



# Fabrication and characterization of all-covalent nanocomposite functionalized screen-printed voltammetric sensors



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## ABSTRACT

We report in this paper an all-covalent method to obtain highly nanostructured carbon screen printed electrodes (SPEs) bearing gold nanoparticles (AuNPs) functionalized by complexing groups using diazonium salts chemistry. SPEs were first modified with 4-aminophenyl functions (SPE-Ph-NH<sub>2</sub>). The amino moieties were then converted into diazonium salts (SPE-Ph-N<sub>2</sub><sup>+</sup> Cl<sup>-</sup>). These reactive SPEs were then used to immobilize AuNPs by electrochemical or spontaneous method. The spontaneous method proved to be a more efficient grafting approach. Two types of AuNPs suspensions were compared: AuNPs obtained via the well-known Turkevich method, citrate-stabilized and having a diameter of about 20 nm, and AuNPs obtained by the method recently described by Eah et al., stabilizer-free with an average diameter of 4 nm. We show that the size of the Au-NPs, their concentration and their surface properties are key parameters that affect the electrochemical properties of the final nanostructured SPEs. The covalent grafting of 4-carboxyphenyl ligands through diazonium chemistry, able to complex metallic cations, at the surface of SPE-Ph-AuNPs allowed their use for the detection of Pb(II). Electrochemical Impedance Spectroscopy, Cyclic Voltammetry, Scanning Electron Microscopy, Rutherford Backscattering and X-ray Photoelectron Spectroscopy were used to characterize these nanostructured materials.

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## 1. Introduction

The nanostructuring of electrodes is an area of research which is continually expanding. The grafting of metallic nanoparticles at the surface of electrodes offers new perspectives in several domains such as catalysis, electroanalysis, etc. Previous studies have shown that screen printed electrodes (SPEs) functionalized with diazonium salts bearing organic functions, able to bind metal cations, showed good sensitivity for trace metals electroanalysis [1–3]. The incorporation of conductive nanoparticles such as gold nanoparticles (AuNPs) in these electrode materials would offer several advantages: metal nanoparticles would promote electron transfer reactions [4], enhance the specific surface and thus ensure higher sensitivity [5]. Moreover, gold nanoparticles were found to facilitate the separation of two neighbouring stripping peaks, which is interesting for the detection of trace metals in the presence of interfering analytes [6]. The nanostructuring of SPEs would thus be an interesting way to improve their performance.

The number of electrode materials containing AuNPs for the detection of trace metals is growing rapidly. Among them, very few associate AuNPs with ionophores [7] or deal with AuNPs functionalized with ligands [8–11]. To our knowledge, only two very recent examples of SPEs modified by functionalized nanoparticles [12,13] are described in the literature.

The immobilization of AuNPs on SPEs may be operated via several methods. One consists in the electrodeposition of gold onto the working electrode surface using a solution of tetrachloroauric acid and applying a fixed potential for a selected time [14–18]. Other methods for the immobilization of AuNPs consist in the immersion of the SPEs in a suspension of AuNPs [12,19,20], in the incorporation of AuNPs in a carbon paste [21] or in the entrapment of AuNPs in a polymer film at the surface of the electrode [22,23].

Self-assembled monolayers (SAMs) are often used for the binding of AuNPs at the surface of electrodes when a strong interaction is needed between the nanoparticles and the electrode. Thiols are generally employed due to the well-known strong sulfur-gold interaction [24]. However, thiol-based SAMs present disadvantages for electrochemical applications: small electroactivity domain, poor electrical conductivity and poor stability against oxidation and during storage [25,26].

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The covalent grafting of AuNPs at the electrode surface would provide a greater robustness of the material. This robustness is required for any further applications as a sensor. The chemistry of diazonium salts allows for the covalent binding of organic molecules onto surfaces by either electrochemical [27], chemical [28], physical [29] or spontaneous methods [28,30]. The grafting of a diazonium salt on gold leads to a C-Au covalent bond, thus resistant to solvents, sonication, etc [31]. The immobilization of AuNPs onto the surface of SPEs through p-aminophenyl diazonium salt ( $\text{NH}_2\text{-Ph-N}_2^+$ ; 4-APD) has been previously described [27,32]. The advantage of 4-APD is that once the diazonium group is reduced and the ligand grafted onto the SPE surface, the remaining amine function may be easily converted into another diazonium function, allowing the covalent immobilization of nanomaterials. Gooding and al described the electrochemical grafting of Turkevich AuNPs on these reactive surfaces, and evidenced the robustness of the resulting material [27]. Palacin and al worked on the spontaneous grafting of different types of nanomaterials such as copper nanoparticles or carbon nanotubes [32].

Until now, no comparison of the effectiveness between electrochemical grafting and spontaneous grafting has been done. In this paper, we compared these two approaches. Two types of AuNPs suspensions were used: Turkevich AuNPs [33], well-defined and commonly used in the literature, or Eah AuNPs [34], which synthesis has been recently published. The aim of this work was to improve the “nano-functionalization” of SPEs in terms of number of AuNPs grafted and homogeneity of their dispersion at the SPE surface, for further sensor applications. Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), chronocoulometry as well as scanning electron microscopy (SEM), Rutherford backscattering spectroscopy (RBS) and X-ray photoelectron spectroscopy (XPS) were used for this comparison. Finally, functionalized SPE-AuNPs were obtained using the 4-carboxyphenyl diazonium salt and we studied the effectiveness of this functionalized nanostructured electrode material for the detection of Pb (II).

