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Electrochemical properties of aryl-modified gold electrodes

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ABSTRACT

The properties of electrochemically grafted gold electrodes surface have been investigated. Electrografting with 1- and 2-naphthyl, biphenyl and 4-bromophenyl groups yielded strongly attached layers and for the latter, electrochemical quartz crystal microbalance (EQCM) and atomic force microscopy (AFM) measurements showed that a multilayer film of bromophenyl groups was formed. This was confirmed by X-ray photoelectron spectroscopy (XPS). The blocking of electron transfer for several redox probes caused by the aryl-modification was investigated using cyclic voltammetry (CV). Oxygen reduction was studied using a rotating disk electrode (RDE) and the data also revealed a strong inhibition of this process by the attached aryl groups. The stability of these functionalised surfaces points to the strength of the Au–C bonds formed.

1. Introduction

There has been an increased research activity in surface modification by the reduction of aryldiazonium compounds [1–6]. This process has been widely employed for the covalent grafting of carbon materials [7–10] but in recent years it has also been adopted for the modification of surfaces of metals such as Fe, Cu, Ni, Co, Zn, Pd and Au [11–22]. The modification of gold surfaces by electrochemical reduction of aryldiazonium cations has attracted considerable attention [4,11,19,23–43]. The Au–C bonds formed yield layers that are more stable than those obtained by chemisorption of alkanethiols regarding long-term storage, ability to withstand repeated cycling and available potential window [27]. The bonding of aryl groups to metal electrode surfaces by electroreduction of the corresponding diazonium compounds in acetonitrile was first demonstrated by Ahlberg et al. [43]. The mechanism of attachment to gold is not entirely clear although there is good evidence for the formation of Au–C bonds [11,24,26,28]. An attractive grafting approach is to use *in situ* synthesised diazonium derivatives [24,37,39]. Aryl-modified Au electrodes can find applications in biochemical sensing [4] due to the possibility of performing additional chemical transformations to the attached film.

The inhibition of electron transfer (ET) reactions by the attachment of aryl groups to gold electrodes have been studied using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The blocking action of aryl films depends on the modifier used and on the modification procedure [2,3]. Typically, thicker and more compact films exhibit a stronger blocking behaviour but the nature of the modifier film and the ionisation of functional groups play an important role in determining the electrochemical response of these modified electrodes.

Laforgue et al. showed that a thin carboxyphenyl (CP) layer attached to gold did not alter the kinetics of ET for the $Fe(CN)_6^{3-/4-}$ probe [23] and the peak potential separation was the same as for bare gold. Stronger inhibition was observed, however, by increasing the grafting time at a constant potential [23,36]. By contrast, Liu et al. observed that a CP film of submonolayer coverage suppressed electron transfer compared with bare gold [27]. Long-term sonication of the freshly prepared Au/CP electrode partially removed the modifier from the surface and the CV became similar to that of unmodified gold. Paulik et al. studied the structure and properties of multilayer CP and methylphenyl (MP) films on gold [28]. The formation of porous films was in evidence. However, the voltammetric peaks of the $Fe(CN)_6^{3-/4-}$ probe disappeared in the presence of an incomplete CP layer. This effect was explained

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by electrostatic repulsion between the $-COO^-$ groups and the $Fe(CN)_6^{3-/4-}$ anions in solution. Both CP and MP multilayer films were affected by long time sonication, which changes their structure and electrochemical properties. Sonication of these functionalised Au electrodes in solvents of different polarities led to different interfacial electrochemistry and hydrophilicity, consistent with a dynamic surface structure that can reorganize in response to the environment [28]. The greater stability of functional residues attached using diazonium chemistry compared with thiol attachment has been recently demonstrated by Schewchuk and McDermott [42].

Surprisingly, the behaviour of the $Fe(CN)_6^{3-/4-}$ couple is not affected by the presence of a thick phenyl film on gold [19], whereas the CV response is completely inhibited on the Au electrodes modified with nitrophenyl (NP) groups [19]. Thick NP and diethylaniline films remarkably decrease the ferri/ferrocyanide electron transfer rate [23]. Electrode modification with aminophenyl groups appears to suppress the response of this redox probe even more strongly than the NP-modified Au electrodes [24]. In this case, AFM imaging showed that the thickness of the aminophenyl layer was approximately 25 nm. Modification of gold electrodes with (4-aminoethyl)benzenediazonium cations had little effect on the voltammetric response of the $Fe(CN)_6^{3-/4-}$ couple [29]. The degree of inhibition increases significantly by attaching glutathione to the modifier film. The EIS results indicate effective grafting of Au electrode surface with a fluorinated diazonium salt [31]. Alkylbenzene monolayers attached by the reduction of diazonium compounds can be used to stabilise Au nanoparticles [44]. The strong attachment of anthraquinone groups to gold by electrochemical reduction of the corresponding diazonium salt has also been recently demonstrated [40] and some attempts have been made to obtain molecular level information regarding the binding of carbon to gold [45,46]. Similarly, electrografting of gold has also been achieved using iodonium salts [47].

