



Microelectrochemical patterning of gold surfaces using 4-azidobenzediazonium and scanning electrochemical microscopy

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ABSTRACT

This work describes for the first time the possibility of performing local micro electrochemical grafting of a gold substrate by 4-azidobenzediazonium by SECM in a single and simple one step without complications from adsorption. The electrografted spots of diazonium were performed by positioning a Pt tip at a given distance above the gold substrate and the SECM was used in a three-electrode configuration (the Pt tip serving as the microanode) in acetonitrile containing 9 mM 4-azidobenzediazonium and 0.1 M Bu₄NBF₄ during 10 ms. The dimensions of the derivatized areas of the substrates were finely tuned by using different experimental conditions (tip distance above the substrate, tip diameter, presence or absence of supporting electrolyte). The use of the azido-derivatized diazonium molecule and these preliminary results open the gate to important applications and developments devoted to the local micro functionalization of electrodes by thin layers that allow the implementation of the emerging and attractive interfacial click reaction.

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1. Introduction

Among the methods of surface modification, electrochemical functionalization is one of the simplest and it is a relatively low-cost technique. As a common example of this method, the electrografting of aryldiazonium salts has been shown to efficiently form stable thin organic layers on several kinds of substrates [1–9]. For example, the use of suitable diazonium salts has been successfully applied to the development of biosensors, biochips and immobilization of enzymes [10–12]. But several studies have also now unambiguously shown the occurrence of a spontaneous adsorption of diazonium species on carbon, gold and copper surfaces from acetonitrile and aqueous solutions [13–19], which may however prevent the precise control of further electrochemical grafting. Thus, the use of diazonium salts for the microstructuring of surfaces by ultramicrotechniques such as scanning electrochemical microscopy (SECM) is restrained owing to the spontaneous derivatization of exposed surfaces. To date, only one example was recently reported on direct electrochemical patterning of a diazonium salt via a one-pot sequential reaction for local electro-generation of the diazonium salt, followed by its electrografting on the substrate [20]. Although this alternative strategy allowed circumventing of the spontaneous adsorption of the diazonium salt on the substrate, the technical protocol needs precise control of the multi step procedure. Indeed, the efficiency of the strategy strongly depends on

the kinetics of the diazotization reaction and the electroreduction of the obtained diazonium salt can also occur at the SECM tip and block the micro grafting process. Besides this approach, one can cite the drawing of patterns of a thin passivating layer on gold electrode surface by electrochemical reduction of an arylidonium salt at very negative potential values by SECM [21].

The search for a local electrochemical strategy with minimized spontaneous adsorption phenomenon and accurate control of substrate surface led us to combine the use of 4-azidobenzediazonium tetrafluoroborate and SECM. The use of 4-azidobenzediazonium tetrafluoroborate offers two major advantages afforded by the azide substituent: (i) its kinetics of adsorption is slower than the commonly used diazonium salts [22,23] and (ii) it offers an emerging attractive and efficient way of further chemical functionalization of the electrografted surface through the well known Sharpless copper(I) catalyzed azide-alkyne cycloaddition reaction [22]. Herein, we perform for the first time the microelectrochemical patterning of gold surfaces by application of SECM in three-electrode configuration using 4-azidobenzediazonium with a very simple approach. The micro patterned surfaces were characterized by SECM approach curve and SECM imaging in feedback mode.

2. Experimental

2.1. Chemicals

All chemicals (reagent grade from Aldrich) were used without further purification. MilliQ water was used to prepare all the aqueous

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