

Electrochemical Hydrogenation of Dimensional Carbon
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The hydrogen adsorption and electrochemical properties of epitaxial graphene (EG) grown on silicon carbide (SiC) and bulk graphite in dilute sulfuric acid (H₂SO₄) and perchloric acid (HClO₄) solutions were investigated by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). HClO₄, which showed similar CV peaks, was added into the study to ensure hydrogen adsorption and exclude the possibility of the adsorption of sulphate ions present in H₂SO₄. Electrochemical hydrogen loading and unloading on epitaxial graphene was also demonstrated and confirmed by Raman spectroscopy and CV. Unlike graphite, graphene has an exceptionally high surface area, with the entire monolayer of carbon atoms exposed to chemical reactants. In the absence of π - π interaction from other graphitic layers, graphene has the affinity for chemically induced changes, not seen in the bulk due to the influence of the underlying SiC substrate. Deformation of the ideal graphene lattice has been predicted to induce a bandgap in the material. Home built electrochemical cell and procedures were developed in previous work. CV, Ag/AgCl reference (0.198V vs. NHE) for HClO₄ and Hg/HgSO₄ reference (0.67V vs. NHE) for H₂SO₄ was used to show the different chemical reactivity of bulk graphite compared to graphene. A dependence on number of layers or substrate is present with no well-defined peaks seen in the bulk graphite electrode. Reduction and oxidation peaks are however, present in graphene, peaks not observed in bulk graphite. According to EIS, hydrogen adsorption on EG appears to be mass transfer control with average hydrogen loading of 33% according to Raman. Using the CV potentials, hydrogen was loaded and unloaded on EG to observe the history dependence of the graphene electrode. These results show that graphene hydrogenation is electrochemically reversible and history dependent. This process demonstrates a new pathway to hydrocarbon bond formation for synthesis of advanced organic/inorganic carbon-based compounds.

Table I. Raman peak positions, peak widths and I(D)/I(G) ratios after each H-loading and unloading cycle with I(D)/I(G) ratio showing changes in sp³ content and peak position and width changes resulting from changes in the lattice constant of graphene.

	D position (cm ⁻¹)	G position (cm ⁻¹)	2D position (cm ⁻¹)	I(D)/I(G)	D width (cm ⁻¹)	G width (cm ⁻¹)	2D width (cm ⁻¹)
Pristine EG	1339	1593	2671	0.15	41.8	18.7	67.1
1 st H-Loading	1335	1591	2663	0.37	25.3	21.9	63.3
H-Unloading	(1345)	1604	2705	0.17	(86.2)	22.8	83.7
2 nd H-Loading	1339	1590	2669	0.33	45.6	26.6	81.3

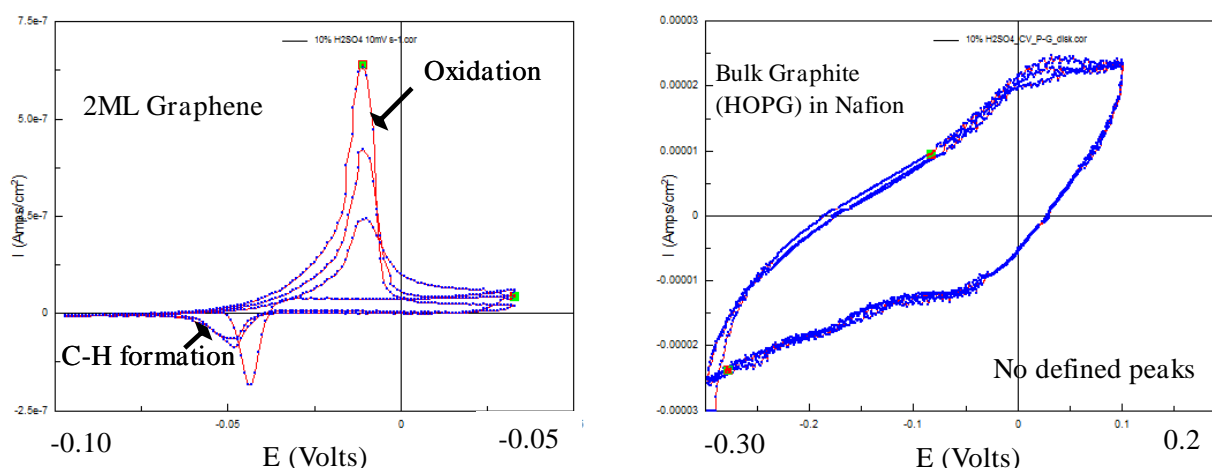


Figure 1. CV of 2ML Graphene and Bulk Graphite in H₂SO₄