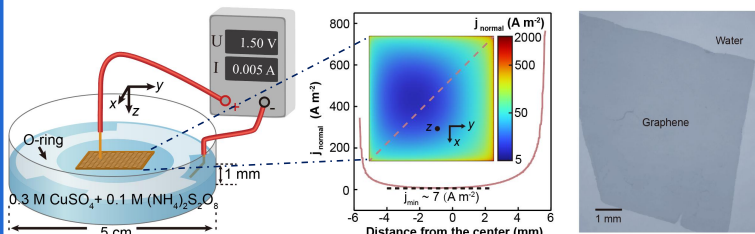


## Abstract

Ion-specific effects at electrode interfaces fundamentally govern interfacial microscopic structure, charge distribution, and reaction kinetics, thereby controlling device performance in electrocatalysis, sensing, and energy conversion applications. Here, we employ electrically tunable, substrate-free monolayer graphene as a model platform to systematically probe the electric double layer (EDL) structure of alkali halide electrolytes at carbon electrode interfaces, using phase-sensitive sum-frequency vibrational spectroscopy (SFVS) complemented by electrochemical measurements. By quantitatively decomposing the total interfacial sum-frequency response into contributions from the diffuse layer, Stern layer, and graphene, we directly determine the density of desolvated halide anions within the SL and reconstruct the molecular-scale structure of the interfacial ionic layers. Remarkably, specifically adsorbed halide anions at the outermost graphene surface exhibit pronounced charge transfer with the electrode, with the magnitude of transfer increasing with ionic size.

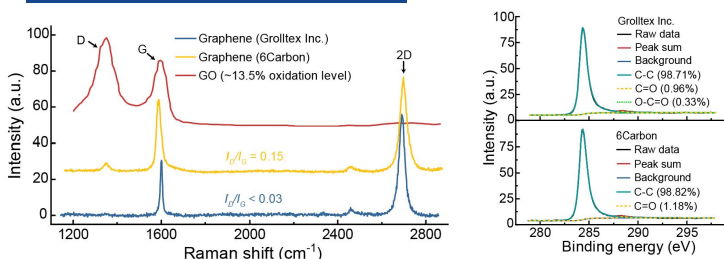
## Sample preparation

### Gradient-etching transfer method



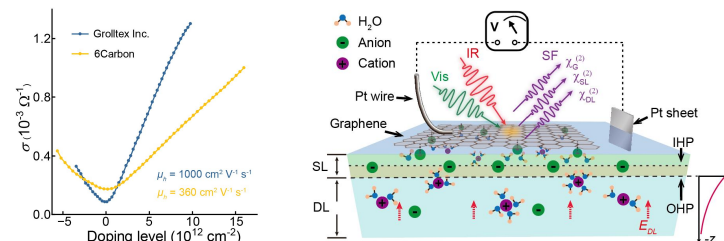
Preparation of large-size freestanding monolayer graphene by building gradient etching rate.

