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Self-assembly of the second-generation of nitroaryl-ended dendrons onto carbon

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ABSTRACT

We report the self-assembly of the second-generation of nitroaryl-ended dendrons onto carbon surfaces. The immobilized layer was characterized by cyclic voltammetry (CV), electrochemical impedance spectroscopy and atomic force microscopy (AFM). The response was analyzed in comparison to the first-generation dendron behavior. Reduction of both layers generates the hydroxylamine product. The resulting redox-active layer exhibits a well-behaved redox response for the adsorbed nitroso/hydroxylamine couple. The thermodynamic of the adsorption of both dendrons on glassy carbon electrodes was also studied by CV. The Frumkin adsorption isotherm was the best to describe the specific interactions. The AFM images showed a network film formation with embedded aggregates that completely covered the carbon surface. The average height suggests a tilted preferential adsorption for both molecules.

1. Introduction

Carbon electrodes are widely used in electrochemical techniques due to their relatively low cost compared to other electrodes such as gold or platinum. However, electron transfer rates observed on carbon surfaces are often lower than those observed on metal electrodes[1]. In particular, the glassy carbon electrodes (GCE) constitute a very good alternative due to its excellent mechanical and electrical properties. GCE are relatively reproducible, chemically inert, and mostly used in a wide potential window. In addition, the carbon surface modification is relevant in the area of electrochemistry and materials science as it is a promising way for a rapid construction of new materials for electrocatalysis and (bio)sensor platforms. Generally, the carbon electrode derivatization is carried out following one of the subsequent strategies. First, through covalent modification of the electrode, for example using oxidized groups (like carboxylic acids) located on the surface of carbon that yields anchoring groups to which the modifiers are connected. In particular, the electrochemical reduction of aryl diazonium salts is a well-established method whereby aromatic organic layers can be covalently tethered to carbon surfaces[2–8]. Second, some electrodes such as carbon paste ones can be doped with species mechanically immobilized during preparation[9–12]. Lastly, by physical adsorption of molecules on the substrates modified *via* supramolecular interactions. It is also well known that when considering immobilization via self-assembly of aromatic molecules on the electrode surface, the presence of functional groups may greatly affect the nature and magnitude of such interaction. Particularly, Wuest et al. recently reported that the adsorption energy of 1,3,5-trinitrobenzene onto carbon surfaces is about three times larger than for nitrobenzene molecules, and that the presence of carboxyl groups on the aromatic ring greatly increases the surface binding on graphite[13].

The aryl-nitro derivatives confined to an electrode surface are well-known redox mediators which exhibit high catalytic activity in the electrooxidation of reduced nicotinamide coenzyme (NADH)[14], and also have been successfully exploited for electrochemical detection of thiols[15]. In general, the aryl-nitro derivative, which is in fact precursor of the real mediator, is electrochemically transformed into the corresponding hydroxylamine

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compound and then, the reversible two-electron oxidation of the hydroxylamine group leads to the nitroso group, which is the catalytically active compound. Several immobilization strategies have been developed for covalent modification of carbon surfaces with nitrophenyl groups, highlighting among them two methods: via spontaneous attachment of the nitrobenzenediazonium salt[16–18] and via self-assembly of nitrothiophenol[19]. The main advantage of both methods is that spontaneous grafting can take place with no electrochemical induction by simple immersing the substrate into a solution of either a diazonium salt or a proper thiol. However, the reactivity of the head group complicates the synthesis of some new aryl diazonium salts and only single component layers have been fabricated[20].

Dendrons are well-defined and highly branched molecules that are of great interest as new materials in many important application areas. They represent a structural component of the parent dendrimer, are also monodisperse, and even more, they are a wedged-shaped section of a dendrimer[21,22]. Dendrons can be used as building blocks to form a molecular self-assembly or adlayer on electrode surfaces. Thus, a common approach to amplify the effective area and quantity of functional groups onto an electrode is to graft dendritic molecules. On account of their controllable geometry, size, and functionality, dendrons rule interest for enlargement of active surfaces; however targeted control of surface architectures requires an understanding of dendron/dendron and dendron/surface interactions, as well as an in-depth knowledge of the structure of the dendrons in the solid state. Dendronization is a synthetic methodology that offers important advantages. The products which are obtained by means of it, present new and specific properties and are called dendronized materials[23].

