Supramolecular Derivation of Graphene Nanomaterials for Chemical Sensors - DTU Orbit (14/12/2018)

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With properties such as high surface area, high conductivity, and low production cost with easy up-scaling, graphene-like materials provide a promising support for many applications, one of which is for chemical sensors. By functionalization with molecular receptors such as supramolecular moieties, which have long been used for chemical sensing, graphene-like materials can be endowed with increasing selectivity to form better and cheaper sensing composite materials.

In this Ph.D. project, reduced graphene oxide (RGO) has been covalently functionalized with supramolecular moieties to create active sensing materials. Two different strategies have been applied to achieve specific functionalization: The first approach consisted of covalently attaching chemically resistant supramolecular moieties, in the present work crown-ethers to graphene oxide (GO); the functionalized GO was then reduced chemically. This resulted in monolayer RGO nanosheets functionalized with crown-ether to an extent of up to 30% of the theoretically available surface area (Figure 1). These materials were shown to selectively bind alkali metal ions, and potentiometric sensing based on the materials was achieved with a detection limit of $10^{-5}$ M.

In the second approach Azido-RGO was prepared as a general platform for post reduction modification. GO was here functionalized with a short linker terminated in an alcohol. The intermediate material was then reduced effectively with NaBH$_4$, followed by chemical transformation of the alcohol into azide, thus providing a chemical handle for click chemistry in the form of CuAAC (Figure 2).

This platform material has then functionalized with ferrocene as a redox probe to accurately determine surface coverage which showed that the material one azido-functionality was attached per 16 RGO-sheet carbon atoms or slightly more than one azide per nm$^2$ of RGO-sheet.

This Azido-RGO was used in successful functionalization with the large supramolecular receptor molecules TTF-calix[4]pyrrole which function as a sensor for Cl$^-$ and potentially for TNB. The coverage achieved was one molecule per 50 – 60 carbon atoms in the RGO-sheet. In view of the size of this molecular moiety, the coverage is actually very high.

The material was used for Cl$^-$ sensing showing sensitivity at very low concentration with linear response in the concentration range $10^{-8}$ – $10^{-5}$ M.

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