

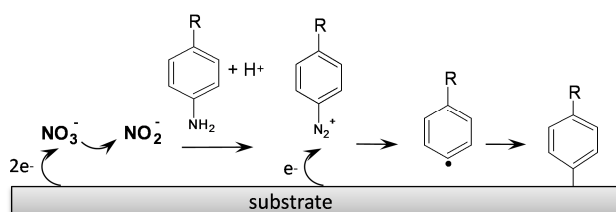
Localized Diazonium Ions Generation Based on the Electrocatalytic Formation of Nitrite

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The covalent modification of surfaces by the electrochemical reduction of aryl diazonium salt has attracted a lot of interest in the past two decades.^{1,2} The high efficiency of this procedure is counterbalanced by a relative instability of some diazonium ions³ and by the spontaneous reduction of the diazonium ions at the electrode surface which is subsequently modified.⁴ Therefore, it is important to develop new methods for the localized functionalization of surfaces. Methods of interest include the local generation of diazonium ions and the reactive corresponding radicals by electrochemical reduction of the corresponding nitro derivative to an amine,⁵ and from aryltriazenes.⁶

Here, we wish to report a new one-step potentiostatic approach for the localized generation of diazonium cations in the diffusion layer of an electrode surface by taking advantage of the electrocatalytic properties of the electrode for the formation of the diazotization agent (nitrite).



Scheme 1. Mechanism suggested for aryl group electrografting by exploiting the electrochemical reduction of nitrate to nitrite to initiate diazotization.

Scheme 1 shows that nitrite anions formed by electrochemical reduction of nitrate in acidic solution⁷ can immediately react with an arylamine to produce the corresponding diazonium cations. The latter can be electrochemically reduced at the electrode surface if the nitrate reduction potential is more negative than the potential required for the electrochemical reduction of the diazonium ions.

The mechanism of the electrode reaction was investigated by cyclic voltammetry at, glassy carbon, gold and copper electrodes in presence of diazonium ions in-situ formed by adding directly nitrite anions to the electrolyte and generating locally nitrite anions was performed. For these electrode materials, the nitrate reduction is highly catalyzed (Cu), poorly catalyzed (carbon) or non-catalyzed (Au). Hence, copper and glassy carbon electrodes act as electrocatalyst for the generation of nitrite anions and could be functionalized by electrochemical reduction of in-situ generated aryl diazonium ions. Electrochemical and X-ray photoelectron spectroscopy analyses were used to confirm the presence of aryl groups on the surface of substrates.

It is also demonstrated, that this approach can be successfully applied for the selective functionalization of one component of two-component electrodes. Due to the different electrocatalytic activity of the electrodes for

nitrate reduction, copper can be selectively functionalized on Cu-Au or Cu-glassy carbon substrates.

Since conducting substrates have different activity for the nitrate reduction⁸ and considering the wide range of reduction potential of substituted diazonium ions¹ it seems that the approach reported herein is versatile and potentially useful for selective surface functionalization and for biosensing and microelectronic applications.^{1,9}

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