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Formation and electroanalytical performance of polyaniline–palladium nanocomposites obtained via Layer-by-Layer adsorption and electroless metal deposition

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ABSTRACT

The Layer-by-Layer (LbL) adsorption technique is used to produce thin composite layers consisting of polyaniline (PANI) and Pd particles in two different ways: (i) multistep adsorption of PANI and presynthesized Pd nanoparticles (NPs) and (ii) multistep adsorption of PANI and polysterene sulfonate (PSS) followed by electroless deposition of palladium particles (Pd_{eless}). The formation of both types of composite layers is characterized by electrochemical and microgravimetric measurements.

Electrochemical measurements for hydrogen peroxide reduction are carried out at neutral pH under voltammetric and amperometric conditions. It is established that the PANI–Pd NPs composites show a sensitive voltammetric response for H_2O_2 reduction in the 40–300 μM concentration range whereas the (PANI–PSS)Pd_{eless} composites have high intrinsic electroactivity that masks the H_2O_2 reductive response. The amperometric data show high sensitivity for both types of composites: PANI–Pd NPs and (PANI–PSS)Pd_{eless} (with Pd incorporated in several electroless deposition steps). For the PANI–Pd NPs material the concentration range of linear response is 10–700 μM and the limit of detection 2.6 μM. The obtained non-enzymatic electrocatalytic materials are suitable for monitoring the levels of H_2O_2 in drinking and waste waters.

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1. Introduction

Hydrogen peroxide is a highly oxidative chemical agent that is used for waste water decontamination [1,2] and for cleaning procedures in the chemical and electronic industries [3]. This compound is involved also in the so called advanced oxidation processes (AOP) for decontamination of industrial waste waters where hydrogen peroxide is used in combination with UV light irradiation [4,5]. Furthermore it is found to be a product of water radiolysis during nuclear fuel storage [6]. Hydrogen peroxide is very toxic for human cells and is associated with progression of different diseases. It is generated in many catalyzed reactions involving enzymes, i.e. uricase, glucose oxidase, cholesterol oxidase, and choline oxidase and corresponding target molecules, i.e. uric acid, glucose, cholesterol, choline, etc. In biomedical research the detection of H_2O_2 as a byproduct of enzymatic reactions is one of the strategies to measure the target compounds. Thus analytical determination of hydrogen peroxide is important from various points of view. Different approaches are used for the electroanalytical determination of H_2O_2 based either on oxidation or reduction, with or without the involvement of enzymatic mediators. The enzyme-based electrodes provide usually high selectivity and sensitivity, but at the same time suffer from a more complicated handling, low stability and reproducibility.

Apart from the enzymatic detection a variety of electrode materials some of them involving noble metals were tested for direct reduction of H_2O_2. Palladium-based materials have been intensively studied [7–12] with the main focus set recently on the attempt to disperse Pd nanoparticles on different substrates [9–12]. PANI-coated electrodes were also investigated for direct electroanalytical determination of hydrogen peroxide [13–17]. Sensitivity in the micromolar range of hydrogen peroxide was obtained in some cases [16,17]. On the other hand several investigations on the electroanalytical determination of H_2O_2 were based on metal particles-modified CP-coated electrodes [18–22]. Metals such as Pt, Au, Cu and Co were used to induce electrocatalytic properties in CP layers different than PANI. Reduction-based electroanalysis was investigated in the case of Pt/poly(o-phenylenediamine) [19], Au/poly(3,4-ethylenedioxythiophene) [20] and Cu/polypyrrole [21]. The use of the reduction (and not the oxidation) reaction provided the

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opportunity to avoid possible interference of coexisting organic compounds that undergo oxidation in the same potential window as H_2O_2.

The aim of the present study is to obtain composite layers of PANI and Pd nanoparticles (Pd NPs) by using different Layer-by-Layer (LbL) adsorption approaches. The combination of both components is expected to be suitable for producing a sensitive material for reductive electroanalytical detection of hydrogen peroxide. The LbL deposition technique for the formation of multilayered structures was originally developed for multistep consecutive adsorption of oppositely charged polyelectrolytes [23]. In the present investigation the LbL technique is used in two variations: (i) adsorption of dissolved PANI (as a cationic polyelectrolyte) is combined with adsorption of anionic-stabilized pre-synthesized Pd NPs and (ii) adsorption of dissolved PANI is combined with adsorption of polysterene sulfonate (PSS) as an anionic polyelectrolyte. In this case Pd is deposited in the LbL adsorbed PANI/PSS structures by electroless reduction of Pd ions involving PANI as reductant [24,25]. The first approach for producing nanocomposite layers consisting of metal (Au or Pd) NPs and PANI was explored in previous investigations [26–31]. It was found that the metal NPs incorporated in the PANI matrix remain electroactive and the composites are suitable for electroanalytical determination of NADH [26,27], hydrazine [29,30], dopamine and uric acid [30,31]. The suggested second approach combining LbL deposition of polyanion-doped PANI and electroless metal deposition (carried out in one or several steps) is so far not investigated. In our study the electroanalytical response of Pd–PANI nanocomposite layers obtained by means of the two LbL approaches mentioned above is compared with respect to H_2O_2 reduction.

