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Electrodeposition of gold nanoparticles on boron doped diamond electrodes for the enhanced reduction of small organic molecules

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Abstract

The performance of gold nanoparticles electrodeposited on boron doped diamond (BDD) electrodes was investigated in respect to the reduction of chloramphenicol (CAP), an antibiotic of the phenicols family. The chosen deposition protocol, three nucleation-growing pulses, shows a remarkable surface coverage, with an even distribution of average-sized gold particles (~50nm), and it was proven capable of generating a three-fold increase in the CAP reduction current. A calibration plot for CAP detection was obtained in the micromolar range (5-35 μM) with good correlation coefficient (0.9959) and an improved sensitivity of $0.053 \mu\text{A } \mu\text{M}^{-1} \text{ mm}^{-2}$ compared to the electrochemistry of CAP at a bare BDD electrode.

Keywords: Boron Doped Diamond, Gold Nanoparticles, Electrodeposition, Chloramphenicol

1. Introduction

Modifying electrode surfaces with gold nanoparticles is a well-established approach to enhance the electrochemical response, especially due to the increase in active surface area and the intrinsic properties of gold in the nanometer size [1,2]. More recently the modification of boron doped diamond (BDD) electrodes with gold nanoparticles (AuNPs) have attracted considerable attention for the analytical determination of biomolecules [3,4] or pollutants [5] as well as spectroelectrochemical applications [6]. Combining the aforementioned characteristics of gold nanoparticles with the wide potential window of BDD in aqueous solvent, low background current, chemical inertness and physical stability of BDD electrodes [7] turns into tempting alternatives for (bio)analytical applications. Song et al. [8] used AuNPs as a substrate for the immobilization of ferrocene-tagged aptamers for the determination of pH while Janegitz et al. [3] developed a biosensor to detect phenols based on tyrosinase, in which the AuNPs were used as a mediator between the enzyme and the electrode surface. Other authors acknowledged the intrinsic catalytic behavior of the AuNPs on BDD electrode [4], realizing the direct electrochemical determination of hemoglobin (Hb) with differently

shaped AuNPs. Also Weng et al. electrodeposited AuNPs on BDD and proved the increase in the oxidation current for the detection of dopamine [9]. According to our knowledge there is only one example of BDD modified with AuNPs for the direct reduction of organic molecules [10]. Wahyuni et al. used AuNPs modified BDD to detect neuraminidase, monitoring the change in its electrochemical behavior upon reaction with zanamivir, a neuraminidase inhibitor. However, the authors deposited the nanoparticles using a non-controlled self-assembly protocol with citrate capped AuNPs on amine terminated BDD.

A controlled electrodeposition of AuNPs could however lead to a better reproducibility of the electrode modification, as well as a better control over particles size and distribution. In this article, a three nucleation-growing pulses protocol (three-pulses deposition) is chosen, developed by Izquierdo et al. for spectroelectrochemical applications [6]. This protocol avoids changes in the surface terminations during the deposition, contributing to the reproducibility. Applying short nucleation pulses (2s), followed by growth pulses at 0 V, a fast reduction of gold nuclei on the surface will be achieved while avoiding hydrogen evolution and maintaining a small cathodic current during the growth pulses. It is known that BDDs surfaces can be oxygen or hydrogen terminated with a change of the electrochemical behavior of the electrode accordingly [11,12]. The proposed deposition protocol ensures that no electrochemical modifications take place at the surface during the deposition protocol, leaving the surface terminations unaltered.