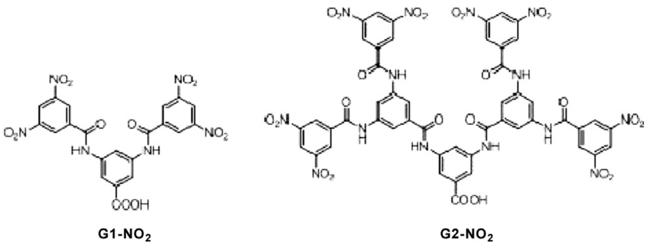
Self-assembly via physical adsorption is a particularly simple way of creating a film onto a surface. It needs neither preformation of oriented films nor special equipments. Physical adsorption is the result of relatively weak Van der Waal's interaction forces, a physical attraction between the electrode surface and the adsorbate. Hence, the method causes little or non-conformational changes of the dendritic molecule, and can be both simple and cheap. Under proper conditions, physical adsorption can result in adsorbed molecules forming multiple layers. However, it has the disadvantage that the adsorbed molecules may detach from the surface due to the weak binding forces[23].

In this paper, we report the self-assembly of the second-generation of nitroaryl-ended dendrons (G2-NO_2) onto carbon surfaces and its comparison to the first-generation dendron behavior (G1-NO_2). The self-assembling process of these adsorbate molecules were monitored by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and atomic force microscopy (AFM). In this way, we report a powerful and versatile modification process, which can be applied to carbon materials without any conductivity or pretreatment requirements that generates promising platforms for electrocatalysis and sensor development.

2. Experimental

2.1. Materials

The synthesis of dendrons (Scheme 1) was obtained following the Kakimoto's procedure[24] (see S1 in the Supplementary Material). The rest of chemicals used within these experiments were reagent grade commercially available chemicals and were used without further purification. All solutions were prepared immediately prior to their use. Phosphate buffer solutions (PBS) used in this work contain Na_2HPO_4/NaH_2PO_4. Deionized water was used after purification in a Millipore Milli Q system and the actual pH of the solutions was determined with a Hanna Instruments pH/ion analyzer model 209.



Scheme 1. Schematic representation of both dendrons: G1-NO_2 and G2-NO_2.

2.2. Glassy carbon electrodes preparation

Prior to its modification, the glassy carbon electrodes (GCE) (CH Instruments, Inc. Austin, TX) of 3.0 mm diameter were polished using 1, 0.3 and 0.05 μm alumina (Buehler) and rinsed with water and ethanol. After its polishing, the electrodes were sonicated for 1 minute in distilled water and dried in a N_2 flux. GCE were incubated in a Dimethylsulfoxide (DMSO) solution containing either G1-NO_2 or G2-NO_2 for different times and concentrations. After the modification, the derivatized surface was subsequently rinsed with copious volumes of ethanol and water, and employed immediately after its preparation.

2.3. Electrochemical measurements

All electrochemical measurements were performed at room temperature with a CH Instruments Multipurpose Electrochemical Analyzer. A conventional three-electrode system, comprising a glassy carbon working one, a platinum foil as the auxiliary, and a Ag/AgCl 3.0 M NaCl electrode (from Bioanalytical Systems, Inc.) as the reference, was used for all measurements. All potentials were reported versus the Ag/AgCl reference electrode at room temperature. Nitrogen gas was used to deaerate all aqueous solutions before their use. If not otherwise mentioned, scans were started at the positive end of the potential range in cyclic voltammetry (CV). The impedance data were analyzed by non-linear least square fits using the Zview software[25]. A sinusoidal potential modulation of 10 mV amplitude was superimposed on a fixed d.c. potential and the amplitude and phase angle of the resulting current were recorded at frequencies ranging from 1×10^{-5}-100 kHz.

2.4. Atomic Force Microscopy (AFM)

AFM images were acquired with a commercial Nanotec Electronic System operating in tapping- mode at an atmosphere pressure and room temperature. Acquisition and image processing were performed using the WS × M free software[26]. V-shaped Olympus RC800PSA cantilevers (Olympus Corporation, Tokyo, Japan) made of silicon nitrite coated with Au/Cr (resonance frequency in the range of 70-90 kHz, nominal spring constant in the range of 0.05-0.1 N/m and a radius of curvature less than 20 nm) were used. The samples for AFM analysis were prepared by immersing freshly cleaved highly oriented pyrolytic graphite (HOPG) in a DMSO solution containing 1 mM of either G1-NO_2 or G2-NO_2 for different reported times. Samples were subsequently rinsed with copious volumes of ethanol and water, dried under nitrogen flux and analyzed immediately.