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The focus of this work is on the synthesis of a 1-Aza-18-crown[6]ether functionalized reduced graphene oxide (RGO-crown[6]) with specific K⁺ binding sites on the RGO surface. Glassy carbon electrodes (GCE) functionalized with RGO-crown[6] were tested for selective potentiometric sensing of K⁺, with a detection limit of 10⁻⁵ M without inference from other ions (Na⁺, Li⁺, NH₄⁺, and Ca²⁺) in concentrations up to 2.5 × 10⁻² M. Similar sensing was achieved with functionalized disposable SPE electrodes. The results demonstrate that RGO-crown[6] is a conductive material full of promise for application in fabrication of new types of ion selective sensors.

Introduction

Selective quantitative ion sensors in solution are critical for environmental monitoring and clinical diagnostics. Cost and speed can limit the use of routine quantification in laboratory setting. We attempt to make low-cost disposable sensing devices for use in remote and resource-limited environments. Selectivity towards single ions is essential as most samples contain many different ions. e.g. the K⁺ to Na⁺ ratio in blood is about 30.

Sensor concept

We utilize potentiometric sensing for our sensor but without a separating membrane by added high concentration of masking salt. The ionophore 18-Crown[6]ether on functionalized RGO ensures selective sensitivity by offering specific binding sites on the electrode. Reduced graphene oxide is used as support material, because of the easy fabrication and functionalization along with its high specific surface area and conductance making it an ideal material for sensing.


Crown-ether functionalization was prepared by thiophosgene activated peptide coupling of boc-protected glycine linker and 1-aza-18-crown[6]ether followed by deprotection in TFA. GO prepared by modified Hummers’ method was then functionalized with this moiety by nucleophilic ring opening of basal plane epoxides under alkaline conditions. Directly following functionalization, GO was reduced in strong alkaline solution at 80 °C. The synthesis procedure is schematically illustrated below.

Functional tests of RGO-Crown[6]

The RGO-crown[6] material on GCE was tested for sensitivity and selectivity of Li⁺, Na⁺, K⁺, NH₄⁺, Ca²⁺ without masking salt. Nernstian response to potential to all salts but no selectivity was obtained. By adding 100 mM of NaNO₃ as masking salt, the response of all ions but K⁺ was quenched up to 25 mM. The specific binding of K⁺ results in retained sensitivity for K⁺ at ~37 mV.


AFM images of GO, RGO and RGO-crown[6] show that single-layer structural feature is retained during synthesis and RGO nanosheets size does not change significantly.


The functionalization ratio is determined through XPS from elemental survey 18-crown[6]ether: graphene carbons is 1 : 46. Further evidence of covalent functionalization from C1s spectrum.

Summery

- 18-Crown[6]ether modified RGO has been synthesized and characterized successfully.
- Sensing of K⁺ on GCE has been achieved with a detection limit of 10 μM.
- Selectivity for K⁺ has been proven up to the presence of 25 mM Na⁺, Li⁺, NH₄⁺ or Ca²⁺.
- The material on SPE displayed the same sensing features as that on GCE.