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Aggregates of gold nanoparticles with complexes containing ruthenium as modifiers in carbon paste electrodes

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ABSTRACT

Gold nanoparticles (AuNPs$^-$) were synthesized through the reduction of $HAuCl_4$ with a solution of sodium citrate 1%, getting negatively charged species. $[Ru^{II}Cl(dppb)(bipy)(py)](PF_6)$ and $[Ru^{III}Cl_2(dppb)(phen)](PF_6)$ were also synthesized as monocationic species (Ru$^+$), where dppb = 1,4-bis(diphenylphosphino)butane, bipy = 2,2′-bipyridine, phen = 1,10-phenantroline and py = pyridine. Aggregates of AuNPs$^-$ with negatively charged and with a cationic complex containing ruthenium (II) and (III) were obtained by means of electrostatic interactions. The AuNPs$^-$ and aggregates (Ru–AuNPs) were analyzed by ultraviolet/visible spectroscopy (UV–Vis), Fourier transform infrared spectroscopy–attenuated total reflectance (FTIR–ATR), nuclear magnetic resonance of phosphorous ($^{31}P\{^1H\}$ NMR), cyclic voltammetry (CV) and field emission scanning electron microscopy (FE-SEM). The AuNPs$^-$ and the Ru–AuNPs were used as modifiers in the preparation of carbon paste electrodes and their performance were evaluated by cyclic voltammetry to determination of acetaminophen.

1. Introduction

Since the work of Kuwana and French [1] in 1964, where modifier materials were introduced in carbon paste electrodes (CPE), developed by Adams [2] in 1958, a large quantity of modifier materials have been widely researched in electroanalysis and in the context of chemical sensors [3–5].

Gold nanoparticles (AuNPs), one of the new promising materials, were used to modify electrodes due to their stable physical and chemical properties, small dimensional size and useful catalytic activities [5–7]. The most common method to synthesize gold nanoparticles is by a process called “arrested nucleation and growth”[8], also known as the Turkevich method [9]. This occurs due to the reduction of $H[AuCl_4]$, by sodium citrate or sodium borohydride, and provides AuNPs with diameters of 20 nm. Further studies done by Frens [10] enabled the control over AuNPs size by varying the feed ratio of gold salt for the sodium citrate. Chow and Zukoski [11] provided the kinetics of the Turkevich process and Yu and co-workers [12] determined an optimal purification method as well as the stoichiometric equation of the AuNPs synthesis through the citrate reduction method. The overall charge of the gold nanoparticles is negative as a consequence of the citrate being weakly bounded to the surface. Citrate is a very common reducting agent and has also been used to prepare other metal nanoparticles, such as Ag, from $AgNO_3$, Pd from $H_2(PdCl_4)$ and Pt from $H_2(PtCl_6)$ [8].

The use of AuNPs as modifier electrodes have been extensively used in chemical and biological sensing, due to their physical and chemical attributes that make them excellent scaffolds for fabrication of novel chemical and biological sensors [6,13]. AuNPs feature excellent conductivity, extensive surface area and catalytic properties that make them excellent materials for the electrochemical detection of a wide range of analytes [14].

However the use of gold nanoparticles to construct modifier electrodes via electrostatic cross-linking of citrate-stabilized AuNPs$^-$ and cationic species has not been systematically investigated. The most cited works in this field in the literature are the works of Wang and coworkers [15], where they described a method for effective immobilizations of cationic ruthenium complexes on an electrode surface, and the work of Willner and co-workers [16], where they reported the construction, via electrostatic cross-linking, of an electroactive multilayer electrode by simultaneously depositing anionic AuNPs$^-$ and oligocationic cyclophanes. In both cases a donor S compound was used to cross-link the AuNPs$^-$ with a derived indium tin oxide (ITO) electrode surface. The electrostatic interaction with the positive charge species can occur after or before the cross-link of the AuNPs$^-$ with the ITO electrode surface.

Herein is described how the negative charge of gold nanoparticles from $HAuCl_4$, reduced with sodium citrate, can incorporate

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cationic ruthenium complexes in carbon paste electrodes without donor S compounds. The resulting electrode (CPE–AuNPs–Ru) was used to acetaminophen detection.

2. Experimental

2.1. Material and Instrumentation

Reagents: All reactions were carried out under an argon atmosphere using standard Schlenk techniques. $RuCl_3 \cdot H_2O$, $HAuCl_4$, triphenylphosphine (PPh_3), 1,4-bis(diphenylphosphine)butane (dppb), 2,2′-bipyridine (bipy), pyridine (py), 1,10-phenantroline (phen) and sodium citrate were purchased from Aldrich and used as received. Reagent grade solvents were distilled prior to use.

Instrumentation: The NMR spectra of the compounds were obtained at Universidade Federal de São Carlos, São Carlos (SP). They were acquired with a Bruker DRX-400 spectrometer (9.4 T) equipped with a 5 mm inverse probe head. Samples for $^{31}P\{^1H\}$ experiments were prepared under an inert atmosphere and measured at room temperature, with methylene chloride (CH_2Cl_2) as solvent and a D_2O capillary. Chemical shifts were reported with respect to the phosphorus signal in 85% phosphoric acid (H_3PO_4).

Optical spectra were obtained on a Perkin Elmer model Lambda 25 spectrophotometer with 1 cm quartz cell between the 300 and 800 nm. The FTIR spectra were recorded on a Jasco FTIR 4000 spectrometer with an ATR apparatus, using a diamond cell as support, or conventional KBr cell of 0.2 mm length in the 4000–400 cm^{-1} range.

