OH⁻ radical degradation of blocking aryl layers on glassy carbon and gold electrodes leads to film thinning on glassy carbon and pinhole films on gold

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ARTICLE INFO

Article history:
Received 18 December 2012
Received in revised form 8 January 2013
Accepted 8 January 2013
Available online 17 January 2013

Keywords:
Diazonium salts
Azobenzene derivatives
Hydroxyl radicals
Hexacyanoferrate

ABSTRACT

Aryl layers on glassy carbon and gold electrodes were degraded by hydroxyl radicals from UV photolysis of hydrogen peroxide. The electrode surfaces were modified via electrochemical reduction of two structurally different azobenzene diazonium derivatives. The degradation of the aryl films was studied by AFM, XPS and electrochemical measurements using [Fe(CN)₆]⁴⁻ as solution probe. While the prepared aryl layers inhibited the electrochemical response of hexacyanoferrate, their degradation with OH⁻ radicals resulted in different electrochemical behaviours for glassy carbon and Au electrodes. The aryl layer on glassy carbon was thinned, indicated by the increasing reversibility of the [Fe(CN)₆]⁴⁻ response, whereas the aryl film on Au showed pinhole formation, indicated by the microelectrode behaviour of the hexacyanoferrate response without retarded reversibility.

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1. Introduction

The hydroxyl radical (OH⁻) is a highly reactive species degrading almost all kinds of organic compounds. They are used in advanced oxidation processes for removal or degradation of pollutants, e.g., azo compounds (dyes), in different wastewaters. OH⁻ radicals can be produced by Fenton reactions or UV photolysis of water and hydrogen peroxide. In the Fenton process, OH⁻ radicals are generated in acid media from H₂O₂ in the presence of Fe²⁺ ions [1]. Besides the removal of dyes [2], Scholz et al. [3] showed that self-assembled monolayers (SAMs) of thiols on gold and mercury electrodes are degraded by OH⁻ radicals. They are also able to remove surface asperities from mechanically polished gold electrodes [4] whereby active centres are knocked out [5].

The electrochemical reduction of aryldiazonium salts on carbon electrodes forms strong covalent bonds between the aryl layer and the carbon surface [6,7]. However, there is still a controversy about the nature of the bonding to gold surfaces. Evidently, compared with alkanethiol-based SAMs, the aryl layers derived from the corresponding diazonium salts are more stable and the bonding of the organic layer to the Au surface is stronger [8–10]. Therefore it would be highly interesting to see how the treatment with OH⁻ radicals could affect the aryl layers derived from the corresponding diazonium compounds.

Since aryl layers on glassy carbon (GC) and Au inhibit the response of hexacyanoferrate in aqueous solution, it was the goal of this study to follow the degradation of the aryl layer by OH⁻ radicals. The latter were generated by UV photolysis of H₂O₂, and the electrodes with degraded films were characterised by electrochemical measurements, X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). Two azobenzene derivatives (Fast Garnet GBC sulphate salt and Fast Black K salt) were used for electrografting of GC and Au surfaces analogously to previously published procedure [11,12].

2. Experimental

Glassy carbon and polycrystalline Au electrodes were prepared by mounting GC (GC-20SS, Tokai Carbon) and Au discs (99.99%, Alfa Aesar) into Teflon holders. The geometric area of the electrodes was 0.2 cm². Prior to surface modification, the GC and Au electrodes were polished with 1.0 and 0.3 μm alumina slurries (Buehler) and additionally with 0.05 μm alumina slurry in case of Au electrodes. Thereafter the electrodes were sonicated in Milli-Q water (Millipore, Inc.), isopropanol (Sigma-Aldrich) and acetonitrile (HPLC grade, Sigma-Aldrich) for 5 min. The polished Au electrodes were cycled between −0.3 and 1.5 V at a scan rate (v) of 100 mV s⁻¹ in N₂-saturated 0.5 M H₂SO₄ (Suprapur, Merck) for surface cleaning.

The surface modification of GC and Au electrodes was performed by electrochemical reduction of the diazonium salts (GC: 1 mM, Au: 3 mM solutions in acetonitrile containing 0.1 M tetrabutyrammonium tetrafluoroborate (Fluka) as supporting electrolyte). The diazonium compounds Fast Garnet GBC sulphate salt (Sigma-Aldrich) and Fast Black K salt (Sigma) were used. The GC and Au electrodes were cycled between 0.6 and −0.4 V for 10 potential scans at 100 mV s⁻¹ in order to attach 2-methyl-4-[(2-methylphenyl)azo]benzene (GBC) and 2,5-dimethoxy-4-[(4-nitrophenyl)azo]benzene (FBK) groups to the
electrode surfaces. The modified electrodes are designated here as GC/GBC, GC/FBK, Au/GBC and Au/FBK. Electrodes were cleaned from physically adsorbed material by sonication in acetonitrile for 3 min.

