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# Chemosensitive nanocomposite for conductometric detection of hydrazine and NADH

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# ABSTRACT

A new chemosensitive material based on palladium nanoparticles and PEDOT-PSS is described. The composite was characterized by transmission electron microscopy, cyclic voltammetry and in situ resistance measurements. The material was applied for conductometric detection of hydrazine and NADH. Upon exposure to these analytes PEDOT is reduced leading to an increase in its conductance. This process is catalyzed by palladium. A model for description of the potential dependence of polymer conductivity was suggested, tested and applied for the development of new calibration procedure of chemiresistors based on electroactive polymers.

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#### 1. Introduction

In the last years conducting polymer-based nanocomposite materials have attracted enormous interest [1-4]. Within this field composites of conducting polymers and metal nanoparticles were shown to be useful materials in chemical sensors [1,5]. Such composites can be prepared by electrochemical deposition of metallic nanoparticles on a surface or immobilization into a conducting polymer matrix [6], by electroless reduction of metal salt precursors by the conducting polymer [6,7], by reduction of metal salt precursors by monomers resulting in polymerisation of the monomers [8], by electropolymerisation of conducting polymers in presence of nanoparticles in solution [9] and by electrostatically driven layer by layer deposition of metal nanoparticles and conducting polymers [10,11]. There are only few publications dealing with the preparation of dispersions from conducting polymers and pre-synthesized nanoparticles [12]. However such dispersions have the advantage that they can be easily transferred to almost any surface by ink-jet printing, spin- or spray-coating [13]. Palladium or platinum nanoparticle conducting polymer composites were used in chemical sensors for detection of hydrazine, ammonia [14], methanol [15], hydrogen, oxygen and pH [16] and in biosensors for detection of glucose via hydrogen peroxide oxidation [17,18]. The composites from conducting polymers and metallic nanoparticles are typically used in amperometric sensors while there are only few publications dealing with the application of such composites in chemiresistors [16]. In most cases they were used as gas sensors [14,15,19]. The nanoparticles in chemiresistors serve as reaction sites for redoxactive analytes. The resulting charge is transferred to the conducting polymer thus changing its conductivity.

Palladium nanoparticles have been successfully used in the electrooxidation of hydrazine [20–22] and NADH [23]. In a comparative study it was further demonstrated that palladium nanoparticles are a unique catalytic material for hydrazine oxidation [24]. Conductometric detection of gaseous hydrazine was reported [25–27], however to our knowledge there was no report on hydrazine detection in aqueous solutions. Polyaniline doped with polyanions which extend its electroactive pH range towards pH 7 can be used in conductometric sensors for NADH [28,29], however polyaniline's conductance is strongly pH dependent, which can influence the measurements.

In this work we present a characterization of a nanocomposite consisting of PEDOT-PSS and palladium nanoparticles and its application for conductometric detection of hydrazine and NADH. Furthermore, a new approach to calibrate such sensors is introduced.

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Fig. 1. Interdigitated electrode for simultaneous two- and four-point measurements.

# 2. Experimental

#### 2.1. Chemicals

PEDOT-PSS (conductive grade),  $Pd(NO_3)_2$ , ascorbate (Na-salt) and hydrazinehydroxide were purchased from Sigma Aldrich. Dimethylsulfoxide (DMSO) and sulfuric acid (98%) were from Merck. Buffers were prepared from equimolar amounts (50 mM) of Na<sub>2</sub>HPO<sub>4</sub> and NaH<sub>2</sub>PO<sub>4</sub> and were adjusted to pH 7 by NaOH. Deionized water additionally purified was used in all experiments.

#### 2.2. PdNPs synthesis

10 mL of a 1 mM solution of  $Pd(NO_3)_2$  in water was heated until boiling. Then 1 mL of a 0.1 M solution of sodium ascorbate in water was quickly added. The solution was further boiled for about 3 min and then allowed to cool down at room temperature [22]. The nanoparticles were characterized by transmission electron microscopy (TEM) on a LEO 912 TEM; the samples were prepared by adsorption of the nanoparticle containing dispersion on a carbon coated copper grid.

