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Full Length Article

XPS and NRA investigations during the fabrication of gold nanostructured functionalized screen-printed sensors for the detection of metallic pollutants

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ABSTRACT

An all covalent nanostructured lead sensor was built by the successive grafting of gold nanoparticles and carboxylic ligands at the surface of self-adhesive carbon screen-printed electrodes (SPEs). Surface analysis techniques were used in each step in order to investigate the structuration of this sensor. The self-adhesive surfaces were made from the electrochemical grafting of *p*-phenylenediamine at the surface of the SPEs *via* diazonium salts chemistry. The quantity of grafted aniline functions, estimated by Nuclear Reaction Analysis (NRA) performed with *p*-phenylenediamine labelled with ^{15}N isotope, is in agreement with an almost complete coverage of the electrode surface. The subsequent diazotization of the aniline functions at the surface of the SPEs was performed; X-ray Photoelectron Spectroscopy (XPS) allowed us to consider a quantitative conversion of the aniline functions into diazonium moieties. The spontaneous grafting of gold nanoparticles on the as-obtained reactive surfaces ensures the nanostructuration of the material, and XPS studies showed that the covalent bonding of the gold nanoparticles at the surface of the SPEs induces a change both in the Au-*4f* (gold nanoparticles) and Cl-*2p* (carbon ink) core level signals. These unusual observations are explained by an interaction between the carbon ink constituting the substrate and the gold nanoparticles. Heavy and toxic metals are considered of major environmental concern because of their non-biodegradability. In a final step, the grafting of the carboxylic ligands at the surface of the SPEs and an accumulation step in the presence of lead(II) cations allowed us to evidence the interest of nanostructured materials as metallic pollutants sensors.

1. Introduction

Nanostructuration proved to be an efficient way to improve the performances of biological and chemical sensors [1,2]. Gold nanoparticles are particularly widely used because of their easy functionalization, high electrical conductivity and interesting catalytic, optical and electrochemical properties [3,4]. Various strategies have been applied in order to fix them on sensor surfaces, such as adsorption [5–8], entrapment in a polymer matrix [9,10], chemical affinity with thiols [11] and amines [12], etc. Among these methods, the use of diazonium salts offers the advantage of a simple grafting process leading to a covalent bonding onto various substrates. The use of diazonium salts for the anchoring of various nanomaterials on substrates has been reviewed recently [13]. Different strategies can be applied, such as the use of aniline-functionalized nanoparticles electrografted at an electrode surface [14] or the use of reactive surfaces bearing diazonium functions, so-called self-adhesive surfaces [15], for the immobilization of various nanomaterials including AuNPs [16]. These surfaces are made starting from the grafting of *p*-aminophenyl diazonium salt at the electrode surface, then the conversion of the remaining amine function may be easily realized, allowing further covalent immobilization of nanomaterials (Fig. 1). The key parameter for the fabrication of the nanostructured material is the anchoring of the

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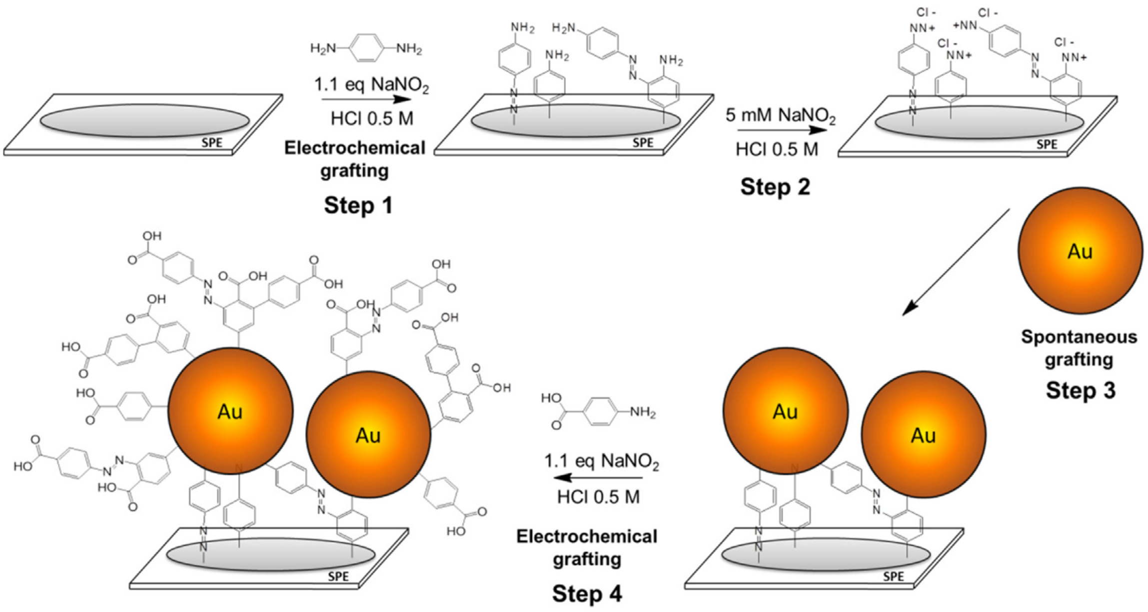

Fig. 1. Reaction scheme showing the different steps for the covalent grafting of AuNPs onto SPEs using diazonium salts chemistry.

