In-situ generation of diazonium cations for electrochemical modification of carbon surface

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The electrochemical and chemical modification of carbon by reduction of diazonium salts attracted a lot of interest in the past decade. The major disadvantage of the modification approach based on aryl diazonium salt is that the synthesis of the salt is required. Indeed, the synthesis and isolation of the diazonium salt are not always straightforward. The synthesis is commonly carried out in acidic media from the corresponding amine by using NaNO2 as a reactant. On the other hand, it might be interesting to have a modification procedure that will avoid this synthesis by using the amine as a precursor. In this work, we have achieved the derivatization of a glassy carbon electrode surface by electrochemical reduction of several in-situ generated diazonium cations. The diazonium cations were synthesized in the electrochemical cell by reaction of the corresponding amines with NaNO2 in aqueous HCl. The versatility of the method was demonstrated by using several diazonium cations. This deposition method, which involves simple reagents and does not require the isolation and purification of the diazonium salt, enabled the grafting of covalently bounded layers which exhibited properties very similar to those of layers obtained by the classical derivatization method involving isolated diazonium salt dissolved in acetonitrile or aqueous acid solution. Cyclic voltammetry and electrochemical impedance spectroscopy carried out in aqueous solutions containing electroactive redox probe molecules such as Fe(CN)6^{3-}/4- and Ru(NH3)6^{3+}/4+ confirmed the barrier properties of the deposited layers. The chemical composition of the grafted layers was determined by X-Ray photoelectron spectroscopy and surface coverage in the range 3 to 6×10^{-10} mol cm^{-2} was estimated for films grown in our experimental conditions.