The goal of this work is (1) to investigate the pretreatment and influence of the surface termination on the AuNPs deposition and (2) to show how the facile electrodeposition of AuNPs on BDD can be used as a tool to enhance the electrochemical reduction of small organic molecules. This work helps to tackle different analytical issues apart from the sensitive electrochemical detection of small organic molecules. Given the fact that AuNPs can act as anchoring sites for biomolecules like antibodies or enzymes, this strategy opens up new perspectives for the development of biosensors. The suggested approach allows an easy modification of BDD electrodes, given their chemical stability and inertness [13]. As a model molecule we choose chloramphenicol (CAP), an antibiotic of the phenicols family. CAP is a low cost and efficient antibiotic used in the treatment of severe infections of the respiratory tract and central nervous system, but due to some serious side effects [14] its use nowadays is very limited and European Union strictly regulated the residual amount that could be present in the environment [15]. There are many different analytical techniques and protocols for the determination of CAP, mainly based on chromatography such as HPLC and GC with different detectors [16,17]. However the redox behavior of CAP is well-known and was already exploited for its detection. Different carbon electrodes were employed for the detection of CAP in pharmaceutical formulations such as electrochemically pretreated glassy carbon electrode (EPGCE) [18,19] or multi-walled carbon nanotubes modified glassy

carbon (MWCNTs-GC) [20]. Also BDD have been used to determine CAP in milk and eye drops both with cyclic voltammetry and flow-injection analysis [21].

For those reasons CAP is a suitable candidate to test the efficiency of the proposed method towards small organic molecules such as antibiotics, pollutants or micronutrients.

2. Materials and Methods

2.1 Chemicals

Boron doped diamond electrodes (3 mm diameter, B content 0.1% - 1000 ppm) were purchased from Windsor Scientific (UK). Chloramphenicol (CAP), gold(III) chloride trihydrate (HAuCl_4), potassium ferrocyanide ($\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$), potassium ferricyanide ($\text{K}_3\text{Fe}(\text{CN})_6$), were purchased from Sigma Aldrich (Belgium). Diamond polishing slurries were obtained from SPI Supplies (West Chester, PA, USA). All the other reagents are of analytical grade and used without further purifications. Buffers and solutions were prepared with MilliQ water.

2.2 Instruments

Cyclic voltammetry (CV) and square wave voltammetry (SWV) were performed with a PGSTAT 302N potentiostat controlled by Nova 1.1 software (Metrohm Autolab B.V., Utrecht, The Netherlands). A conventional three-electrode cell was employed with BDD as working electrode, a platinum coil as counter and a saturated calomel electrode (SCE) as a reference in a 3 mL solution. Scanning electron microscopy (SEM) images were taken using a Quanta TM 250 FEG (FEI, Eindhoven, The Netherlands). Data analysis and manipulation were performed with Origin 8.0 software (OriginLab Corporation, Northampton, MA, USA).

2.3 Polishing protocol

Before electrodeposition, the electrodes were polished using diamond slurries. Briefly, the electrode was polished for one minute on a nylon cloth pad and thoroughly rinsed with ethanol (EtOH), then left in an ultrasonic bath for one minute to remove all slurries residues. The procedure was repeated with three different particles sizes (15, 6, 1 μm) and after the last polishing step, the electrode was left in EtOH in an ultrasonic bath for five minutes.

2.4 Electrochemical pretreatment

To test the effect of electrode surface terminations on the AuNPs deposition, electrochemical pretreatments were performed after the polishing step. Cathodic

pretreatment was carried out at -2 V for 30 min in 0.1 M phosphate buffer pH 2 and anodic pretreatment at +2 V for 30 min in 0.1 M phosphate buffer pH 2.

2.5 Chloramphenicol detection

CAP detection was carried out in 0.1 M Phosphate Buffer pH 7.5 with CV (between 0.4 V and -1.2 V, 100 mV/s) and SWV (between 0.4 V and -1.2 V, Amp: -0.05, Freq: 20 Hz). To calculate the analytical parameters (E_p and I_p) the blank was subtracted from the CAP voltammogram.

2.6 AuNPs deposition

The electrochemical deposition of AuNPs on the surface of BDDs was carried out in a 0.1 M H_2SO_4 solution containing 0.5 M $HAuCl_4$. The protocol includes three nucleation-growing pulses (three-pulses deposition) [6]. The potential and duration of the pulses induce a fast reduction of gold avoiding extensive hydrogen evolution and thus maintaining the surface termination of the electrode. A nucleation pulse consists in 2 s at -0.7 V, followed by growth pulses at 0 V (150 s, 300 s, 800 s respectively). After rinsing the electrode with dH_2O the electrode is further characterized. To assess the presence of AuNPs, the electrode was analyzed in a 2 mM $Fe(CN)_6^{3-/4-}$ solution with 0.5 M KCl with CV (between -0.4 V and +0.6 V, 100 mV/s) and in 0.5 M KCl (CV between 0V and +1.4 V, 100 mV/s). The AuNPs deposition was also confirmed by SEM analysis.