#### 2.3. Sensor fabrication

250  $\mu$ L of the PEDOT-PSS dispersion was diluted with 9.75 mL of water. 500  $\mu$ L of this solution was mixed with the PdNP solution resulting in a stable dispersion of the PdNPs in the PEDOT-PSS solution. 1% of DMSO was added to this solution before deposition onto the electrodes. An addition of DMSO to PEDOT-PSS is known to enhance the conductivity of PEDOT-PSS layers. The chemiresistors were prepared by drop-coating of 0.5  $\mu$ L of this dispersion on electrodes with a working area of 0.64 mm<sup>2</sup> consisting of four interdigitated gold strips separated by an 8  $\mu$ m gap (Fig. 1). Then the chemiresistors were dried at about 80 °C for 10 min. For the NADH sensor, 0.2  $\mu$ L instead of 0.5  $\mu$ L was used. Before coating the electrodes were cleaned subsequently by acetone, ethanol, piranha solution and water.

The samples for cyclic voltammetry were prepared by dropcoating of  $6 \,\mu$ L of the composite dispersion on a glassy carbon electrode (3.14 mm<sup>2</sup>) and drying at 80 °C for 10 min.



Fig. 2. TEM images of palladium particles in the PEDOT-PSS matrix.

#### 2.4. Measurements

Electrochemical measurements were done using a CHI-660A electrochemical analyzer. Either Ag/AgCl electrodes or saturated calomel electrodes were used as a reference electrode. The type of the electrode used is indicated in the corresponding figures. A platinum wire was used as a counter electrode.

Simultaneous two- and four-point measurements (S24) were used as described in [30,31]. Shortly, potential difference pulses of alternating polarity were applied between the outer two electrodes and the resulting current was measured. Simultaneously the potential drop between the two inner electrodes was measured. To avoid effects due to a potential difference between the outer electrodes, only a small potential difference (10 mV) was applied. Potential control during simultaneous two- and four-point measurements was performed by programmed a Keithley 617 connected to a reference electrode (SCE) [31]. Phosphate buffer solution (pH 7, 100 mM) was used in all experiments. Hydrazine hydrate solutions were made by dilution of a 1 M stock solution in buffer. To measure the effect of hydrazine the sensor was placed in a flow cell. Each concentration was pumped through the flow cell till the response of the sensor reached the steady-state value. In case of NADH additions of NADH from a 10 mM stock solution do the pH 7 buffer containing the sensor were performed.

#### 3. Results and discussion

## 3.1. Material characterization

TEM images of the PEDOT-PSS/PdNP composite obtained by adsorption of the composite on a carbon coated copper grid, show 5–10 nm big palladium particles (Fig. 2). A characterization of these nanoparticles including TEM and light scattering data was presented elsewhere [22]. It seems that the particles are stacked together in a loose random structure. It is known that PEDOT-PSS consists of 30–200 nm particles [32,33], but they scatter the electrons much smaller than the palladium nanoparticles and therefore are not observed in the TEM image.

Optical microscopy of a film of the composite on an interdigitated electrode shows homogeneously distributed small black particles with the size of around  $1 \,\mu$ m along with some bigger aggregates within a thin film of PEDOT-PSS. It has to be noted that



Fig. 3. Picture of a thin film of the composite on an interdigitated electrode, acquired by optical microscopy.

the film covers the whole surface (Fig. 3). Furthermore no connections of the microelectrodes by big agglomerates of palladium were found in all experiments.

Cyclic voltammograms were recorded to evaluate the presence, electroactivity and stability of palladium particles in the layers. The voltammogram shows the typical features of palladium; e.g. the currents corresponding to the hydrogen adsorption (<-0.2 V) and desorption (-0.05 V) and oxide formation (>0.7 V) and reduction (0.5 V) (Fig. 4a). The voltammogram is very similar to that of a PEDOT-PdNP composite obtained by electroless deposition of palladium in previously reduced PEDOT films [7]. For compar-

ison, the voltammogram for pure PEDOT-PSS on the glassy carbon electrode is shown in Fig. 4b. The currents of the PEDOT oxidation are much smaller than the currents observed for hydrogen adsorption/desorption on the palladium nanoparticles. At the starting potential of -0.35 V versus Ag/AgCl PEDOT is already partially oxidized, therefore only partial oxidation and reduction of PEDOT takes place during this voltammetric experiments.

The catalytically active palladium nanoparticles are electrically connected by PEDOT-PSS. This is proved by in situ conductance measurements. The potential dependent conductance of the nanocomposite is very similar to that of PEDOT-PSS without palladium nanoparticles and seems therefore not influenced by the presence of the PdNPs (Fig. 5). This is in contrast to the PANI-PdNP composite obtained by layer by layer deposition from diluted PANI solutions in [22], where PdNPs are assumed to build conducting pathways in the PANI matrix.