## 2. Experimental

### 2.1. Chemicals and reagents

Sulfuric and chlorhydric acid standard solutions (1 M) were purchased from Fluka; p-phenylenediamine, potassium chloride and tetrafluoroboric acid (48%) from Sigma; 4-aminobenzoic acid, hexaammineruthenium (III) chloride (98%) and sodium borohydride from Aldrich; sodium nitrite from Acros Organics; hydrogen tetrachloroaurate (III) trihydrate and trisodium citrate from Alfa Aesar. All solutions were prepared with purified water ( $18.2 \text{ M}\Omega\cdot\text{cm}^{-1}$ ) 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. Electrochemical measurements

All electrochemical measurements were performed with an Autolab (low current PGSTAT302 N, Metrohm) with a conventional three-electrode system, comprising SPEs or grafted SPEs as a working electrode, a platinum counter electrode and a saturated calomel electrode (SCE) as a reference purchased from Radiometer Analytical. All the potentials reported in this work are relative to SCE at room temperature. EIS measurements were performed using an EG&G (273A, Princeton Applied Research) coupled with a SI 1255 Frequency Response Analyzer (Solartron). A platinum foil was used as the counter electrode.  $0.4 \text{ mM } [\text{Ru}(\text{NH}_3)_6]^{3+}$  in  $0.1 \text{ M KCl}$  solution was used as the electrolyte solution. EIS measurements

were recorded at room temperature within the frequency range of  $10^2\text{--}10^6 \text{ Hz}$  superimposed on a DC potential of  $-0.175 \text{ V}$ , with AC of  $10 \text{ mV}$  peak to peak amplitude, and 5 points per decade of frequencies.

### 2.3. Surface analysis

SEM was carried out using a LEO 1530 SEM-FEG coupled with an energy dispersive X-ray (EDX) spectrometer Imix (Princeton Gamma Tech). The pictures presented were recorded in compositional contrast.

RBS was performed on the SAFIR Platform of the University Pierre and Marie Curie (UPMC), with a HVEE 2.5 MeV Van de Graaff accelerator,  $^4\text{He}^+$  particles at  $1.5 \text{ MeV}$ ,  $35 \text{ nA}$  and a scattering angle of  $165^\circ$ . The density of Au was determined using a certified reference sample of silicon implanted with  $5.53 \cdot 10^{15} \pm 2\% \text{ atoms cm}^{-2}$  of  $^{209}\text{Bi}$ . The reference spectra were acquired immediately after the analysis of the SPE-Ph-AuNPs samples and in the same conditions so as to minimize errors related to beam current fluctuations and charge collection. The areal density of Au was from the Au peak area in the spectra, allowing the density of AuNPs per  $\text{cm}^2$  to be calculated.

XPS analyses were carried out with a Kratos Axis Ultra DLD using a high-resolution monochromatic Al K $\alpha$  line X-ray source at  $150 \text{ W}$ . Fixed analyzer pass energy of  $160 \text{ eV}$  for survey scans and  $40 \text{ eV}$  for core-level scans were used. The photoelectron takeoff angle was normal to the surface, which provided an integrated sampling depth of approximately  $5 \text{ nm}$ . A survey spectrum and core-level spectra of C 1s ( $277\text{--}293 \text{ eV}$ ), O 1s ( $526\text{--}538 \text{ eV}$ ), and N 1s ( $396\text{--}411 \text{ eV}$ ) regions were recorded. The energy scale of the instrument was calibrated by setting  $\text{Au } 4f_{7/2} = 84.00 \text{ eV}$ . Spectra were treated with Casaxps software. The scanned area was  $700 \times 300 \mu\text{m}^2$ .

### 2.4. Synthesis of the diazonium salts

4-Aminophenyldiazonium tetrafluoroborate (4-APD) was synthesized from p-phenyldiamine.  $4.4 \text{ mmol}$  of p-phenyldiamine were dissolved in  $10 \text{ mL}$  of  $10\% \text{ HBF}_4$ . The solution was cooled  $15 \text{ min}$  in ice then  $1.1$  equivalent of  $\text{NaNO}_2$  in  $1 \text{ mL}$  of water were added dropwise under vigorous stirring. The solution was stirred  $15 \text{ min}$ . The dark brown precipitate was then filtered on Buchner, washed with cold ether and dried under vacuum. 4-Carboxyphenyldiazonium tetrafluoroborate (4-CPD) was synthesized as previously described [35]. NMR and IR data are given in the supporting information.

### 2.5. Synthesis of gold nanoparticles

Before the synthesis, all the glassware was washed with aqua regia and then thoroughly rinsed with deionized water.

Turkevich [33] and Eah [34] AuNPs were synthesized according to the literature.  $15\text{--}20 \text{ nm}$  diameter AuNPs were obtained with Turkevich procedure and  $3\text{--}5 \text{ nm}$  diameter AuNPs were obtained with Eah procedure.

All AuNPs suspensions were characterized by UV-vis spectroscopy and Dynamic Light Scattering (DLS). Spectra are given in the supporting information (Figure A.1).

### 2.6. Electrode preparation and modification

The working electrodes were carbon-based SPEs. SPEs were prepared according to Authier and al [36] by a printing process which consists of the deposition of a thin layer of a commercial conducting ink (Electrodag PF-407A purchased from Circuit Imprimé Français (CIF)) on a polystyrene support, through a screen supplied by CIF,

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