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Study of an AuNPs functionalized electrode using different diazonium salts for the ultra-fast detection of Hg(II) traces in water

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ABSTRACT

Chemically-prepared gold nanoparticles (AuNPs) were drop-casted onto bare glassy carbon (GC) and on GC functionalized by two different diazonium salts bearing either nitro (NO_2) or thiol (SH) groups. The resulting interfaces were characterized by field emission gun scanning electron microscopy (FEG-SEM) and cyclic voltammetry in H_2SO_4. The micrographs evidenced different densities of AuNPs depending on the substrate, bare GC affording denser deposits than diazonium-functionalized GC. The stability of the interfaces was evaluated over one month and showed higher recovery of active surface area (up to 91% depending on the storage conditions) for AuNPs deposited on diazonium-functionalized GC than on bare GC. The three electrodes were also tested for Hg(II) trace detection by using Square Wave Anodic Stripping Voltammetry (SWASV) and a preconcentration time shortened from 300 s to 30 s. In such conditions, a linear response was obtained in the range 1–10 nmoll^{-1} together with a normalized sensitivity up to 17 times higher than that reported in our previous works dealing with electrodeposited AuNPs.

1. Introduction

As a member of the heavy metals family, mercury is one of the most problematic pollutants causing major environment contaminations. It is present in the ecosystem because of natural processes such as volcanism, but mostly because of anthropogenic discharges from gold mines or industries. It is then widespreaded in soils [1,2], atmosphere [3,4] and animals [5,6]. In his organometallic form (methylmercury MeHg) it bioaccumulates all along the food chain [7,8] and may thus be present in quite high quantities in the human food. When a poisoning occurs, effects on health include lungs, heart, liver, kidney and brain pathologies [9,10]. To control the widespreading of this micropollutant, the World Health Organization has delivered a guideline value of 6 $\mu g l^{-1}$ (ca. 30 nmol l^{-1}) for drinking water [11], but in Europe, the European Water Framework Directive set an even more strict standard of 0.07 $\mu g l^{-1}$ (ca. 0.3 nmol l^{-1}) in addition of classifying mercury and his compounds as priority dangerous substances [12]. Thus, there is a need for detection tools against this pollutant capable of detecting traces levels.

In analytical laboratories, mercury in surface water is detected with classical spectroscopic techniques such as cold-vapor atomic absorption spectrometry or cold-vapor atomic fluorescence spectrometry with good accuracy, sensitivity and selectivity. However, in addition of the cost of these equipments, the measurements are ex-situ meaning that water samples have to be collected, transported and even stored prior to analysis. Concerning mercury, this is a great cause of contamination during the samples storage and transportation [13,14]. It then appears necessary to develop portable sensors which can provide in-situ measurements and real time analysis. To this purpose, electrochemical sensors can be a good alternative due to their portability, low costs production and maintenance, and good sensitivity. They are also a great choice for traces detection in regards of the possibility of electrode functionalization that affords better selectivity and sensitivity [15]. Electrode modification can be operated with graphene [16], biological materials like DNA [17], carbon nanotubes [18] and so on. In particular, gold nanoparticles (AuNPs) are an interesting sensing material for electrode modification because of their good affinity with mercury and their electrocatalysis features [19–21].

In our group, AuNPs were electrodeposited on a glassy carbon electrode throught different electrochemical techniques and

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showed a great ability to detect mercury traces [22]. Because chloride ions were shown to play an important role in the detection, a desorption step was added to the detection process and a concentration of mercury of 19 pmol l^{-1} was reached for a submarine groundwater discharge sample [23]. In an alternative way, chemically prepared AuNPs were used to functionalize a GC electrode reaching a LOD of 1 pmoll^{-1} [24]. However, the remaining sensor suffered a poor stability over time and electrochemical treatments.

In this present study we used diazonium salts diazonium salts in order to improve the stability of the particle deposits on the carbon surface by acting as a link between AuNPs and glassy carbon. It has been shown many times that the organic layer obtained by reduction of diazonium ions is covalently bonded to the glassy carbon [25,26]. Besides, harsh treatments like power sanding or radical attacks are the only ways to remove this layer as it resists ultrasonic treatments [27]. Then, the most interesting question is to determine the optimal terminal group on the diazoniums that could strongly interact with the AuNPs in order to stabilize them. In the literature, one of the most and commun diazonium used is the 4-mercaptobenzene diazonium, that is call SH in this present paper. Indeed, it is known that the interactions between sulfur and gold are covalent with a binding energy of 154.4 kJ mol^{-1} [28]. This strong bonding was confirmed for AuNPs deposited on a SH-modified electrode [29–31]. However, like the commonly studied alkanethiols Self-Assembled Monoloyers, the S—Au in this configuration is labile and can be destabilized by oxidation [32]. The use of nitrobenzene diazonium (NBD) for the improvement of the AuNPs stability is not as popular as SH. In most studies, NBD is used in order to reduce its terminal nitro group in an amine before AuNPs deposition [33]. Indeed, the bonding energy of NH—Au is 153.6 kJ mol^{-1} [34] whereas the NO_2—Au was calculated to be 8.37 kJ mol^{-1} [35]. However, this NBD diazonium is known for growing in multilayer structure, especially when the grafting is not controlled (cyclic voltammetry) or when the amount of charge used is important (long time electrolysis). It presents a rough morphology where holes or globuled structures appear [36,37]. Thus, AuNPs may be suspected to interpenetrate into the layer at differents depths [38] allowing the current to run from the analyte solution to the electrodes through the metallic particles. The NBD diazonium may be then supposed to afford a stabilizing effect on the AuNPs mostly because of steric interactions.

