Real-Time, Operando Characterization of Aryl Diazonium Functionalized Bilayer Graphene

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Potentiometric sensors are widely used for ion-sensing applications. Graphene field effect transistor (GFET) based sensors enabled by wafer-scale synthesis and thin-film processing methods offer several advantages over semiconductor sensors [1]. We introduce a **covalently functionalized bilayer graphene** (BiG) **sensor** to address the outstanding challenge of achieving improved long-term stability in sensor response. This architecture combines a conductivity sensitive to surface potential and covalently immobilized selective analyte adsorption sites. To realize BiG sensors, it is required to achieve control over bilayer graphene functionalization. While various methods such as gate controlled functionalization of monolayer graphene have been demonstrated [2], research on controlled functionalization of bilayer graphene is comparatively limited [3],[4].

We present here a novel method for **real-time, operando characterization** of both **monolayer** and **bilayer graphene gate-controlled functionalization**. This approach integrates ac Hall instrumentation with electrochemical functionalization in a microfluidic chamber for simultaneous measurement of resistance and charge carrier density. This technique has enabled us to achieve functionalized bilayer graphene with about 50% reduction in conductivity with aryl diazonium salt chemistry. This method enables a **comprehensive characterization** of graphene, including the measurement of charge carrier density, Hall mobility, field effect mobility and capacitance. We will present operando measurement of charge carrier density during functionalization, with complementary Raman spectroscopy characterization of functionalization. Charge transfer from functional groups to bilayer graphene in response to environmental pH changes will be presented, giving insight into potentiometric pH sensing with bilayer graphene field effect transistors.

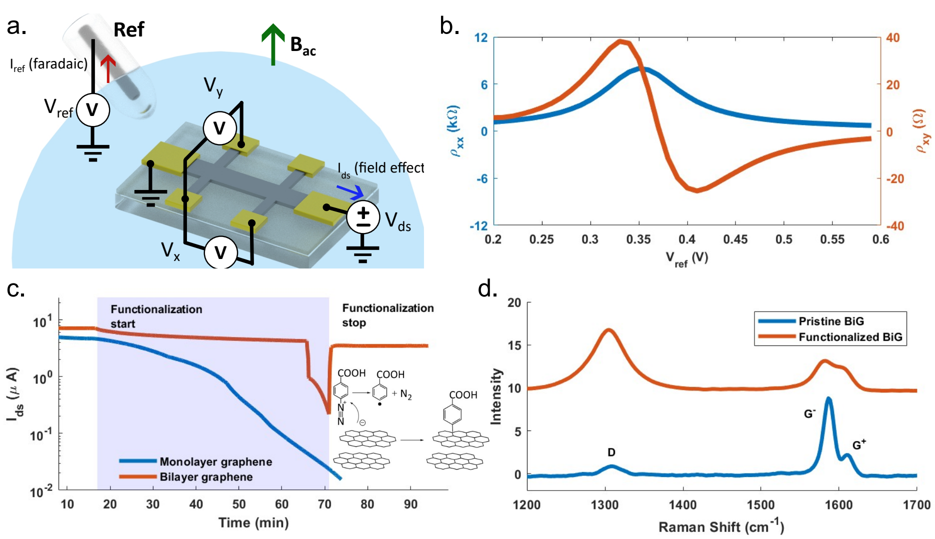

Fig. 1. **a.** Schematic of real time operando characterization of functionalized graphene. **b.** Measured longitudinal and transverse resistance versus reference potential of monolayer graphene. **c.** Measured source-drain current versus time during functionalization of monolayer and bilayer graphene showing that functionalized bilayer graphene maintains its conductivity, in contrast to monolayer graphene, inset: scheme of covalent attachment of carboxylic aryl diazonium salt with bilayer graphene. **d.** Raman spectra of pristine and functionalized bilayer graphene, confirming covalent functionalization.

References

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