Characterization of organic coating grafting on metals and carbon surface via electrochemical reduction of diazonium salts

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Interest in surface modification and derivatization is growing in the fields of material science, catalysis, chemical and biological sensing, molecular electronic, corrosion protection… A recent approach involving the electrochemical reduction of aryldiazonium salts[1] led to the synthesis of thin layers (thickness in the nanometer range) on to a large variety of materials such as carbon, Pt, Au, Si, Fe, Zn[1-5]… This procedure involves the formation of a covalent bond to the electrode according to scheme 1 when R is a substituent such as nitro, caboxy, fluoro…

Recently surface grafting via electrochemical reduction of aryldiazonium salt has been mentionned for various applications in numerous papers. Thus a complete understanding of the deposition and the structure of these layers is required for their successful applications. It was currently proposed that a covalently bound monolayer was obtained on electrode surface[6-7]. However Kariuki at al.[8-9] have investigated the binding of diethylamine radicals on HOPG or on glassy carbon electrodes. Their works indicated that aryl multilayers can be obtained.

The purpose of this work is to examine and to control the structure of the organic layer grafted on various electrodes: Fe, Au, Pt and glassy carbon (GC). The deposition of 4-nitrobenzene is investigated with the use of cyclic voltametry, the infrared reflectance absorption spectroscopy and the X-ray photoelectron spectroscopy.

The growth of the layer is tracked in situ by quartz micobalance and ex situ by atomic force microscopy. The grafting of the aryl layer to various electrode can be achieved via chronoamperometry or cyclic voltametry.

Infrared spectroscopy clearly showed that NO_2 groups and aromatic are present on the grafted electrodes surface (figure 1). The investigation of the structure have been completed by XPS.

The quartz microbalance studies indicated that multilayer films are formed on electrodes from the reduction of nitrobezenediazonium salt. The growth rate and the stability of the coating is dependent on the overpotential applied during the grafting. These results are corroborated by the AFM imaging.

Scheme 1

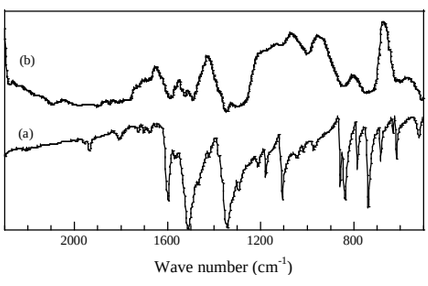

Figure 1
FTIR spectra of (a) Au grafted with 4-nitrophenyl groups and (b) 4-nitrobenzène diazonium tetrafluoroborate

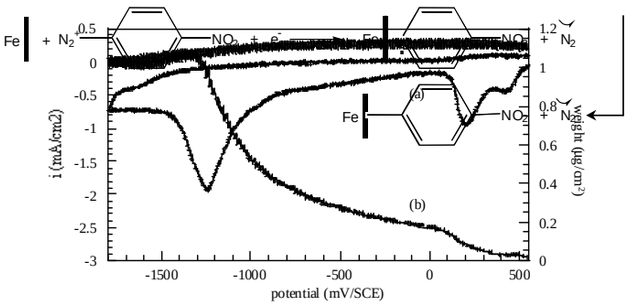

Figure 2
Cyclic voltametry of a gold electrode in a 2 mM solution of 4-nitrobenzene diazonium tetrafluoroborate in CH_3CN + Nbu_4BF_4 0.1M (a) Voltammogram, (b) weight variation using quartz microbalance

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