Probing the Electronic Density of States of Electrochemically Reduced Graphene Oxide *via* Quantum Rate Spectroscopy

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Quantum Rate Theory Spectroscopy (QRS) is a novel technique based on Quantum Rate Theory (QRT, a framework for understanding charge transfer/transport rates in quantum systems) that enables the characterization of nanostructures anchored to a probing electrode. In QRS analysis, the electrode applies an electric-field perturbation (a way of applying electric force to the system) of an 'electron reservoir' (a source or sink for electrons) that maintains 'quantum coherence' (the preservation of phase relationships between quantum states) with an ionic electrolyte bath (a liquid containing charged particles, or ions). This allows access to the dynamics of quantum states by measuring the quantum capacitance (the system's ability to store charge due to quantum effects) at the interface. Because quantum capacitance is directly proportional to the electronic density of states (DOS, a measure of the number of electronic states available at a given energy), it allows us to investigate the electronic structure of an anchored material at the electrode.

Building on this foundation, this research investigates the electronic structure of reduced graphene oxide (rGO) by measuring its quantum capacitance. QRS [1] shows that the widely accepted charge-storage mechanism, often linked to high surface area, is governed by a dissipative quantum limit – a threshold where energy loss affects charge storage [1]. We study how atomic-level changes affect both electronic and capacitive behavior. The reduction protocol removes preferential oxygen-containing groups – such as hydroxyl (-OH) and epoxy (C-O-C) – and increases the carbon-to-oxygen (C:O) ratio. This also raises the sp^2-to-sp^3 carbon-hybridization ratio and creates chemical and structural defects, which have been reported to drive charge storage (supercapacitance). The DOS is measured directly *in situ* using QRS and correlated with XPS (X-ray photoelectron spectroscopy) data. This links electrochemical behavior to surface chemistry. Importantly, partially restoring the sp^2-hybridized carbon network – mainly by removing hydroxyl and epoxy groups – increases orbital overlap and enhances the DOS near the Fermi level. Beyond the extended (delocalized) electronic states, the DOS profile also shows localized states, attributed in the literature to certain defect types and edge sites [2]. Like disordered semiconductors, these localized states create defect-related energy levels, whose occupancy depends on the ratio of different carbon oxidation states. Overall, this interdisciplinary approach connects quantum electrochemistry, surface spectroscopy, and semiconductor physics to describe quantized processes at room temperature.

REFERENCES

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