In the present work we compared the stability of GC electrodes functionalized with chemically prepared AuNPs with or without the presence of a layer of diazonium (NBD or SH) between the substrate and the particles. The functionalization of the electrodes was followed with respect to two electrochemical probes, ferricyanide and hexaammineruthenium(III), and the resulting interfaces were characterized by field emission gun scanning electron microscope (FEG-SEM) observations and electrochemical processes. The stability of the sensors in different storage conditions was evaluated and discussed. Finally, the analytical performances of the modified electrodes were determinated against the detection of Hg(II) traces.

2. Experimental

2.1. Reagents and apparatus

All the solutions were prepared using ultrapure water (Milli-Q, Millipore, 18.2 MΩ cm). 99.5% $NaNO_2$, 4-aminothiophenol (97% $NH_2C_4H_4SH$) and 4-nitrobenzene diazonium tetrafluoroborate (97% $C_6H_4N_3O_2BF_4$) were purchased from Sigma Aldrich. $HAuCl_4.3H_2O$ pro-analysis grade and 99% KNO_3 were supplied by Acros Organics. Sodium citrate ($C_6H_5Na_3O_7$) and $Ru(NH_6)Cl_3$ were purchased from Alfa Aesar. $K_3[Fe(CN)_6]$ was purchased from Merck. 95% H_2SO_4 Normapure grade was obtained from VWR Prolabo. Hg(II) solutions were prepared by dilution of [separate-uncertainty] 1000±(4) mg l^{-1} $Hg(NO_3)_2$ standard solution (TraceCERT grade, Sigma Aldrich) and acidified to pH 2 with concentrated 34–37% HCl (Plasmapure grade, SCP Science). All the experiments were performed at room temperature in a three-electrode glass cell using a PGSTAT 128 N potentiostat (Metrohm Autolab, Utrecht, Netherlands) connected to a computer running with NOVA 1.10 software package. A Radiometer saturated calomel electrode Hg/Hg_2Cl_2/KCl(sat) was used as a reference electrode and a Metrohm glassy carbon (GC) wire as the auxiliary electrode. The working electrode was a Radiometer rotating GC disk sealed in Teflon (3 mm diameter, A = 7.07 mm^2) or a pyrolized photoresist film (PPF) plate (6 mm diameter, A = 28.3 mm^2) prepared at the Institut des Sciences Chimiques de Rennes according to published procedure [39,40]. PPF was used for diazonium layer thickness measurements, as it is known to react like GC while being as flat as HOPG [41]. The electrochemical cell was constantly maintained in a Faraday cage in order to minimize the electrical interferences. The solutions were deaerated with a N_2 stream for 10 min prior to each experiment. A N_2 atmosphere was also maintained over the solution during the corresponding experiments.

2.2. Synthesis of the gold nanoparticles (AuNPs)

The AuNPs were synthesized by the classical Turkevich method [42]. Prior to any use, all glassware was cleaned with aqua regia (3:1 HCl/HNO_3) and rinsed with ultrapure water. 22 mg (8.5×10^{-5} mol) of sodium citrate was dissolved in 30 ml of Milli-Q water and then heated under reflux. 10 ml of an aqueous $HAuCl_4$ solution (9.9 mg, 2.5×10^{-5} mol) was then added followed by 10 ml of ultrapure water. The mixture was heated for 20 min and left to cool at room temperature for at least 1 h before storing at 4 °C. The final solution had a concentration of AuNPs of 4.8 nmol l^{-1} calculated with Equation (1).

$$C_{AuNPs} = \frac{N_{AuNPs}}{V_{Sol} N_a} \tag{1}$$

where V_{sol} is the volume solution, N_a the Avogadro number and N_{AuNPs} the gold nanoparticles number in the solution calculated with Equation (2).

$$N_{AuNPs} = \frac{V_{Au}}{V_{AuNP}} = \frac{m(Au)}{\rho_{Au}} \frac{3\pi R^3_{AuNPs}}{4} \tag{2}$$

where V_{Au} is the gold volume in the solution and V_{AuNP} the volume occupied by one gold nanoparticle considering a diameter of 15 nm (see Section 3.1).

The final colloidal solution was stable for one month.

2.3. Synthesis of 4-thiophenol diazonium

To synthesize the 4-thiophenol diazonium (SH), 120 µl of a 0.1 mol l^{-1} $NaNO_2$ aqueous solution was slowly added to a 0.1 mol l^{-1} HCl solution containing 1 mg (0.01 mmol) of 4-aminothiophenol at 4 °C. The solution became yellow immediately and the reaction was left to run for 10 min before use.

2.4. Preparation and modification of the electrode

Before each modification the GC surfaces were sanded with silicon carbide grinding paper (grit 1200) for 5 s in order to remove