



Surface and electrochemical characterization of aryl films grafted on polycrystalline copper from the diazonium compounds using the rotating disk electrode method



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ARTICLE INFO

Keywords:

Electrografting
Diazonium salts
Copper electrode
Oxygen reduction
Ferricyanide reduction
Rotating disk electrode

ABSTRACT

In this paper, aryl films are grafted via electrochemical reduction of two different diazonium salts, 4-nitrobenzenediazonium tetrafluoroborate and Fast Red AL salt, in different conditions on polycrystalline copper electrodes. For the surface modification, “normal” electrografting, redox grafting (RG) and for the first time, RG and rotating disk electrode combined method are used. The obtained aryl films are characterized by X-ray photoelectron spectroscopy and atomic force microscopy. Surface concentrations of redox active moieties are determined in acetonitrile and highest values of ca. 25 and 12 nmol cm⁻² are obtained in case of nitrophenyl and anthraquinone films, respectively. Different aryl films exhibit unequal blocking action toward ferricyanide probe and also variable degree of inhibition of the O₂ reduction rate.

1. Introduction

The research of aryldiazonium salts and their practical applications has very rich and versatile history [1,2]. Since the first demonstration in 1992 [3], the reduction of diazonium salts has been frequently employed for the covalent modification of surfaces [1,2]. In short, during this process aryldiazonium cation (R-N₂⁺) is reduced to highly reactive aryl radical (R·) which bonds to the surface of a substrate material [2]. The reduction of R-N₂⁺ can be induced electrochemically or by non-electrochemical method (e.g. reducing surfaces or chemical agents). In the latter case, usually monolayer or thin modifier films are obtained and the control over the film growth is complicated [2]. By using the “normal” electroreduction method [4], thicker modifier films and more efficient control over the film growth can be achieved [5]. Nevertheless, the thickness of the aryl film on the electrode does not exceed usually 10 nm using the “normal” electrografting method because of the restricted electron transfer between the electrode and R-N₂⁺ [4,6,7].

To overcome the problem (electron transfer restriction), the redox grafting (RG) method has been presented, in which aryldiazonium salts with the redox active moieties (e.g. nitro, quinone) are employed and the electrode is cycled over the redox potential of the redox active moiety [4,6,7]. By doing this, the electron transfer in the film does not

become restricted and enables the film growth up to 900 nm for example in case of Au electrode modified with nitrophenyl (NP) groups [6]. The film growth can be additionally promoted by the combination of RG and rotating disk electrode (RDE) methods [8]. By using the combined method, the surface concentrations of electroactive species have been achieved 2 to 3 times higher on the Au and glassy carbon (GC) electrodes electrografted with anthraquinone (AQ) groups compared to the electrodes modified only by the RG method [8]. Until now, several electrode materials with different properties have already been electrografted using the RG method: GC [4,6,9,10], Au [4,6,7], stainless steel (SS) [6,11,12], Ni [13], highly oriented pyrolytic graphite (HOPG) [10], chemical vapor deposition (CVD)-grown graphene [10,14]. Furthermore, the combination of RG and RDE method has been used to prepare thick AQ films on GC and Au electrodes [8], however no information could be found about the use of RG and RDE combined method for modification of Cu electrode.

Cu is one of the most important materials in the industry and therefore, the inhibition of its corrosion is challenging [15,16]. Recently, for the corrosion protection quite different coatings (e.g. thiol-based self-assembled monolayers (SAMs) [17], adsorbed caffeic acid [18], polyaniline/zeolite nanocomposite [19], polypyrrole [20]) on Cu have been studied. The aryl films obtained by the reduction of

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aryldiazonium salts have also been proposed to be suitable for the corrosion protection [21,22]. In addition, thick organic films could be beneficial for the development of sensors and supercapacitors [6,7]. For the record, copper electrodes have already been grafted with AQ and NP films via the reduction of aryldiazonium cations using the spontaneous [21,23–26], electrochemical (via “normal” electrografting) [15,27,28], and photochemical [29] approach. Furthermore, it has been demonstrated by Bernard et al. that the redox waves of nitrobenzene and AQ molecules can be registered on Cu electrode in acetonitrile solution [30]. But there is no information about the aryl film formation in varied electrografting conditions and no electrochemical characterization of the blocking behavior of the obtained films. The oxygen reduction reaction (ORR) can be used for studying the blocking behavior of the aryl films on the surface of Cu electrodes. The reduction of O₂ on Cu electrodes proceeds predominantly via 4-electron pathway in a broad pH range [16,31–37].

The aim of the present work is to electrochemically graft anthraquinone and nitrophenyl groups on the surface of Cu electrodes via diazonium reduction. For the aryl film formation RG method and in addition, the RG and RDE combined methods in varied conditions are employed. To our knowledge, this is the first time the combination of RG and RDE method is applied for the modification of Cu electrodes via the reduction of aryldiazonium salts. The prepared aryl films are characterized by physical and electrochemical methods. Since no comparative information is available in the literature about ferricyanide reduction on bare and aryl-modified polycrystalline Cu electrodes, then herein, the electrochemical properties of bare and aryl-modified Cu toward the ferri/ferrocyanide redox probe are investigated. The electroreduction of O₂ on bare and aryl-modified Cu electrodes is also studied. To our knowledge, the ORR has not been studied before on Cu electrodes functionalized with AQ or NP films via reduction of aryldiazonium salts.