### Graphene transparent electrode



Raman spectra of freestanding graphene samples

XPS of graphene on silicon

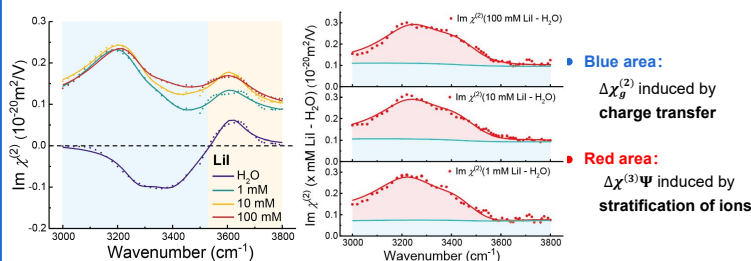


Mobilities of graphene samples

Graphene-based electrochemical cell

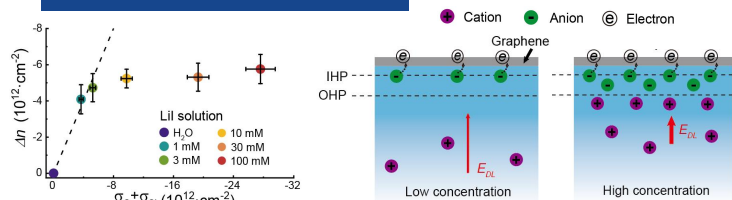
## Results and discussion

### Spectra at Graphene/LiI solution interfaces



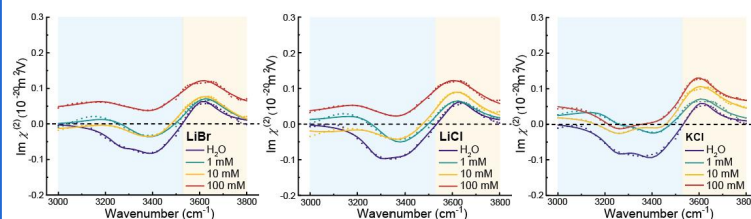
Specific adsorption of LiI — driving charge transfer with graphene ( $\Delta\chi_g^{(2)}$ ) and generating interfacial electric field ( $\Delta\chi^{(3)}\Psi$ ) — significantly alters the interfacial SFG spectra.

### Ionic Structure at the interfaces

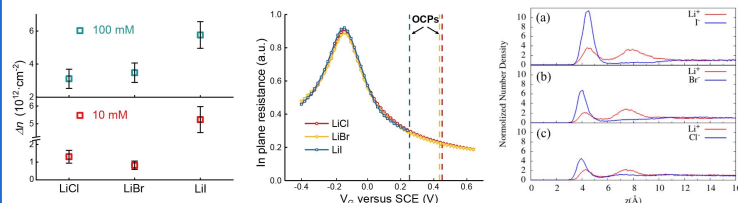


The illustration of the ionic structure at the graphene/LiI solution interface.

### Adsorption of Different Anions



(1). Anions, rather than cations, are always adsorbed on the graphene surface.  
(2). The adsorption properties exhibit significant differences among different anions.



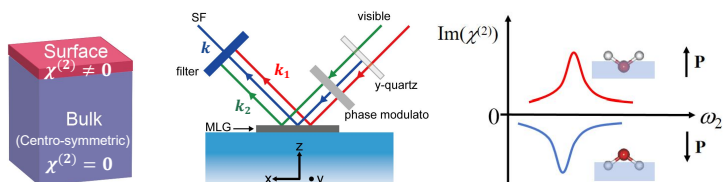
Anions charge transfer abilities follow the trend of  $\text{Cl}^- < \text{Br}^- < \text{I}^-$ .

## Conclusion

- We studied the structure of the interfaces between substrate-free floating graphene/electrolyte solution using *in situ* sum-frequency vibrational spectroscopy techniques.
- Combined with EDL model, we quantified the interfacial electric field induced by specific adsorption. By comparing with graphene's doping level, we extracted fundamental characteristics of the interfacial ionic structure.
- We found that differences in ion-graphene interactions will induce significant structural differences at carbon electrode interfaces, offering critical insights for interfacial studies.

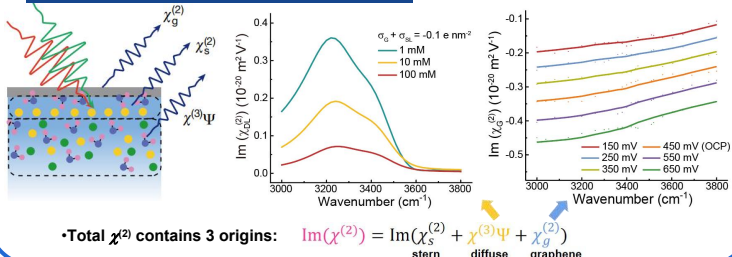
## Experimental Method

### Sum-frequency Spectroscopy



SFVS is a surface-specific technique which can work at normal temperature and pressure.

### SF signal from graphene interface



## Reference