3. Results and Discussion

Three pulses aiming nucleation and growth of gold nanoparticles were applied on the BDD electrodes in an acidic 0.5 M $HAuCl_4$ solution (see 2.6 AuNPs deposition). The electrode surface was characterized with SEM as well as CV. A well-known redox couple, $Fe(CN)_6^{3-/4-}$, was used to assess the presence of gold in the nanometer range on the surface. It is expected that the redox behavior of $Fe(CN)_6^{3-/4-}$ is enhanced by the catalytic effect of AuNPs as well as by the increased active surface area. The comparison between the response of the redox couple at the bare BDD and the AuNPs-BDD electrode clearly indicates a successful deposition (Fig. 1A). It is possible to observe an increase in both the oxidation and reduction peak current for $Fe(CN)_6^{3-/4-}$. Additionally, a characteristic voltammogram of Au (an intense oxidation peak at +1.2 V related to the oxidation of the gold particles and a smaller double reduction couple at +0.7 and +0.5 V standing for the reduction of gold oxides/hydroxides) appears (Fig. 1B). At the bare BDD electrode no AuNPs redox chemistry can be observed in the voltammogram.

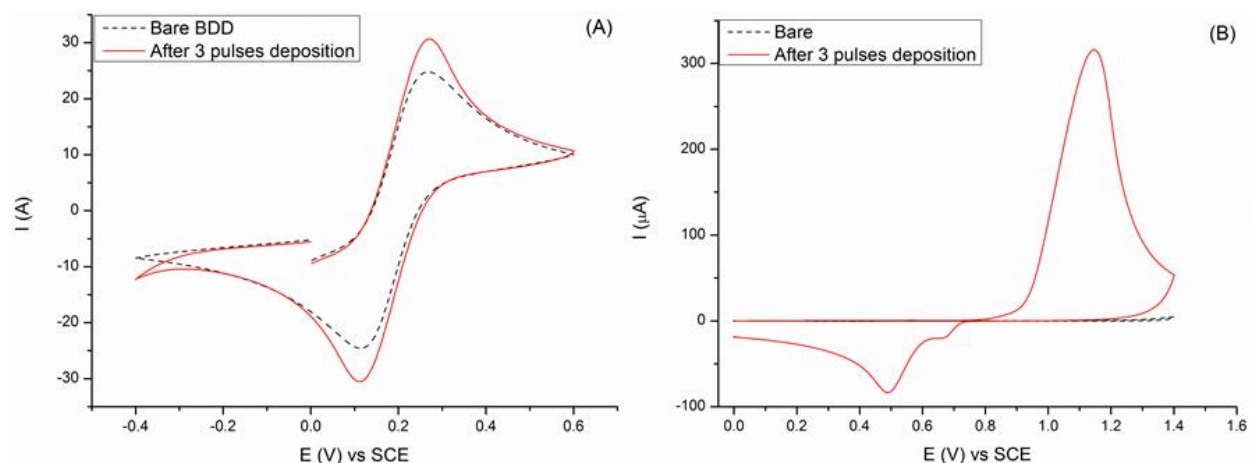


Fig.1: (A) CV of $\text{Fe}(\text{CN})_6^{3-/4-}$ in 0.5M KCl before (black dashed line) and after (red full line) three-pulses deposition; (B) CV in KCl 0.5 M for BDD before (black dashed line) and after (red full line) three-pulses deposition

SEM images at different magnifications (Fig. 2) show that the AuNPs are uniformly distributed on the BDD surface, with almost complete surface coverage, and an average NPs diameter of 50 nm. Fig. 2A shows the nanoparticles around an imperfection of the electrode surface: the AuNPs are distributed in an ordered monolayer with some aggregates, probably due to a higher B content of the underlining surface.