The aryl-modified surfaces were then treated with OH \(^-\) radicals generated by UV photolysis of a 10% \(\text{H}_2\text{O}_2\) solution (Merck) with the help of a high-pressure mercury lamp (500 W). The solutions were housed in quartz test tubes. The disc electrodes used for electrochemistry were positioned in such a way that only some diffuse stray radiation could shine on the electrode surface. In case of the electrodes for AFM the modified surface was not irradiated at all.

The aryl-modified and \(\text{H}_2\text{O}_2/\text{UV}\) treated GC and Au electrodes were characterised by cyclic voltammetry (CV) in \(\text{N}_2\)-saturated 0.1 M \(\text{K}_2\text{SO}_4\) containing 1 mM \(\text{K}_4[\text{Fe(CN)}_6]\). An Autolab potentiostat/galvanostat PGSTAT30 (Eco Chemie B.V., The Netherlands) with a three-electrode cell configuration, saturated calomel electrode (SCE) as reference and Pt wire as counter electrodes, were used. All potentials are given with respect to the SCE.

XPS and AFM studies were performed only with GBC and FBK modified Au substrates (Schröer GmbH, Lienen, Germany) before and after the OH \(^-\) radical attack. These Au/glass substrates were annealed in a butane flame until a weak dark-red glowing of the surface appeared. After this they were cooled down to room temperature in a \(\text{N}_2\) stream, in order to get flat gold terraces with preferential Au\{111\} orientation. The AFM measurements were carried out with a DualScope 95-50 microscope (DME, Denmark) in non-contact mode using the Software DME Scan Tool Version 1.2.1.0. The XPS experiments were performed with a SCIENTA SES-100 spectrometer using an unmonochromated Mg K\(_\alpha\) X-ray source (incident energy = 1253.6 eV), a take-off angle of 90\(^\circ\) and a source power of 300 W.

### 3. Results and discussion

The GBC and FBK layers were reproducibly electrografted on GC and Au electrodes. The electrografting scans for GC and Au surfaces (data not shown) were similar to that previously reported\[11,12\]. In all cases, the reduction currents decreased during consecutive potential cycles indicating the growth of a blocking aryl layer.

The GC/GBC, GC/FBK, Au/GBC and Au/FBK electrodes were treated with OH \(^-\) radicals formed in UV photolysis of \(\text{H}_2\text{O}_2\), first using a 10% \(\text{H}_2\text{O}_2\) solution and a UV treatment time of 1 min. Since the effect of a 1 min treatment was very small, in further experiments 5 min photolysis times were used and these 5-minute-treatments were repeated to follow the degradation over a longer period.

The grafted aryl layers on GC completely blocked the response of the \([\text{Fe(CN)}_6]^{4-}\) probe. During the degradation of the layers by OH \(^-\) radicals the response returned, accompanied by an increasing electrochemical reversibility (Fig. 1a, c) as indicated by a decrease of CV peak potential difference (\(\Delta E_p\)) from 0.32 V to 0.12 V in case of GC/GBC electrodes, after 10 and 25 min treatment time, respectively. The CVS exhibited the typical response of planar infinite diffusion\[13\].

The shape of CVS for aryl-modified Au electrodes was rather sigmoidal which is in good agreement with our earlier report\[12\]. Furthermore, in the course of degradation of the aryl layers by OH \(^-\) radicals, the shape of the CVS was kept constant and exhibited the sigmoidal signals typical for microelectrode arrays and an electrochemically reversible couple (Fig. 1b,d). The microelectrode behaviour taken together with the full electrochemical reversibility of \([\text{Fe(CN)}_6]^{4-}\) can be explained by the formation of pinholes in the film which act as microelectrodes.

