Sum-frequency Vibrational Spectroscopic Study of an Intrinsic Graphene Electrode Interface

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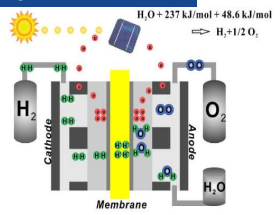
Abstract

Graphitic electrode is commonly used in electrochemical reactions.Being the two-dimensional building block of graphite, graphene shares similar chemical properties with graphite, while its unique physical and chemical properties offer more varieties and tunability for developing state-of-the-art graphitic devices. Hereby we have obtained cm-sized substrate-free monolayer graphene suspended on electrolyte surface with gate tunability. Using sum-frequency spectroscopy,we have observed the structural evolution versus the gate voltage at the graphene/water interface. The suspended pristine graphene offers a new platform to unravel the microscopic processes at the graphitic electrode interfaces.

Introduction

Graphitic electrode



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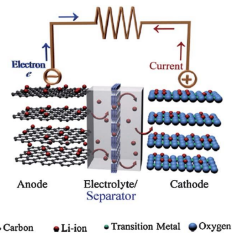
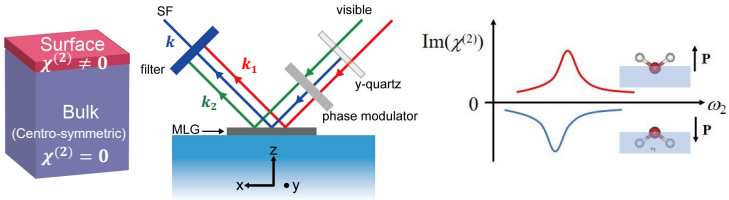


* Journal of Materials Chemistry A 1.38 (2013): 11513-11528.

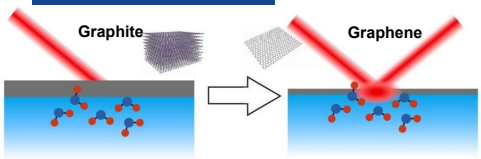
- **Graphitic electrode is widely applied in energy conversion and storage.**

Sum-frequency spectroscopy



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

Graphene electrode

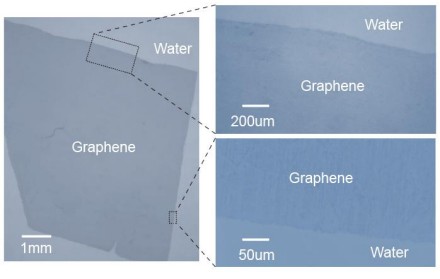


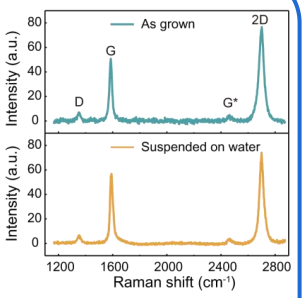
- **Graphene is transparent to visible and IR.**

➢ **How to obtain a gate-tunable cm-sized substrate-free monolayer graphene sample suspended on electrolyte surface?**

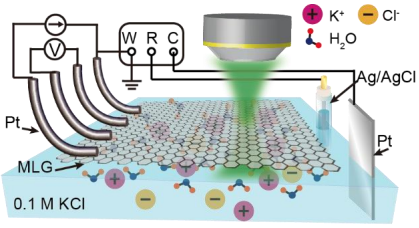
➢ **How does the microstructure of water molecules at the graphene electrode interface changes with gate voltage?**

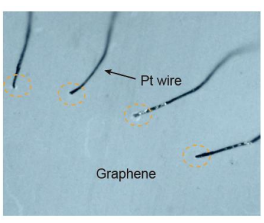
Sample preparation





- **The graphene sample was intact without folding or shrinkage and had few lattice defects.**

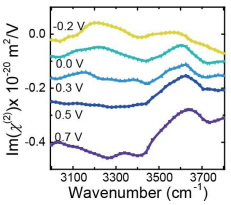


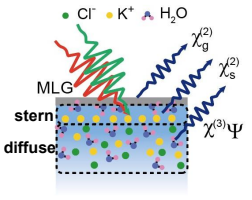


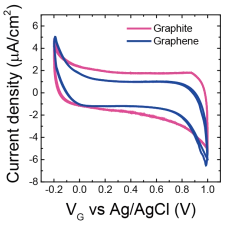
- **The gate-tunability of graphene was achieved by putting Pt in contact with graphene sheet.**

Results

SFVS spectra of graphene interface

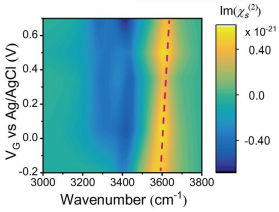


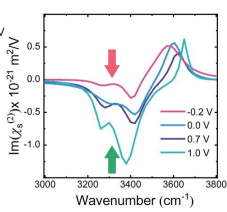


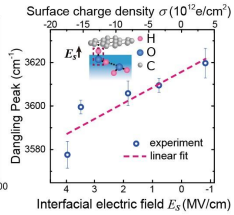


- **Total $\chi^{(2)}$contains three origins:** $\mathrm{Im}(\chi^{(2)}) = \mathrm{Im}(\chi_s^{(2)}) + \chi^{(3)}\Psi + \chi_g^{(2)}$ (stern, diffuse, graphene)

Stern layer spectra ($-0.2\,V < V_G < 1.0\,V$)

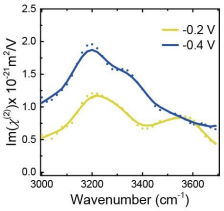


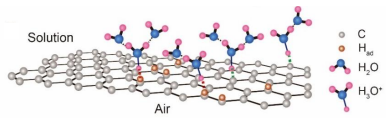




- **Bonded-OH is nearly independent of V_G between +0.7 V and 0.0 V, and changes drastically at V_G = 1.0 V and -0.2 V. The dangling-OH frequency shifts bacause of Stark effect.**

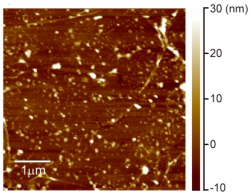
Stern layer spectra at HER



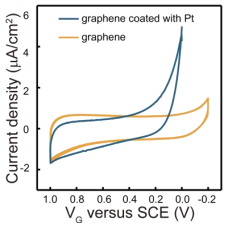


- **Dangling-OH mode disappears when V_G is tuned to -0.4V where the hydrogen evolution reaction (HER) is set off.**

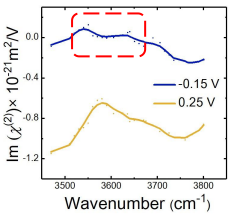
Decorating graphene with Pt nano-paticles



- **AFM image of MLG coated with Pt**



- **Pt nano-paticles promotes the HER**



- **Dangling-OH disappears at higher V_G**

Conclusion

➢ **We have obtained pristine cm-sized free-standing monolayer graphene samples suspended on water surface. The carrier density in graphene can be tuned continuously.**

➢ **We have studied the hydrogen bond network structure at the graphene/ electrolyte interface with SFVS. The interfacial structure changes drastically when chemical reactions are set off.**

➢ **Our work demonstrated that substrate-free pristine graphene is essential for unraveling the intrinsic microscopic structure at the graphene electrode interface.**

Reference

[1] Xu Y, Ma Y B, Gu F, et al. Structure evolution at the gate-tunable suspended graphene–water interface[J]. *Nature*, 2023: 1-5.

[2] Gu, F., & Tian, C. S. Unpublished work