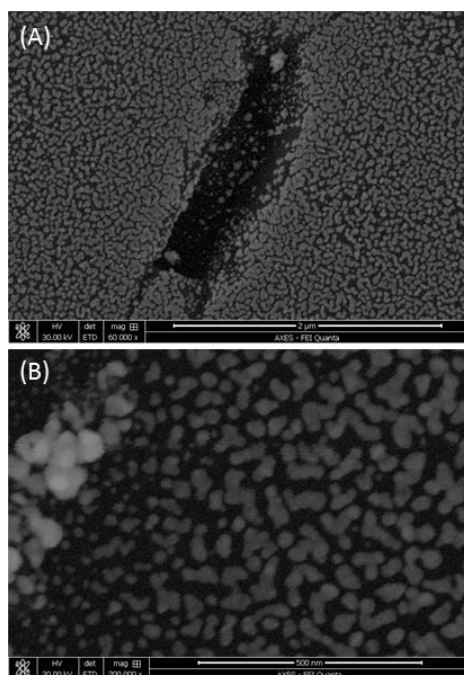


Fig.2: SEM images of the BDD surface after AuNPs deposition: (A) 60000x; (B) 200000x.

The electrochemical behavior of CAP, a small organic molecule, on bare BDD was investigated. Fig. 3A shows the CV for 50 μM of CAP in a 0.1 M phosphate buffer

solution (pH 7.5). The reduction peak present at ca. -0.9 V (vs SCE) can be explained as the four electron four proton reduction of the nitro group as described in equation 1 [19]:



This same process on macro Au electrodes (blue dotted line in Fig.3A) results in a peak at c.a. -0.6 V with a current comparable to that obtained at a bare BDD. After the three-pulses deposition (Fig. 3B), the background current increases and a small peak appears around -0.7 V, due to gold reduction. When adding CAP, a peak at -0.95 V appears, due to NO₂ reduction. Comparing the peak current at a bare BDD ($I_p^{\text{Red}} = 10 \mu\text{A}$) and at AuNPs-BDD ($I_p^{\text{Red}} = 29 \mu\text{A}$), a three-fold increase in the signal intensity is observed for the same analytical conditions, suggesting the enhancing effect of the AuNPs on the CAP reduction.