![Fig. 1. Cyclic voltammograms of bare and aryl-modified electrodes and after treatment with OH \(^-\) radicals for various time periods: (a) GC/GBC, (b) Au/GBC, (c) GC/FBK and (d) Au/FBK electrodes in \(\text{N}_2\)-saturated 0.1 M \(\text{K}_2\text{SO}_4\) containing 1 mM \(\text{K}_4[\text{Fe(CN)}_6]\). \(\nu = 100\) mV s\(^{-1}\).](image-url)
In case of the films on GC, the degradation obviously leads to a thinning (decreasing thickness) of the aryl film without pinhole formation. The continuous thinning of the aryl layer improved the electrochemical reversibility of [Fe(CN)₆]⁴⁻, practically shifting from complete irreversibility to an almost complete regained of reversibility. This behaviour strongly reminds to the effect of alkyl chain length of SAMs on the reversibility of dissolved redox probes [14], and corroborates the interpretation that the OH radicals are thinning the film. According to recent reports it is reasonable to assume that the aryl layers on GC electrodes are more closely packed than on Au and therefore the blocking effect is stronger on GC [9, 15].

To obtain more information about the degradation process, the elemental composition of aryl films before and after OH radical attack was investigated for the Au/GBC and Au/FBK electrodes by XPS (Fig. 2). First, the formation of the GBC and FBK layers on Au surface was confirmed. The survey spectrum revealed the presence of nitrogen (N1s), oxygen (O1s), carbon (C1s) and gold (Au4f, Au4d) on the electrode surface. The XPS peak at 406 eV was detected for both modifiers and it is attributed to azo groups (Fig. 2a, c insets). Moreover, the attachment of FBK groups on Au electrode was further confirmed by the peak at 406 eV, which corresponds to nitro groups (Fig. 2c inset). These results are in agreement with earlier observations using different substrates along with gold [11, 12, 16]. As can be seen in Fig. 2b, d, no XPS peak in the N1s region was detected for GBC and FBK grafted Au electrodes after 10 and 5 min of H₂O₂/UV treatment. This indicates that after the OH radical treatment for that time period, the aryl layers were degraded so much that XPS could not detect the film residue. The electrochemical measurements showed that these aryl layers on Au behaved like a microelectrode array with the electron transfer occurring at the gold/solution interface at the bottom of the pinholes. Mixed SAMs on gold have shown a similar behaviour [17]. In current work, after a 5 min of H₂O₂/UV treatment, a sigmoidal CV response was obtained for the Au/GBC electrode (Fig. 1b) and the pinholes of the film were confirmed by AFM measurements. Fig. 3 presents the AFM images of the GBC and FBK modified Au electrodes before and after the OH⁻ attack. Fig. 3a shows an AFM micrograph of a GBC covered gold surface: the GBC film has a granular structure. Fig. 3b depicts the surface after 5 min of OH⁻ attack. Small holes in the polymer are clearly detectable (see the marks). After further 5 min attack (Fig. 3c) the film was obviously extremely thin and only the fact that the Au crystallites underneath could not yet be seen and some remaining grains of polymer on the surface can be taken as a proof of its existence. This explains the above mentioned XPS results. Fig. 3d shows the FBK covered gold surface before OH⁻ attack. Also this film is rather granular, although less pronounced, and probably very thin, since the grain boundaries of the Au crystallites are still visible. With the help of AFM measurements the thickness of the formed FBK layer during modification was determined as follows: one part of an annealed gold surface was covered by a polysiloxane layer and the gold surface was modified with FBK in the described way. After the cleaning process the silicon layer was removed and the thickness of the FBK layer was determined by AFM as 38 nm. Fig. 3e presents the FBK film after 5 min of H₂O₂/UV treatment. The aryl film appears to be similar like the GBC film after 10 min of OH⁻ attack. The invisibility of the typical Au[111] triangle structures indicates that a very thin film is still present.

4. Conclusions

We have shown here that aryl films on GC and Au electrodes can be degraded by OH⁻ radicals. Most interestingly, the degradation of

![Fig. 2. XPS spectra for: (a) Au/GBC, (b) Au/GBC after 10 min of H₂O₂/UV treatment, (c) Au/FBK, and (d) Au/FBK after 5 min of H₂O₂/UV treatment. The insets show the XPS spectrum in the N1s region.](image-url)
the films on these two substrates follows two different pathways: the thickness of aryl layers on GC is decreased by OH• and the reversibility of the dissolved redox probe [Fe(CN)₆]⁴⁻ is returning, whereas aryl film on Au shows a degradation with pinhole formation, so that the electrode exhibited microelectrode behaviour and reversibility of [Fe(CN)₆]⁴⁻. These observations allow us to assume that the treatment of blocking surface films with OH• radicals may be a versatile tool to produce arrays of microelectrodes, and in other cases, the tuning of the reversibility of electrode systems is feasible.

Acknowledgements

This research was supported by the Estonian Science Foundation (Grant No. 9323) and by a grant of the Rector of the University of Greifswald for supporting the cooperation with Baltic countries.

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