



Research Paper

Carbon black supported Au–Pd core-shell nanoparticles within a dihexadecylphosphate film for the development of hydrazine electrochemical sensor



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ABSTRACT

An amperometric method for the determination of hydrazine (HDZ) using a glassy carbon (GC) electrode modified with carbon black supported Au–Pd core-shell structured nanoparticles (Au@Pd/CB) within dihexadecylphosphate (DHP) film (Au@Pd/CB-DHP/GCE) is proposed. Au@Pd nanoparticles were synthesized by chemical reduction of AuCl₃ and PdCl₂ using ethylene glycol as a reducing agent, and the nanoparticles supported on CB were characterized by scanning electron microscopy, transmission electron microscopy, energy dispersive X-ray spectroscopy and X-ray diffraction techniques. The proposed Au@Pd/CB-DHP/GCE and CB-DHP/GCE (without Au@Pd) electrodes were used to investigate the electrochemical behavior of HDZ using cyclic voltammetry. When the Au@Pd/CB-DHP/GCE was used, an electrocatalytic effect was observed, the analytical signal was substantially increased (87%) and the oxidation potential decreased, i.e. in 728 mV. Additionally, the apparently heterogeneous electron-transfer rate constant (k^0) obtained for the Au@Pd/CB-DHP/GCE ($0.15 \text{ cm}^2 \text{ s}^{-1}$) was about two orders of magnitude greater than that obtained using the CB-DHP/GCE ($0.068 \text{ cm}^2 \text{ s}^{-1}$). Under the optimized conditions for the amperometric technique, a linear analytical curve for HDZ was obtained in the range of $2.50\text{--}88.0 \mu\text{mol L}^{-1}$, with a limit of detection of $0.23 \mu\text{mol L}^{-1}$ (0.0074 ppm). The proposed method was satisfactorily applied to determine the concentration of HDZ in natural lake and tap water samples.

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1. Introduction

The development of chemically modified electrodes has attracted considerable attention due to the new challenges posed by samples of industrial, clinical, and environmental interest [1–4]. Thus, the use of hybrid nanomaterials like carbon materials and metal nanoparticles is growing, since when used together, they can produce a synergistic effect, promoting improved analytical conditions (sensitivity and selectivity) [5,6]. One of the biggest challenges in this area is the search for suitable electrode modifier materials able to promote a better electron transfer between the electrode surface and redox species.

In this context, the metal nanoparticles may be composed of a single metal or mixture of metals, forming alloys or core-shell structures. The alloys and core-shell structures have attractive electronic, optical, and catalytic properties different from those of the corresponding single metals [7,8]. The addition of a second metallic component can enhance the activity, selectivity, and stability of a pure metal [9–11].

Core-shell bimetallic nanoparticles are structures where a thin shell composed of one metal envelops a core composed of another metal. Noble metals, such as Pt, Au, Ag, and Pd have been widely used for this purpose [12].

Due to the high cost of noble metals, it is common to synthesize supported catalysts in other materials such as carbon materials [13–17], phthalocyanine [18–20], among others. This strategy, besides reducing costs, can also contribute to the enhancement of the catalytic performances of the supported nanoparticles, facilitating electron transfer, improving mass transportation, and increasing active surface area [21].

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Among various bimetallic nanoparticles, core-shell structures formed by Au-Pd have been widely used as catalytic materials for a variety of reactions, because Au and Pd are miscible at any ratio, as can be seen from their phase diagram presented previously [22,23].

Some studies have demonstrated that Au-Pd nanoparticles supported on different materials, such as graphene [24,25], TiO₂ nanotubes [26], and phthalocyanine [27] show high catalytic activity for the HDZ oxidation. Some of those approaches used graphene or phthalocyanine as an electrode modifier; however, it is known that these materials are of high cost, and are difficult to reproduce synthetically.

As an alternative to these materials, CB is a nanostructured carbonaceous material of low cost (~\$1 per kg), interesting for the synthesis of electrocatalytic nanocomposites that offer excellent conductivity, chemical stability, and a large specific surface area. Moreover, stable aqueous dispersions without the need for sophisticated procedures can be prepared using this material for the preparation of modified electrodes for further applications in electroanalysis [28,29]. Among the range of CB applications in different fields, the use of this material as a support for the production of metallic nanocomposites has been one of the most suitable applications for electroanalysis, mainly because they incorporate the features of CB conductivity and the catalytic properties of the metallic nanomaterials, besides being a material of low cost [30,31].

Hydrazine (HDZ-N₂H₄) is a chemical compound, well-known for its extensive industrial applications, including its use in agricultural chemicals, pharmaceutical intermediates, corrosion inhibitors in boilers and industrial pipes, and catalyst agents as well as rocket propellant [32,33]. However, environmental agencies have reported hydrazine as a possible carcinogen to humans since some studies showed an increased incidence of lung and liver tumors in rats exposed to hydrazine [34,35].

Further, due to its high solubility, there is great concern about the contamination of soil and water by HDZ. In this context, considering the environmental pollution concerns, simple, rapid, and low cost methods for the quantification of HDZ in natural water is of great interest to assist environmental monitoring and control.