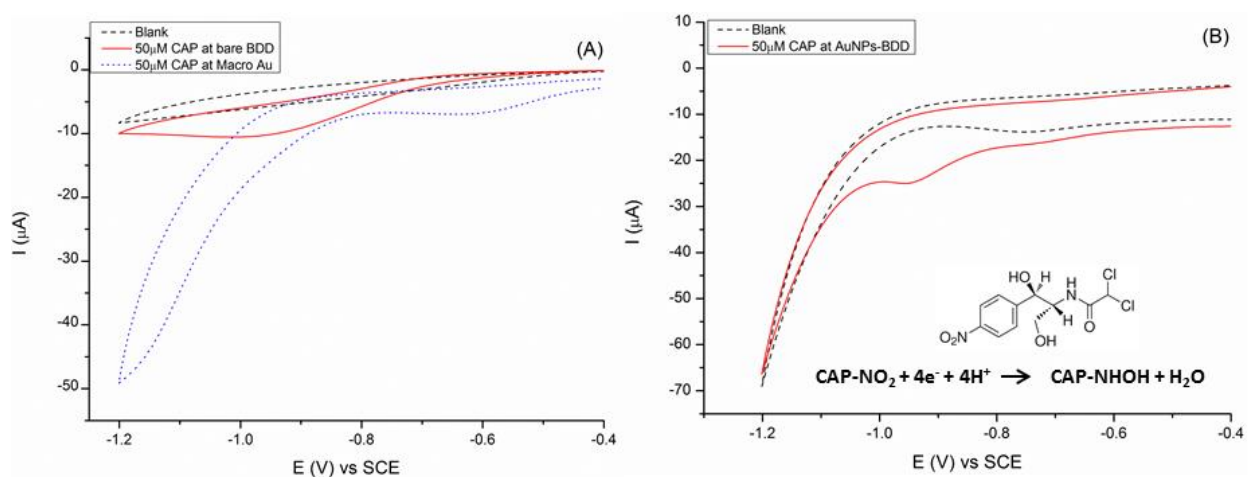


Fig.3 (A) CV in 0.1 M phosphate buffer (pH 7.5): blank (black dashed line), 50 μM CAP at bare BDD (red full line) and at macro Au (blue dotted line)(B) CV with AuNPs-BDD in 0.1 M phosphate buffer (pH 7.5): blank (black dashed line), 50 μM CAP (red full line), inset: CAP structure and reduction reaction pathway.

To optimize the protocol, the deposition time was investigated: three different deposition protocols (Table 1) were employed, applying only one nucleation and one growing pulse (one-pulse), then two nucleation and two growing steps (two pulses) and then the complete three nucleation three growing pulses protocol (three-pulses).

Table 1: Summary of the investigated electrodeposition protocols.

	One pulse	Two pulses	Three pulses
Nucleation (-0.7 V)	2 s	2 s	2 s
Growth (0 V)	150 s	150 s	150 s
Nucleation (-0.7 V)	-	2 s	2 s
Growth (0 V)	-	300 s	300 s

<i>Nucleation</i> (-0.7 V)	-	-	2 s
<i>Growth</i> (0 V)	-	-	800 s

The surface coverage (Γ) was calculated from the area of the gold oxidation peak obtained in 0.5 M KCl solution. Table 2 summarizes the values for the coverage, together with the CAP reduction potential and current for the different protocols. When increasing the number of pulses, Γ increases and the CAP peak potential slightly shifts towards more negative potentials. Also the peak current increases steadily (from 10 μ A of the bare BDD up to 29 μ A for three-pulses).

Table 2: Summary of the analytical parameters for one, two, and three pulses deposition protocol, also compared with the responses at a bare BDD. E_p and I_p are for the reduction of 50 μ M of CAP in 0.1M phosphate buffer (pH 7.5).

	$\Gamma_{\text{gold@BDD}}$ (mol/cm ²)	$E_{p,\text{CAP}}$ (V)	$I_{p,\text{CAP}}$ (μ A)
Bare BDD	-	-0.90	10.5
One-pulse AuNPs@BDD	$5.45 \cdot 10^{-12}$	-0.90	12.6
Two-pulses AuNPs@BDD	$2.73 \cdot 10^{-11}$	-0.93	18.4
Three-pulses AuNPs@BDD	$4.14 \cdot 10^{-11}$	-0.96	29

