



Short Communication

4-Azidoaniline-based electropolymer as a building block for functionalisation of conductive surfaces

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ABSTRACT

We propose in this work to compare three approaches using 4-azidoaniline combined with “click” chemistry and electrochemistry to anchor ferrocene moieties at glassy carbon surfaces. The immobilisation of a newly synthesised molecule, 4-(4-ferrocenyl-1H-1,2,3-triazol-1-yl)aniline, through direct electropolymerisation or via *in situ* diazotization followed by electrografting is studied by analysing the samples by XPS and electrochemistry.

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1. Introduction

The controlled immobilisation of molecules on conductive surfaces is the subject of considerable research due to the large potential applications ranging from sensors to biomaterials. A quite recent and versatile approach consists of applying the concept of “click chemistry” – using the copper(I) catalysed azide–alkyne cycloaddition (CuAAC) reaction [1,2] – to interfacial reactions for the functionalisation of conductive substrates through adsorption of thiols (to form SAMs) or electrografting of azido-diazonium salts [3–6]. SAMs are, however, not adapted to all electrode materials, making the “diazonium strategy” appealing for modifying conductive surfaces [7–9]. Moreover, scarce and recent studies have reported on electropolymerisation of pyrrole synthesised with terminal azide or alkyne groups and on the use of poly(3,4-(1-azidomethylethylene)dioxythiophene) (PEDOT) bearing azide groups for interfacial click chemistry [10–12]. But, to our knowledge, no study has been reported yet on electropolymerisation of 4-azidoaniline for use in click chemistry.

We report here on “diazonium-like” electrochemical approaches using CuAAC click chemistry to produce versatile functionalisation of conductive materials starting from 4-azidoaniline

(noted **1**, Scheme 1). Click chemistry was performed either before or after electrochemical functionalisation, as explained below. The long-term purpose of comparing the modification of electrode surfaces by electropolymerisation versus electrografting lies in the difference in properties of the resulting surfaces for the preparation of electrochemical sensors. Using a starting molecule, **1**, as a basis for making such diverse surfaces is then more attractive when looking at multiple applications of sensors.

In this work, the strategies defined in Scheme 1 were applied to the immobilisation of ferrocene groups at a glassy carbon surface. Indeed, research on ferrocene-based polymers has many applications, such as the conception of biosensors [13]. The choice of **1** is dictated by its versatility for click chemistry. It was used in this work to synthesise (by CuAAC reaction from **1** and ethynylferrocene, **2**) [14,15] new electrodeposable moieties possessing an aniline group, namely 4-(4-ferrocenyl-1H-1,2,3-triazol-1-yl)aniline (**3**). Two routes were followed for immobilisation of **3**, either through its direct electropolymerisation (*route A*) or by *in situ* diazotization [16] of the aniline part of **3** to form the species 4-(4-ferrocenyl-1H-1,2,3-triazol-1-yl)benzenediazonium (**4**) that was further electrografted (*route B*), as illustrated in Scheme 1. The direct electropolymerisation of **1** followed by immobilisation of ferrocene via click reaction with **2** (*route C*) was also investigated here for the first time for this aniline derivative. These modification routes were compared to the “classical” modification of electrodes by a two-step method [5], consisting of the *in situ* diazotization of **1** to form 4-azidobenzenediazonium salt (**5**) followed by

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