Aryl-modified gold electrodes provide a good platform for the development of biosensors [4]. Aminophenyl and carboxyphenyl groups are most suitable for the covalent attachment of DNA, enzymes, redox proteins, antibodies and cells. These techniques have been used, for example, for the immobilisation of horseradish peroxidase on a Au electrode surface [37,39] and therefore methods for the functionalisation of gold electrodes are of great current interest. Of these, spontaneous modification with aryl groups from diazonium salts solutions presents advantages in terms of simplicity and has been recently demonstrated [48–51].

Gold electrodes modified with aryl groups could be applied in electroanalytical devices, for instance for the determination of dopamine. Dopamine is an important target because it is a central player in the brain "reward" system, although its precise function is not understood. Catecholamine neurotransmitters are well suited for electrochemical detection because the potential required for their oxidation is well within the potential limits for carbon and metal electrodes in physiological buffer [52]. Gold and platinum microelectrodes have been used to detect directly catecholamines in vitro. The noble metals are typically protected with a polymer film to prevent biofouling. In this respect, it is of interest to test electrochemically the barrier properties of aryl films on gold towards dopamine oxidation, as it has been carried out in the present work.

The purpose of this work was to explore the electrochemical properties of gold electrodes modified with different aryl groups to investigate the resulting blocking of electron transfer reactions. The molecules were chosen to provide attached aromatic rings of different sizes and an example of a phenyl group containing a polar group. For the latter, phenyl bromide was chosen since the dipole moment of bromobenzene is 1.70 D [53].

2. Experimental

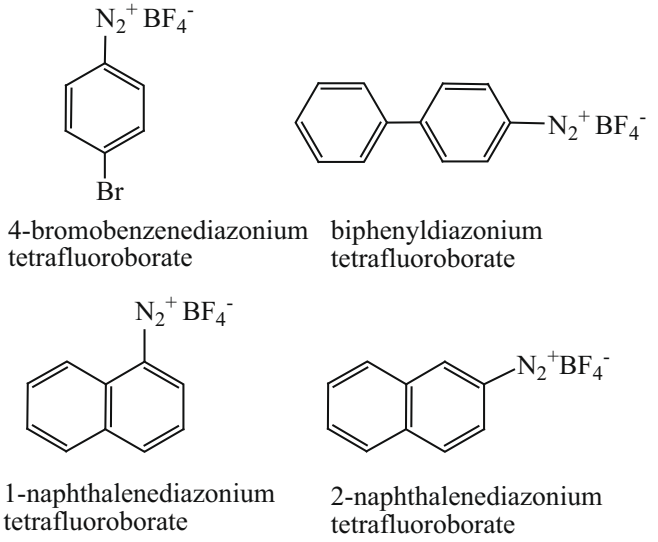
2.1. Electrode preparation

A gold disk electrode with a geometric area (A) of 0.196 cm^2 was employed for the electrochemical measurements. The disk was cut from a Au rod (99.99%, 0.5 cm in diameter, Alfa Aesar, UK) and was pressed in a Teflon holder. The electrode was polished before use to a mirror finish with 1.0, 0.3 and 0.05 μm alumina slurries (Buehler) followed by sonication in Milli-Q water (Millipore, Inc.). The polished Au electrodes were electrochemically cleaned in Ar-saturated 0.5 M H_2SO_4 by cycling the potential 50 times at 100 mV s^{-1} between −0.3 and 1.5 V. H_2SO_4 (Suprapur) was supplied by Merck.

2.2. Electrografting of Au electrodes with aryl groups

The covalent attachment of aryl layers to the gold surface was performed by electrochemical reduction of the corresponding diazonium cations. Four aryldiazonium salts were used in this study and their chemical structures are shown in Scheme I. 4-Bromobenzenediazonium tetrafluoroborate was a product from Aldrich. Three other aryldiazonium derivatives were synthesised according to a published procedure [54]. Briefly, an ice-cooled solution of 50 mmol of $NaNO_2$ in 7.5 ml water was added slowly (dropwise ~0.5 h) to a mixture of 45 mmol of the aryl amine dissolved in 30 ml of 48% HBF_4 cooled to 0 °C. The temperature was kept at 0–2 °C while stirring the solution for an additional 0.5 h. The compound was filtered, washed once with ice cold HBF_4, once with ice cold water, twice with ice cold ethanol and finally three times with diethyl ether. The product was then dried in vacuum or air (yield up to 90%).

Surface grafting was carried out in acetonitrile (ACN, Riedel–de Haën) containing 0.1 M tetrabutylammonium tetrafluoroborate ($TBABF_4$, Fluka) as base electrolyte. The concentration of the aryldiazonium salts was 3 mM. The potential was cycled between 0.5 and −1.0 V and then held at −0.2 V for 10 min, followed by sonication in ACN for 5 min. The electrodes modified with biphenyl, 1-naphthyl, 2-naphthyl, and 4-bromophenyl groups are designated as Au/BP, Au/Naph1, Au/Naph2, and Au/PhBr, respectively. Assessment of the surface coverage of Au/PhBr film was performed by cyclic voltammetry in Ar-saturated 0.5 M H_2SO_4 by cycling the Au/PhBr electrode between −0.3 and 1.5 V [28,42].



Scheme I. Chemical structures of the diazonium salts used.