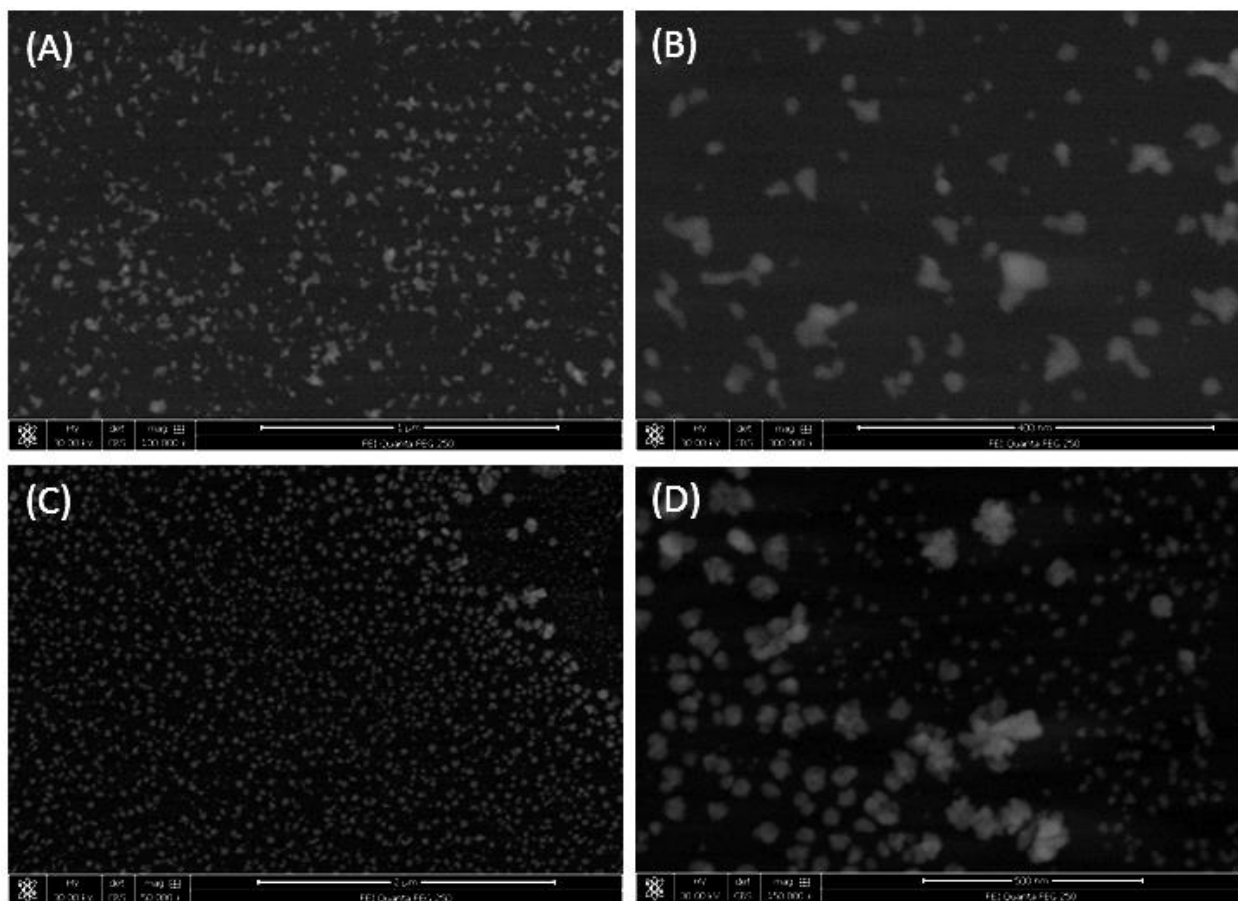


Fig.4: SEM images of BDD surface after one-pulse (A: 100000x, B: 300000x) and two-pulses (C: 50000x, D: 150000x) deposition protocol.

SEM analysis of the surface shows that, for one-pulse deposition, the obtained nanoparticles are smaller (ca. 20 nm) with an uneven distribution (Fig. 4A) while with two-pulses deposition the surface coverage improves but the nanoparticles are of different sizes (Fig. 4D). The smaller particles (ca. 15 nm in diameter) are probably gold nuclei not fully grown, while others have the same size (50 nm) as the ones obtained with three pulses deposition. In conclusion to achieve a good surface coverage and a uniform size distribution, coupled with the highest increase of CAP reduction peak, the three-pulses deposition protocol is suggested as the best approach. It is worth noting that this nucleation-growing pulses approach allows remarkable flexibility and control over the nanoparticles size and distribution. Tuning the amount of nucleation pulses and the length of the growing pulses allows to create different configurations of nano objects on the electrode surface with different possible applications such as biomolecules immobilization and multiple metals deposition.

Additionally, the influence of the electrochemical pretreatment of the BDD surface (surface termination) on the AuNPs deposition was also investigated. It was already

