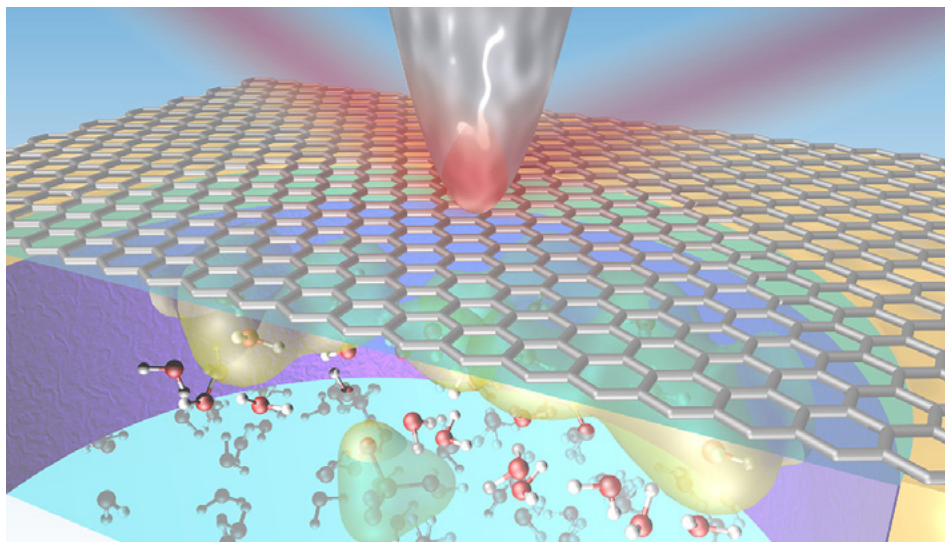


Infrared Nanospectroscopy at Graphene-Liquid Interfaces



Infrared (IR) light is focused onto the sharp metallic tip of an atomic force microscope (AFM), enabling the acquisition of vibrational spectra from a graphene-liquid interface. Since the enhancement of the IR around the AFM tip decays exponentially with distance, with a decay length on the order of the tip radius, the resulting spectra should be sensitive to the layers of water within the decay length, which includes the first few molecular layers.

Interface investigations: deep undercover

Solid-liquid interfaces are vital to physical and chemical processes in many subjects, including corrosion, the generation and storage of energy (fuel cells, batteries), biology (ion transport through cell membranes), and environmental science (chemical weathering). However, solid-liquid interfaces are difficult to experiment on because they are buried under the bulk of the materials on either side of the interface. Furthermore, the interface region is extremely thin—only a few atomic layers. Many techniques for probing materials reveal just surface information, or, if they can penetrate more deeply, provide information averaged over a large volume, rather than from a thin slice close to an interface. Now, researchers

have demonstrated a way to overcome these challenges, using synchrotron infrared nanospectroscopy (SINS) at the ALS.

Double-checking the double layer

Numerous theories have been developed to describe the structure of solid-liquid interfaces, including the electrical double layer (EDL) concept first proposed by Hermann von Helmholtz in the 1800s. In this model, a charged solid surface (an electrode) exposed to a liquid with free-floating ions (an electrolyte solution) will attract a layer of oppositely charged ions. A second layer of ions, more diffuse and loosely bound, extends into the electrolyte. Despite its importance to basic phenomena such as charge transfer,

Scientific Achievement

At the Advanced Light Source (ALS), researchers developed a new infrared approach to probing the first few molecular layers of a liquid in contact with a graphene electrode under operating conditions.

Significance and Impact

The work offers a new way to study the interfaces that are key to understanding batteries, corrosion, and other bio- and electrochemical phenomena.

adsorption, and capacitance, the EDL model requires further experimental validation at the molecular level, for a deeper understanding of interface chemistry that can be applied toward the improvement of many technologies.

SINS in a graphene-capped liquid cell

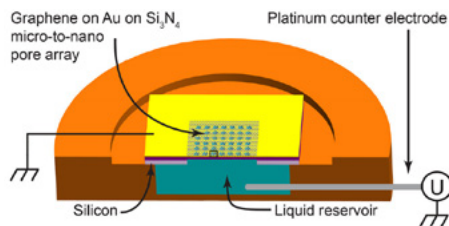
In this work, researchers from several Berkeley Lab divisions—Materials Sciences, Energy Storage and Distributed Resources, the Molecular Foundry, and the ALS—developed a way to collect infrared vibrational spectra at a graphene-electrolyte interface with nanoscale spatial resolution. In SINS experiments at ALS Beamlines 2.4 and 5.4, the light scattered from the interaction between the tip of an atomic force microscope probe and the sample is

analyzed using Fourier transform infrared nanospectroscopy (nano-FTIR).