The potential dependent conductance of PEDOT can be described with a simple model assuming that the polymer composite has two states: one conducting state A and one non-conducting state B. In equilibrium the potential influence on the concentrations of these states can be described using the Nernst equation.

$$E = E_{AB}^{0} + \frac{RT}{n_{AB}F} \ln \frac{c_{B}}{c_{A}}$$
(1)

Let's indicate the molar conductivities of the corresponding states of the polymer as  $g_x$ , where the index x is either A and B. The behaviour of different states of the polymer is assumed to be independent. The total conductivity of the polymer is the sum of conductivities of all polymer states:

$$G = c_A g_A + c_B g_B \tag{2}$$



Fig. 4. Voltammogram of the nanocomposite of PdNP with PEDOT-PSS (a) and voltammogram of PEDOT-PSS (b). Electrolyte: 0.5 M H<sub>2</sub>SO<sub>4</sub>. Sweep rate: 0.1 V/s.



Fig. 5. Potential influence on the conductance of the nanocomposite from PdNP with PEDOT-PSS (a) and on PEDOT-PSS without palladium nanoparticles (b). Electrolyte: 100 mM phosphate, pH 7.



**Fig. 6.** Increased concentrations of hydrazine lead to increase of the current on voltammograms of the nanocomposite of PdNP and PEDOT-PSS deposited on a glassy carbon electrode. The hydrazine concentrations are: 0, 20, 100, 200, 400  $\mu$ mol/L. Electrolyte: 100 mM phosphate, pH 7. Sweep rate: 0.1 V/s.

By combining Eqs. (1) and (2) one and substitution of  $c_{A}g_{A}$  and  $c_{B}g_{B}$  with  $g_{A}'$  and  $g_{B}'$  one gets an equation for the potential dependent conductivity of the polymer.

$$G = \frac{g'_{\rm A} + (g'_{\rm B} \, 10^{(E_{\rm 0\_PEDOT} - E)/a})}{1 + 10^{(E_{\rm 0\_PEDOT} - E)/a}} \tag{3}$$

where  $a = 2.3(RT/n_{AB}F)$ 

As one can see in Fig. 5, Eq. (3) describes the potential dependent conductance of the film quite well, especially in the conducting region. The model is similar to that proposed by Amemiya et al. to describe the spectroelectrochemical behaviour of polypyrrole [34]. It has to be stated that a logarithmic plot of the conductance versus the potential would give a better view of the potential dependence of the composite as with the linear plot the small changes in the highly oxidized state are overestimated [35], however in this work the high conducting region is of more interest as even with high concentrations of hydrazine we do not reach potentials less than -0.25 V.

The electroactivity of the nanocomposite from PdNP and PEDOT-PSS towards hydrazine oxidation was studied by cyclic voltammetry in a pH 7 buffer. A set of cyclic voltammograms registered by using a glassy carbon electrode coated by the composite at various concentrations of hydrazine in the range 40–800  $\mu$ M is presented in Fig. 6. The figure shows the stationary voltammograms obtained after three cycles carried out at each concentration of hydrazine in the solution. The oxidation of hydrazine



**Fig. 8.** Open circuit potential of the interdigitated gold electrode coated by the nanocomposite of PdNP and PEDOT-PSS as a function of hydrazine concentration.



**Fig. 9.** Comparison of the dependencies of the conductance of nanocomposite from PdNP and PEDOT-PSS on the applied electrode potential (squares) and on the open circuit potential defined by hydrazine additions (circles). The line presents theoretical curve according to Eq. (3).

seems to start at about  $-0.3\,\text{V}$  and has a maximum at about 0.15 V.

#### 3.2. Conductometric detection of hydrazine and NADH

As expected, an exposure of the nanocomposite of PdNP with PEDOT-PSS to hydrazine or NADH leads to the reduction of PEDOT



Fig. 7. Influence of hydrazine (a) and NADH (b) on the conductance of the nanocomposite from PdNP with PEDOT-PSS and pure PEDOT-PSS (inset a). Electrolyte: 100 mM phosphate, pH 7.