Thus, we used carbon material (carbon black) as an alternative low cost support for Au@Pd nanoparticles deposition. Then, we explored the construction of an electrochemical sensor using the carbon-supported core-shell nanoparticles (Au@Pd/CB) within a dihexadecylphosphate (DHP) film for the development of an amperometric method for the determination of HDZ in water samples.

2. Experimental

2.1. Reagents and standards

All reagents were of analytical grade: dihexadecylphosphate, hydrazine sulfate, palladium (II) chloride (PdCl₂), gold (III) chloride (AuCl₃), and ethylene glycol were purchased from Sigma-Aldrich. The Vulcan-XC72R carbon black was kindly supplied by Cabot Corporation. The supporting electrolyte used was a 0.2 mol L⁻¹ phosphate buffer (pH 10.0) deoxygenated solution. All solutions were prepared using nanopure water supplied by a Milli-Q system (Millipore®) with resistivity ≥ 18.2 M Ω cm.

All electrochemical measurements were performed under N₂ atmosphere to avoid the reaction of HDZ with molecular oxygen.

2.2. Apparatus

A potentiostat/galvanostat model μ -Autolab type III (Eco-Chemie, the Netherlands) was used for the electrochemical measurements. A three-electrode cell system was used, with the

proposed sensor as the working electrode, a Pt wire as the auxiliary electrode, and an Ag/AgCl (3.0 mol L⁻¹ KCl) as the reference electrode.

The pH measurements were performed using an Orion Expandable Ion Analyzer (model EA-940, USA), employing a combined glass electrode with an Ag/AgCl (3.0 mol L⁻¹ KCl) external reference electrode.

The morphologic analysis of the nanomaterials was carried out using images acquired by field-emission gun scanning electron microscopy (FEG/SEM, Magellan 400 L, operated at 25 kV) and by transmission electron microscopy (TEM, FEI Tecnai G2F20) 200 kV.

For SEM analysis, an aliquot of 20 μ L of Au@Pd/CB aqueous dispersion (preparation procedure described in the next section) was dropped onto a 1 cm \times 1 cm GCE plate, and then left to dry at room temperature. For TEM analysis, the Au@Pd/CB samples were suspended in isopropyl alcohol using an ultrasound bath. An aliquot of each solution was dropped onto a porous carbon film supported on a copper grid and then left to dry at room temperature.

The structural characterization of the samples was completed with powder X-ray diffraction (XRD) measurements. XRD analyses were performed in a Bruker-AXS D8-Advance diffractometer with CuK α radiation ($\lambda = 1.5418$ Å) in the 2 θ range of 15°–90° at a scanning rate of 0.5° min⁻¹.

HDZ determination was carried out by a comparative spectrophotometric method using a Shimadzu UV–vis spectrophotometer (Model UV-2550) set at 458 nm with a quartz cuvette (optical path length of 10 mm) and a 1:99 v/v HCl solution as solvent and *p*-dimethylaminobenzaldehyde as chromophore [36].

2.3. Synthesis of core-shell nanoparticles

The Au@Pd nanoparticles were prepared by chemical reduction of salt precursors using an ethylene glycol aqueous solution as a reducing agent. Initially, 6 mg of AuCl₃, 5 mL of ultrapure water and 20 mL of ethylene glycol were put in a 250 mL flask. Then, 190 mg of CB was added to the mixture. The mixture was stirred for 4 h in an ultrasonic bath. The reduction reaction was then performed at 120 °C for 24 h under constant stirring. The obtained AuNPs/CB dispersion was filtered, washed with deionized water, and dried at 80 °C in an oven.

Second, 10.3 mg of PdCl₂ was dissolved in 15 mL of 0.4 mol L⁻¹ HCl solution under sonication for 1 h. Subsequently, 150 mg of the powder (AuNPs/CB) obtained in the first synthesis step, and 60 mL of ethylene glycol were added to a 250 mL flask. The mixture was stirred for 4 h in an ultrasonic bath. The reduction reaction was also performed at 120 °C for 24 h under constant stirring to obtain a 5 m/m% of Au@Pd catalyst in CB. Once the Au@Pd/CB dispersion obtained, it was filtered, washed with deionized water, and dried at 80 °C in an oven.

2.4. Sensor preparation

Firstly, the surface of a glassy carbon electrode (GCE, $\phi = 3.7$ mm) was polished with alumina suspension on a polishing cloth after being rinsed with ultrapure water, then sonicated for 2 min in ultrapure water to remove adsorbed particles.

An Au@Pd/CB-DHP aqueous dispersion was prepared by the addition of 1 mg of Au@Pd/CB and 1 mg of DHP in 1 mL de H₂O, using ultrasonic agitation for 60 min. Afterwards, an aliquot of 8 μ L was dropped onto the GCE surface and the solvent was evaporated at room temperature for 3 h. Thus, a GCE modified with Au@Pd/CB within a DHP film was obtained, as described in detail elsewhere [37,38]. This sensor was designated as Au@Pd/CB-DHP/GCE.

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