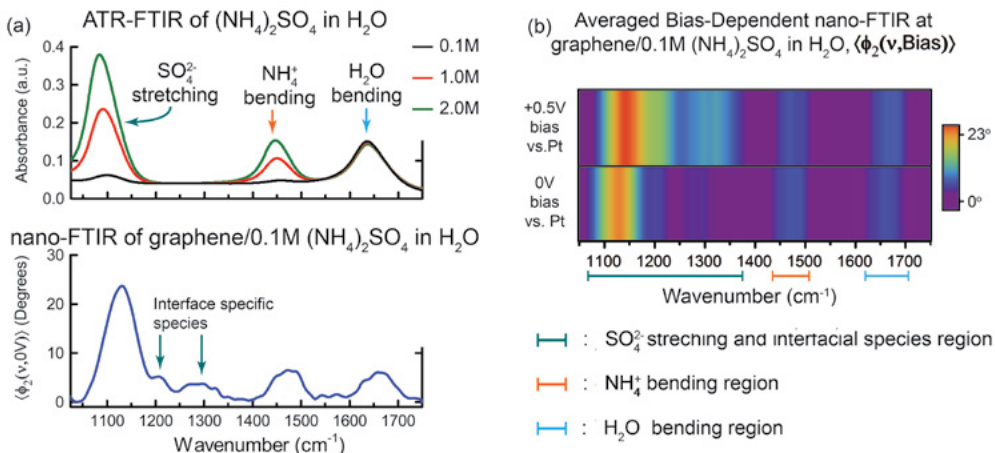
A key component of the technique is a liquid cell with a reservoir of several microliters, capped by a graphene membrane. The graphene is transparent to photons, impermeable to gases and liquids, and acts as a working electrode for studies performed under an applied voltage. With this arrangement, the researchers performed infrared spectroscopy studies with water, propylene carbonate, and aqueous ammonium sulfate electrolyte solutions.

Comparison with conventional FTIR

The nano-FTIR spectra of water and propylene carbonate matched those measured using conventional FTIR (ATR-FTIR), indicating the success of the liquid-cell platform. More importantly, the power of the method was demonstrated by the results on ammonium sulfate, which contains ions identifiable by their vibrational characteristics. Several additional peaks appeared in the nano-FTIR



Schematic of the graphene-capped liquid cell design with a cross-sectional view. A cavity in the body center is the liquid electrolyte reservoir. A platinum counter electrode is fed through the cell wall. The cell is sealed by a silicon chip covered with a 50-nm-thick perforated silicon nitride (Si_3N_4) membrane, coated with gold (~20 nm) and capped with graphene. The perforations have diameters ranging from hundreds of nanometers to micrometers and allow measurement of the graphene-liquid interface.



(a) ATR-FTIR spectra of three concentrations of ammonium sulfate solution (top) and nano-FTIR of the 0.1 M solution. The nano-FTIR peaks appear slightly blue-shifted. (b) Voltage-dependent nano-FTIR displayed as a color map for +0.5 V (top) and 0 V (bottom). The application of positive bias between the graphene and platinum electrodes increases the relative concentration of sulfate and interfacial species, resulting in a larger measured signal.

spectrum, and the relative peak intensities differed from the ATR-FTIR spectra. In measurements under an applied voltage, a clear bias-dependent feature appeared.

These results demonstrate the ability to obtain spectroscopic data from within the EDL and diffuse layer not seen using conventional FTIR, opening the door to

future simulation work identifying the composition of these layers. In the longer term, the approach paves the way for nondestructive, in situ, and operando investigations of liquid environments and solid-liquid interfaces, particularly for applications in biology, energy storage, and electrochemistry.

Contact: Yi-Hsien Lu (yhlu@lbl.gov) and Jonathan Larson (jmlarson@lbl.gov)

Publication: Y.-H. Lu, J.M. Larson, A. Baskin, X. Zhao, P.D. Ashby, D. Prendergast, H.A. Bechtel, R. Kostecki, and M. Salmeron, "Infrared Nanospectroscopy at the Graphene-Electrolyte Interface," *Nano Lett.* **19**, 5388 (2019), doi:10.1021/acs.nanolett.9b01897.

Researchers: Y.-H. Lu, J.M. Larson, A. Baskin, P.D. Ashby, D. Prendergast and R. Kostecki (Berkeley Lab); X. Zhao and M. Salmeron (Berkeley Lab and UC Berkeley); and H.A. Bechtel (ALS).

Funding: U.S. Department of Energy, Office of Science, Basic Energy Sciences Program (DOE BES); and Energy Biosciences Institute (EBI)-Shell Research Program. Operation of the ALS is supported by DOE BES.



Published by the
**ADVANCED LIGHT SOURCE
COMMUNICATIONS GROUP**