shown that surface pretreatment/termination of BDD affects the deposition of metals [22,23]. For this reason, before the three pulses deposition, the BDD electrode underwent a cathodic or anodic electrochemical pretreatment (see 2.4 Electrochemical pretreatment). The amount of gold deposited on the electrochemically pretreated BDD surface (Fig. 5A) is low compared to that of a non-pretreated electrode and even more, the peak for CAP reduction is absent for both cathodically and anodically pretreated AuNPs-BDD. This phenomenon can be explained by the fact that, for anodic pretreatment, the repulsion between the negatively charged surface and the negatively charged CAP ($pK_a = 5.5$) is too strong to allow efficient electron transfer between the electrode and the analyte. Thus even in the presence of AuNPs, the redox reaction is hindered due to charge effects. For the cathodic pretreatment, instead, the available potential window is more narrow than the one for bare BDD. This effect is probably due to the buffer composition used for the pretreatment [24]. Thus the comparison of the CVs of the cathodic pretreated BDD before and after the addition of CAP suggest that the H_2 evolution starts at more positive potential than the non-treated electrode and therefore covering the peak of CAP reduction, even in the presence of AuNPs. The increase in oxidation and reduction peak current of $Fe(CN)_6^{3-/4-}$ for cathodic pretreatment (blue line in Fig. 5B) is due to the increased electron transfer between the H-terminated surface of the cathodic pretreated electrode and the redox probe, rather than for the catalytic effect of the AuNPs [25]. Based on the above results, it is also now clear that the suggested nucleation-growing approach maintains the BDD surface modifications, which might affect the gold deposition.

The optimal protocol for the AuNPs deposition is the three pulses deposition without any pretreatment of the electrode. As far as the stability of the deposited nanoparticles is concerned, repeated CV analysis of the same electrode shows a decrease in the CAP reduction current of only 7% after six consecutive cycles.

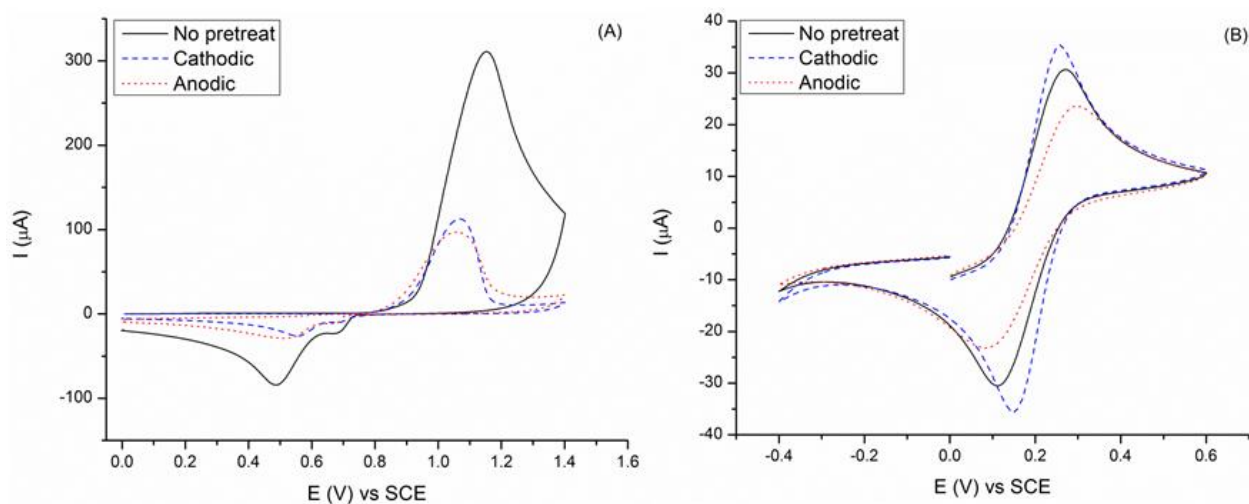


Fig.5: Effect of the pretreatment on the AuNPs deposition; no pretreatment (black full line), cathodic (blue dashed line), anodic (red dotted line). (A) CVs in 0.5M KCl; (B) CVs of 2mM $\text{Fe}(\text{CN})_6^{3-/4-}$ in 0.5M KCl;

For the construction of the calibration plot, square wave voltammetry was employed; the peak current reported is obtained by subtracting the blank voltammogram from the one recorded after adding CAP in the solution. In Fig.6 the voltammograms of CAP at different concentrations, from 5 to 35 μM , are shown for the bare BDD (Fig. 6A) and the AuNPs-BDD (Fig. 6B). The peak potential obtained at the bare BDD is more positive (-0.77V) compared to AuNPs-BDD (-0.93 V). Looking at the parameters of both calibration plots (Table 3 and Fig.S1) the effect of the AuNPs is self-evident. The correlation coefficient is increased, as well as the sensitivity. A better reproducibility is achieved for AuNPs-BDD, with a lower experimental LOD.