AuNPs at the electrode surface, *e.g.* their number or the nature and robustness of the linkage, etc. However, very few studies deal with nanostructured materials made by a multi-step functionalization. As both the robustness of the sensor and its electrochemical behavior are dependent of the nature of the connexion between the nanoparticles and the surface, a good knowledge of the interface is crucial. Gooding et al. showed that the thickness and uniformity of the organic layer between the substrate and the AuNPs can affect the efficiency of electron transfer between the nanoparticles and the electrode surface [17]. Our group has recently used self-adhesive surfaces in order to develop highly nanostructured screen-printed electrodes (SPEs) for lead electrochemical sensing [18]. The size and the surface properties of the AuNPs used, as well as the choice of the grafting method, were key parameters that affected the electrochemical properties of the final functionalized SPEs. In this work, we investigate more specifically the structuration of the grafted organic layer as well as the nature of the interaction between the substrate and the AuNPs. An all covalent nanostructured lead sensor was built by spontaneous grafting of "Eah" AuNPs [19] at the surface of carbon SPEs; these nanoparticles were then functionalized by carboxylic ligands in order to ensure lead complexation. As shown in Fig. 1, four steps are required, *step 1*: the *in situ* generation of *p*-aminophenyl diazonium salt and its electrografting onto the SPE surface; *step 2*: the generation of a reactive surface by conversion of amine into diazonium functions; *step 3*: the anchoring of AuNPs by spontaneous reduction of the diazonium functions and *step 4*: the electrografting of the *in situ* generated *p*-carboxyphenyl diazonium salt at the nanostructured surface. The detailed synthesis of this nanocomposite material can be found in a previous article [18]. Here, surface analysis techniques, such as X-ray Photoelectron Spectroscopy (XPS) and Nuclear Reaction Analysis (NRA) were used in each step of the material fabrication to estimate the coverage of the SPEs by amino groups, the diazotization yield and the strength of the organic layer-AuNPs interactions. The grafting of the carboxylic ligands at the surface of the nanostructured material was also investigated. Finally, an accumulation step in the presence of lead (II) cations allowed us to evidence the higher complexation of metallic pollutants in the case of nanostructured SPEs.

2. Material and methods

2.1. Chemicals and reagents

Sulfuric and hydrochloric acid standard solutions (1 M) were purchased from Fluka; *p*-phenylenediamine, potassium chloride and tetrafluoroboric acid (48%) from Sigma; *p*-aminobenzoic acid, sodium borohydride from Aldrich; sodium nitrite from Acros Organics; hydrogen tetrachloroaurate (III) trihydrate from Alfa Aesar. All solutions were prepared with purified water ($18.2\,\mathrm{M\Omega\,cm^{-1}}$) from a milli-Q system from Millipore®. All solutions were deoxygenated with argon for 10 min and blanketed with an argon atmosphere during electrochemical analysis.

2.2. Synthesis of the AuNPs

Before the synthesis, all the glassware was washed with aqua regia and then thoroughly rinsed with purified water. AuNPs were synthesized according to the literature [16]. AuNPs with a diameter of 3–5 nm were obtained.

2.3. Preparation and modification of the SPEs

The working electrodes were carbon-based SPEs. SPEs were prepared according to Authier *et al.* [20] The working disk geometric area was of 10 mm^2. All electrodes were sonicated in a 0.1 M H_2SO_4 solution for 10 min then pretreated by cyclic voltammetry (4 scans at 0.1 V s^{-1} between −0.1 and 0.8 V) in a 0.1 M H_2SO_4 solution prior to use.

Modification of the SPEs by electrochemical reduction of *in situ* generated diazonium salt was achieved according to a method already described in the literature [21,22]. *p*-aminophenyl diazonium salt was obtained from *p*-phenylenediamine 2 mM in a 0.5 M HCl solution with 1.1 eq of $NaNO_2$. The electrochemical reductive modification of the SPE surface was then carried out by scanning in a potential range between 0 and −1.0 V for 5 cycles at a scan rate of 0.1 V s^{-1}. Once functionalized by the *p*-aminophenyl (SPE-Ph-NH_2), the electrodes were sonicated in a 0.1 M H_2SO_4 solution for 2 min.