Electrochemistry at the edge of a single graphene sheet

Kannan Balasubramanian, A. Yadav, M. Wehrhold, T.J. Neubert, R.M. Iost
Department of Chemistry, SALSA & IRIS Adlershof, Humboldt-Universität zu Berlin, Germany
nano.anchem@hu-berlin.de

Abstract
The investigation of electron transfer at an isolated edge of a single graphene sheet is important to evaluate the (electro) chemical reactivity of the edge at a single object level and assess the prospects for applications. Here, we first outline a simple photolithography-based method to realize a high aspect ratio (millimeter-to-nanometer) nanoelectrode at the edge of an isolated graphene monolayer on an insulating substrate. Subsequently, we present the electrochemistry of two redox probes at such electrodes. The voltammetric response at these graphene edge (GrEdge) electrodes show quasi steady state behavior exhibiting high mass transfer rates, attributed to their nanoscale geometry and a unique diffusion profile. Consequently, the heterogeneous electron transfer is found to be kinetically limited at the GrEdge – a behavior similar to that observed at single nanowire electrodes. These characteristics allow the observation of fast electron transfer kinetics at such electrodes and enable the detection of molecules such as the reduced form of nicotinamide adenine dinucleotide (NADH) or flavine adenine dinucleotide (FAD) down to low micromolar concentrations. Furthermore, we demonstrate the use of electrochemical modification to attach nanoparticles or organic moieties selectively to the graphene edge. In contrast to an unmodified GrEdge, gold nanoparticle modified GrEdge electrodes show steady state voltammetric response for the classical redox probes, indicating that the electron transfer is reversible and mass-transport-limited. After the modification, the sensitivity to the detection of FAD could be improved, while the performance for sensing NADH was only slightly affected. These results indicate that single edge nanoelectrodes with or without chemical modification are promising candidates for electrocatalytic and sensing applications.

References

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