**Fig. 10.** Calibration curve of the conductometric hydrazine (a) and NADH (b) chemiresistors based on the theoretical model describing redox conversions of PEDOT. The squares indicate the measured conductance, whereas the lines represent theoretical dependencies obtained from Eq. (5) with corresponding parameters for hydrazine and NADH.

accompanied by the decrease in the conductance (Fig. 6). It was possible to observe an effect on addition of so low concentrations as 0.5  $\mu$ M of hydrazine or 10  $\mu$ M of NADH. At such concentrations the signal changes were at least three times higher than typical fluctuations of the base line, therefore it can be considered as the detection limit. Although the simple and crude sensor fabrication technique without precise control of the layer thickness led to some variation of absolute values of the sensor response from electrode to electrode, the values of the detection limit where about the same for all sensors. It has to be noted that for NADH a thinner layer of the composite was used resulting in a less conducting layer. In comparison to hydrazine the reduction of the composite by NADH was rather slow and the conductance changes where lower. One can assume that hydrazine can diffuse into the composite whereas NADH oxidation probably takes place only on the surface. Probably the PdNPs immobilized in the polymer matrix serve as reaction sites for hydrazine/NADH oxidation and the released electrons reduce PEDOT. This assumption is supported by the fact that the pure PEDOT-PSS covered electrode showed only weak changes upon exposure to hydrazine (14% change at 10 mM in comparison to 45%; see inset Fig. 7).

Alternatively, the analytical information can be obtained from potentiometric measurements. The open circuit potential of the composite decreased by 39 mV per decade with increased hydrazine concentration (Fig. 8). This value can be used to analyze stoichiometry of the reaction, however in this work we consider it as an empiric parameter which can be used for quantitative analysis of the hydrazine concentration. The equation for the potential of the nanocomposite coated electrode is:

$$E = E_0 - 0.039 \log(c(N_2H_4))$$
(4)

where  $E_0 = -0.26$  V.

Taking into account this dependence and the dependence of the conductance of the composite on applied electrical potential it is clear why the response is not linear with increasing concentration, but almost linear in the logarithmic concentration scale. By assigning the open circuit potential values to the conductance values for each hydrazine concentration and plotting these data together with the potential dependent conductance of the nanocomposite of PdNP and PEDOT-PSS, one can see that the data match each other perfectly (Fig. 9). Thus chemical and electrical control of the redox potential of the film yield quantitatively the same result.

Combining the equation used for the description of the potential dependent conductance of the composite (Eq. (3)) with the equation used for description of the electrode potential in dependence of the hydrazine concentration (Eq. (4)), one gets an equation which describes the dependence of the conductance on the concentration

of hydrazine in solution.

$$G = \frac{g'_{\rm A} + (g'_{\rm B}10^{(E_{0}\_{\rm PEDOT}-E_{0}\_N_{2}H_{4}}-0.039\log(c(N_{2}H_{4}))/a)}{1+10^{(E_{0}\_{\rm PEDOT}-E_{0}\_N_{2}H_{4}}-0.039\log(c(N_{2}H_{4}))/a}$$
(5)

Fig. 10 shows that Eq. (5) describes the concentration dependence of the conductance of the layer. It has to be noted that the all parameters used for this description were determined from the potential dependent conductivity of the composite and the potentiometric response of the composite on increasing hydrazine concentrations. No fitting procedure was used to describe the dependence. The same approach was used for NADH, however in this case the sensitivity of the conductance was 59 mV per decade. At high conductance but before saturation (Fig. 9) Eq. (5) predicts linearisation of the concentration dependence in semilogarithmic scale what is observed in Fig. 10.

Another approach suggested in literature to calibrate chemiresistors is based on the response time of the sensor after analyte addition [28,36,37]. However this approach requires that the sensor is switched to its initial potential before each concentration determination and is therefore not suitable for continuous monitoring of analyte concentration.

# 4. Conclusion

A new chemosensitive nanocomposite material was obtained from palladium nanoparticles and PEDOT-PSS. The composite forms a stable dispersion in aqueous media which can be used for deposition on various surfaces via drop-, spray- or spin-coating. The composite was found to be chemosensitive towards reducing agents like hydrazine or NADH and belongs therefore to the class of broad-selective chemosensitive materials for detection of reducing compounds. Conductometric or potentiometric transducing was used. The chemosensitivity is probably based on electrocatalytical activity of palladium nanoparticles corresponding by the reduction of PEDOT. A simple model describing redox conversion of PEDOT provided quantitative description of this system and was used for the development of a new calibration approach.

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