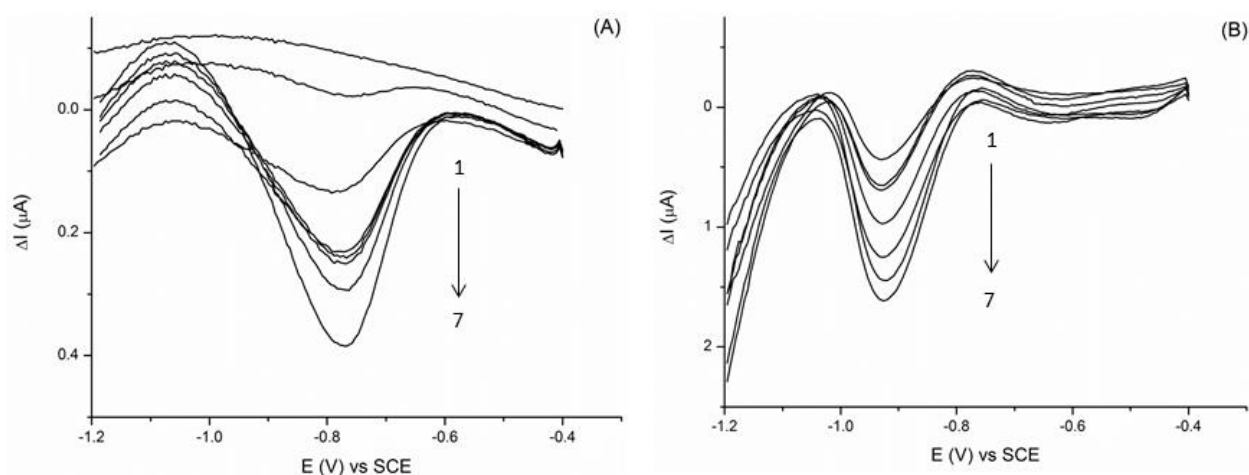


Fig.6: (A) SWV with bare BDD (A) and AuNPs-BDD (B) in 0.1M phosphate buffer pH 7.5 with different concentrations of CAP 5 (1), 10 (2), 15 (3), 20 (4), 25 (5), 30 (5), 35 (7) μM .

Table 3: Summary of the calibration plot parameters for the detection of CAP at bare BDD and AuNPs-BDD.

	R^2	Sensitivity ($\mu\text{A } \mu\text{M}^{-1} \text{mm}^{-2}$)	Experimental LOD (μM)	%RSD (n=4)
Bare BDD	0.7953	0.0013	10	33%
AuNPs-BDD	0.9959	0.0530	5	5%
BDD[21]	0.9948	0.0216	100 (CV)/0.1 (FIA)	3.5%
EPGCE[18]	0.9990	0.0269	0.16	-
EPGCE[19]	0.9990	-	0.1	3.7%
MWCNTs-GC[20]	0.9987	-	0.3	5.3%

4. Conclusion

Electrodeposition of gold nanoparticles on BDD electrodes was achieved via a three nucleation-growing pulses protocol. The obtained NPs are well dispersed with a good

surface coverage. The nucleation-growing approach also ensures that no modification in the BDD surface terminations takes place during the deposition. The obtained AuNPs-BDD shows an improved catalytic effect toward the reduction of CAP, compared with the bare BDD electrode. A three-fold increase in the faradaic current for the reduction of the NO₂ group of CAP is observed. The analytical performances were improved by the nanoparticles especially in term of sensitivity, compared to other electrochemical methods. AuNPs decorated BDD has been proven as a promising alternative for the registration of reduction reactions of small organic molecules, combining the advantages of boron doped diamond with the enhancing effect of Au in the nanometer size.

Acknowledgments

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