Our goal is to develop a Pd-based non-enzymatic electrocatalytic material suitable for H_2O_2 detection in neutral solutions in the range of concentrations corresponding to the levels of H_2O_2 in drinking water and in waste waters treated by the H_2O_2/UV AOP. According to the European standard EN 902:2009 the H_2O_2 treatment dose of drinking water can be up to 17 mg/l, i.e. 500 μmol. The amounts of H_2O_2 used for decontamination of organic substances (natural organics, dyes and surfactants) in waste waters vary in large limits although the general trend is to use concentrations in the several hundreds of μmol range.

2. Experimental

2.1. Reagents

Aniline, sulfuric acid, phosphate buffer components (Na_2HPO_4 and NaH_2PO_4), H_2O_2 (30% aqueous solution) and ammonium persulfate were obtained from Merck. $Pd(NO_3)_2$, dimethylacetamide, PSS (Mr = 70,000) and sodium ascorbate were purchased from Sigma–Aldrich.

2.2. PANI and Pd NPs synthesis

PANI was synthesized by chemical oxidative polymerization in the presence of 0.1 M aniline, 0.1 M ammonium persulfate and 0.5 M sulfuric acid for 6 h at 4 °C under continuous stirring. The product, obtained as emeraldine salt, was transformed to emeraldine base by treating with 8% ammonia aqueous solution. In accordance with the procedure developed in [30] the obtained product was washed, dried at 40 °C for 5 h and dissolved in dimethylacetamide (20 mg dried emeraldine base per mL solvent) under continuous stirring and subsequent ultrasonication. After filtration, the solution was diluted 1–100 using diluted HCl (pH 3.1). Finally, the pH of the PANI containing solution was adjusted to pH 2.6.

Pd NPs were synthesized by fast addition of 1 mL of a 0.1 M sodium ascorbate dissolved in water to 10 mL boiling aqueous solution of 1 mM $Pd(NO_3)_2$. The solution was further boiled for about 3 min and then cooled to room temperature. The particles size of the freshly synthesized Pd NPs was determined by dynamic light scattering using a Zetasizer Nano (Malvern Instruments Ltd.). The size distribution dependence of a freshly synthesized Pd NPs shows an average diameter of 7 nm [29]. TEM images indicate sizes between 4 and 10 nm.

2.3. LbL deposition procedure

The solutions used for LbL adsorption were obtained from the original PANI dimethylacetamide solution by 1/100 v/v dilution with HCl (pH 2.6) and from the Pd NPs suspension by 1/1 (v/v) dilution with Millipore water, respectively. The first step in every LbL deposition sequence was always adsorption of PANI on the carrying substrates (gold or glassy carbon electrodes) followed by adsorption in the Pd NPs solution. The duration of the adsorption steps was fixed to 10 min. Between the depositions steps the substrates were rinsed thoroughly with diluted HCl (pH 2.6) in order to wash out the non-adsorbed particles. Composite layers consisting of PANI and Pd NPs (denoted further as LbL PANI–Pd NPs) were obtained by using typically 10–14 adsorption steps (i.e. 5–7 adsorption steps in each solution).

In the PANI–PSS experimental series LbL multistep deposition was carried out by using 1 mM solution of PSS instead of the Pd NPs solution [32]. Also in this case the adsorption step duration was fixed to 10 min. The LbL PANI–PSS layers were further used to deposit metallic Pd by means of electroless metal deposition (see below).

2.4. Pd electroless deposition

Palladium deposition of metal particles was carried out in a 5 mM solution of $PdNO_3$ by using reduced LbL deposited PANI–PSS layers that may undergo oxidation at the expense of the metal ions reduction. For this purpose the PANI–PSS layers were subjected to electrochemical reduction in 0.5 M H_2SO_4 solution by applying a potential of −0.2 V vs. Ag/AgCl reference electrode for about 15 min. In a next step, the electrode was disconnected and set at open circuit potential while 2 mL of 10 mM $Pd(NO_3)_2$ solution was immediately injected to the initial electrolyte. Open circuit potential (OCP) transients were measured in order to follow the electroless deposition process. Electroless metal deposition was carried out by using the reductive capacity of the conducting polymer layers without any additional reducing agent. This is a self-limited process that allows for fine control over the amount of deposited metal [24,25,33,34].

In some sets of experiments Pd was deposited by means of the electroless process carried out at the final LbL deposited PANI–PSS layer. These layers will be further denoted as n(PANI–PSS)/Pd_{eless} where n denotes the number of adsorbed bi-layers. In other sets of experiments Pd electroless deposition occurred several times, e.g. after adsorption of each two PANI–PSS bi-layers. Thus the notation 3(2(PANI–PSS)/Pd_{eless}) means that the composite was obtained by 6 PANI and 6 PSS adsorptive steps and Pd was deposited three times, after each 2(PANI–PSS) bi-layers.

2.5. Voltammetric, microgravimetric measurements and SEM

Electrochemical characterisations were carried out using a potentiostat/galvanostat Princeton Applied Research EG&G 263A in a three electrode configuration. A freshly polished glassy carbon electrode with a surface area of 0.071 cm^2 was used as working electrode. A platinum plate and a saturated Ag/AgCl electrode were used as counter and reference electrodes, respectively. All

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