Robust Electrografting on Self-Organized 3D Graphene Electrodes

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Abstract

A self-organized three-dimensional (3D) graphene electrode processed by pulsed laser deposition with thermal annealing is reported. This substrate shows great performance in electron transfer kinetics regarding ferrocene redox probes in solution. A robust electrografting strategy for covalently attaching a redox probe onto these graphene electrodes is also reported. The modification protocol consists of a combination of diazonium salt electrografting and click chemistry by means of Cu\textsuperscript{1}-catalyzed alkyne–azide cycloaddition. Our modification strategy applied to 3D graphene electrodes was analyzed by means of atomic force microscopy, scanning electron microscopy, Raman spectroscopy, cyclic voltammetry, and X-ray photoelectron spectroscopy (XPS). For XPS chemical surface analysis, special attention was paid to the distribution and chemical state of iron and nitrogen in order to highlight the functionalization of the graphene-based substrate by electrochemically grafting a ferrocene derivative. Dense grafting was observed, offering $4.9\times10^{-10}$ mol cm\textsuperscript{-2} surface coverage and showing a stable signal over 22 days. The electrografting was performed in the form of multilayers, which offers higher ferrocene loading than a dense monolayer on a flat surface. This work opens highly promising perspectives for the development of self-organized 3D graphene electrodes with various sensing functionalities.

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