2. Experimental

2.1. Electrochemical grafting of Cu electrodes with aryl groups

In the present work, polycrystalline Cu electrodes with geometric area (A) of 0.196 cm² were employed. The electrodes were prepared by mounting the Cu disks (99.999% Cu, Puratronic®, Alfa Aesar) into Teflon® sheath. The Cu electrodes were polished on SiC paper with consecutive grits (600, 1200 and 4000, Buehler) and then with 1.0 and 0.3 μm alumina slurries (Buehler). For removing the polishing debris, an ultrasonic bath was used; the electrodes were sonicated in Milli-Q water (Millipore, Inc.) and acetonitrile (ACN, 99.8%, anhydrous, Sigma–Aldrich) for 5 min in each solvent. Prior to electrografting the polished Cu electrodes were immersed into CH₃COOH (99.8%, puriss p.a., Sigma–Aldrich) for 30 s and rinsed with Milli-Q water [21,24,38].

The electrografting process was carried out in Ar-saturated (99.999%, AGA) anhydrous ACN solution containing 3 mM corresponding diazonium salt and 0.1 M tetrabutylammonium tetrafluoroborate (TBABF₄, dried under vacuum for 12 h, Fluka) as a supporting electrolyte. The used diazonium salts were Fast Red AL (FRA, Sigma–Aldrich) and 4-nitrobenzenediazonium tetrafluoroborate (NBD, 97%, Aldrich); the procedures for the Cu surface modification are given in Table 1. For the electrografting and electrochemical measurements, an Autolab PGSTAT30 potentiostat/galvanostat (Metrohm-Autolab, The Netherlands) was used and controlled with General Purpose Electrochemical System (GPES) software. To conduct the rotating disk electrode (RDE) experiments, the CTV101 speed control unit (Radiometer) and an EDI101 rotator were employed. After electrochemical functionalization with aryl groups, the modified electrodes were sonicated in ACN for 5 min to remove the physically adsorbed compounds.

2.2. XPS experiments

For the X-ray photoelectron spectroscopy (XPS) studies, the 11 × 11 mm² Cu (99.999%, extra pure) plates were employed. The electrografting of the Cu plates was performed by the same procedures as described in Section 2.1 (Table 1). For the XPS measurements, the SCIENTA SES-100 spectrometer was employed with an 300 W unmonochromated Mg K_α X-ray source, incident energy = 1253.6 eV, electron take-off angle 90°. During the experiments pressure below 10^{−9} Torr was maintained in the analysis chamber. Different step sizes, 0.5 eV for the high-resolution and 0.1 eV for the survey spectra were used with the pass energy of 200 eV.

2.3. AFM experiments

The atomic force microscopy (AFM) experiments were conducted with the same electrodes as described in Section 2.1. AFM experiments were carried out with a multimode AFM Autoprobe CP II (Veeco). All images were recorded in non-contact mode using HA-HR (NT-MDT) series cantilevers under ambient conditions. The Gwyddion free software ver. 2.44 (Czech Metrology Institute) was employed for the image processing using the first-order flattening for background slope removal. If necessary, the contrast and brightness were adjusted. For thickness measurements, AFM was used in contact mode to scratch off the modifier layer. The scanning continued until a typical image of a clean electrode surface was obtained. Then the height difference was measured in non-contact mode.

2.4. Electrochemical measurements

The blocking behavior of different aryl films on the Cu electrodes was studied using cyclic voltammetry (CV) and the RDE method. The ferri/ferrocyanide redox probe experiments with bare and grafted copper electrode were carried out in Ar-saturated aqueous solution of 0.1 M KOH (puriss p.a., Sigma-Aldrich) containing 1 mM K₃Fe(CN)₆ (ACS reagent, Aldrich). The reduction of O₂ was studied in O₂-saturated (99.999%, AGA) aqueous solution of 0.1 M phosphate buffer (pH = 7) containing 0.1 M NaClO₄ × H₂O (pro analysi, Merck). The background was recorded in Ar-saturated solution. The buffer solution was prepared from Na₂HPO₄ (puriss p.a., Fluka) and KH₂PO₄ (pro analysi, Merck). For the determination of the amount of redox active groups within the aryl film, cyclic voltammograms were recorded in Ar-saturated anhydrous ACN containing 0.1 M vacuum dried TBABF₄. Saturated calomel electrode (SCE) was employed as the reference electrode and all the potentials presented in the paper are given with respect to the SCE. Pt foil was used as the counter electrode; during the electrochemical measurements a continuous flow of gas passed through the electrolyte cell and the experiments were conducted at ambient temperature (23 ± 1 °C). For all presented electrochemical data, the experiments were repeated at least three times to ascertain the consistency of the results.

3. Results and discussion

3.1. Electrografting of copper electrodes with aryl groups

Firstly, cyclic voltammogram between −0.35 and −2.0 V was recorded in ACN containing 3 mM corresponding diazonium salt (FRA or NBD) and 0.1 M TBABF₄. In case of FRA, two redox waves with the redox potentials (E_r) of −0.88 and −1.52 V were observed (Fig. S1a in the Supplementary material). The first redox wave corresponds to the AQ/AQ^{•−} redox couple and the second one to the AQ^{•−}/AQ^{2−} redox couple [39]; both waves have been also recorded on a Cu electrode in ACN solution containing AQ molecules [30]. In NBD containing solution only a single redox wave with E_r of −1.19 V was observed (Fig. S1b), which has been also registered previously on Cu in nitrobenzene

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