

Layer by Layer Electrode Surface Functionalisation Using Carbon Nanotubes, Electrochemical Grafting of Azide-Alkyne Functions and Click Chemistry

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Abstract

Ferrocene was covalently bonded to a layer of adsorbed single-walled carbon nanotubes on a glassy carbon electrode surface using electrochemical grafting and click chemistry. Grafting of the 4-azidobenzene diazonium salt onto the surface was accomplished by electrochemical reduction. The surface-bound azide groups, with the use of a copper(I) catalyst, were reacted with ethynylferrocene to form covalent 1,2,3-triazole bonds by click chemistry. This layer by layer construction of the electrode surface results in stable electrodes by combining good electrical conductivity and increased surface area of the nanotubes with the versatility of the Sharpless click reaction.

Keywords: Diazo compounds, Carbon nanotubes, Click chemistry, Grafting, X-ray photoelectron spectroscopy

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1 Introduction

Surface modification of electrodes is an important area of research in the production of sensors with improved selectivity and sensitivity to various analytes, as well as better reproducibility and greater resistance to passivation. There are a multitude of approaches to surface functionalisation, however formation of a uniform monolayer on a surface is often more effective through covalent bonding as opposed to adsorption, due to the greater reproducibility and stability of the former [1–4].

Self-assembled monolayers (SAMs) have been extensively explored as a fairly simple and straight-forward method of modification, and are often highly reproducible [4–7]. SAM layers commonly exhibit fast electron transfer kinetics, and can be used as a bridge or link between biologically active or catalytic molecules and an electrode surface [8]. However, in most cases SAMs are formed with thiolated compounds on gold, utilising the strong attraction between sulfur and gold, and so this method is very limited by the substrate. Grafting of aryl-diazonium compounds on to a surface through electrochemical reduction is also an interesting and useful method that is more versatile than SAM formation, and has been used to form stable and uniform monolayers on a variety of conductive surfaces [9]. In particular, grafting has been shown to work successfully on gold [2,10], glassy carbon [3], iron [11] and other conductive sub-

strates including semiconductors [12] for a range of different diazonium salts. This, in combination with the click chemistry reaction proposed and utilised by Demko and Sharpless among others [13–15], has been shown to provide a particularly useful method in which electrode surfaces can be functionalised with a great deal of potential for further applications and modifications [1,5,16]. The “Sharpless click” chemistry reaction uses Cu(I)-catalysed azide-alkyne cycloaddition (Huisgen 1,3-dipolar cycloaddition), where the starting azide and acetylene can be bound to a number of complexes, from ferrocene and diazonium to biomolecules [1,5,13–17]. This reaction has been utilised for synthesis of various compounds [17–20]. The versatility, mild conditions, high yields and stability of the resulting 1,2,3-triazoles makes them particularly attractive for surface, and thus sensor, modification [1,4–7,16,17,21,22]. Evrard et al. [1] and Collman et al. [5] have shown that, following electrochemical grafting with either azide- or acetylene-bearing diazonium salts, ferrocene can be attached to the electrode through click chemistry. In most cases, the Cu(I) catalyst needs to be stabilised to afford easier modification of the entire grafted surface with ferrocene groups.

Another interesting area that has been investigated during the last decade is the use of carbon nanotubes (CNTs) in the construction of electrodes. CNTs have been used in the fabrication of sensors for the enhanced detection of a range of analytes [23], and have proved to