Electrochemical data were obtained using a potenciostat/galvanostat Micro-autolab type III. Solutions of the complexes (10^{-3} mol L^{-1}) were prepared in dichloromethane (CH_2Cl_2) using 0.10 mol L^{-1} tetrabutylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. Measurements were made with a three-electrode configuration cell. A platinum foil was used as the working and the auxiliary electrode and Ag/AgCl as the reference electrode. In this condition ferrocene is oxidized at +0.43 V.

The morphology and the particles size were investigated using a Supra 35-VP FE-SEM (Carl Zeiss, Germany) operated at 6 kV.

2.2. Synthesis

2.2.1. Preparation of gold nanoparticles (AuNPs)

AuNPs with a diameter of 10–18 nm were prepared by citrate reduction of HAuCl4 in an aqueous solution according to the well-known method described by Frens [10]. In brief, 20 μL of solution, containing HAuCl4 (Au 58%) was added to 100 mL of water. The resulting solution was brought to reflux, and 3 mL of sodium citrate solution (1%) was introduced while stirring. The solution was then kept boiling for another 30 min, while the colors changed from yellow to deep blue and then to red. Afterwards the solution was left to cool until room temperature.

2.2.2. Synthesis of ruthenium complexes

The $[Ru^{II}Cl(dppb)(bipy)(py)](PF_6)$ and $[Ru^{III}Cl_2(dppb)(phen)](PF_6)$ complexes were synthesized as described previously [17].

2.2.3. Aggregates of gold nanoparticles with ruthenium complexes

$[Ru^{II}Cl(dppb)(bipy)(py)](PF_6)$ (71.1 mg; 75.1 μmol) was dissolved in acetone (10 mL) under magnetic stirring at room temperature. After complete dissolution, it was transferred to a stock solution of AuNPs in water (100 mL, 0.5 mmol L^{-1}), which was previously synthesized. Therefore, the formation of a quantitative brown precipitate occurred. It was collect by centrifugation, washed three times with water, and then dried under vacuum. The same procedure was used with $[Ru^{III}Cl_2(dppb)(phen)](PF_6)$, producing a quantitative red brown precipitate.

2.3. Preparation of the carbon paste electrodes with modifiers

2.3.1. With gold nanoparticles (CPE–AuNPs)

CPE were prepared using powder graphite (20 μm diameter, 180 mg), and AuNPs as modifiers (different amounts were used for each electrode: 0, 0.1, 0.5, 1.0, 2.0, 5.0 and 10 mL, respectively, from a stock solution of AuNPs {0.05 mmol L^{-1}} containing 9.9 mg of Au). The mixtures were homogenized and kept at 60 °C for 5 h in order to dry. The paraffin (90 mg) was then added and homogenized again. The resulting paste was introduced in a Teflon tube with a 2 mm inner diameter to cool down at room temperature.

2.3.2. With the complex containing ruthenium and CPE–AuNPs (CPE–AuNPs–Ru)

A stock solution of $[RuCl(dppb)(bipy)(py)](PF_6)$ (1.0×10^{-3} mol L^{-1}) was firstly prepared in acetone, having afterwards the introduction of a series of modifier electrodes CPE–AuNPs$^-$ for 0.10, 1 and 10 min. The best time to produce an efficient CPE–AuNPs–Ru was at 1 min. The CPE–AuNPs–Ru was then dried at room temperature and used for the detection of acetaminophen by cyclic voltammetry.

3. Results and discussion

3.1. Synthesis and characterization of gold nanoparticles with complexes containing ruthenium (Ru–AuNPs)

The cationic complexes containing ruthenium (II) and (III), $[RuCl(dppb)(bipy)(py)](PF_6)$ and $[RuCl_2(dppb)(phen)](PF_6)$, were synthesized by ligand exchange using –P and –N donor groups, as published in previous works [17]. A synthetic route is ascribed in the Scheme 1.

These cationic ruthenium complexes were used as positive charge species "Ru^+" in order to aggregate onto the negative surface of gold nanoparticles (AuNPs$^-$), using the combination of acetone and water solution of related species. The Ru–AuNPs specimen was collected as a precipitate and stored as powder under vacuum for further applications. These interactions, using the classical $[Ru(bipy)_3]^{2+}$ complex as a positive charge in water solution, are well known and described by Wang and co-workers [15].

The process of interaction between Ru^+ and the AuNPs$^-$ specimen can be accompanied by optical measurements with the UV–Vis spectroscopy. The UV–Vis data is consistent with a colloidal suspension of AuNPs, and shows a plasmon band at 520 nm (solid line in Fig. 1), which is reasonable with gold nanoparticles that have a 10–18 nm of diameter. A stock solution of $[RuCl_2(dppb)(phen)](PF_6)$, and $[RuCl(dppb)(bipy)(py)](PF_6)$ (4×10^{-4} mol L^{-1} in acetone) was added in small amounts until 840 and 540 μL respectively. Fig. 1 summarizes how the aggregation process occurs in the solution.

Yang and co workers [18a] describe that the aggregation of AuNPs$^-$ in solution is influenced by cationic and oligocationic species. The polarization of the conduction electron oscillations in adjacent gold nanoparticles causes a new red-shifted plasmon absorbance, attributed to the coupling of the plasmon absorbance of the particles. This phenomenon occurs when 40 μL of $[RuCl(dppb)(bipy)(py)](PF_6)$ (4×10^{-4} mol L^{-1} in acetone) is added to the AuNPs$^-$ solution (0.5 mmol L^{-1}). As a result an enlarged band, centralized at 670 nm, arises and there is a significant decrease of the original plasmon band of AuNPs$^-$ (see Fig. 1B). Additional amounts of $[RuCl(dppb)(bipy)(py)](PF_6)$ decreases the plasmon band even more, until it is suppressed and therefore it