

Photo-Electrochemical Detection of Nitrite Ions on a SPE Functionalized with TiO₂ Nanoparticles for Environmental Monitoring

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Abstract

In this paper, a highly sensitive photo-electrochemical sensor based on a screen printed carbon electrode SPE was developed for nitrite detection. The sensor was functionalized with titanium oxide nanoparticles having excellent photo-catalytic properties. The functionalization of the working electrode was investigated by performing scanning electron microscopy imaging and energy-dispersive-X-ray (EDX). Both methods confirmed the successful modification of the electrodes. In addition, an optimization of pH value of the phosphate buffered saline (PBS) solution was performed as it can influence the surface charge properties of the sensor. After the optimization, the sensor performance was characterized by means of cyclic voltammetry (CV) and square wave voltammetry (SWV) under illumination of an UV light source at a wavelength of 254 nm. The results show that in CV, the oxidation peaks have been enhanced around 20% by UV irradiation. This is the effect of the creation of electron/hole pairs in the structure of the TiO₂. The Square Wave Voltammetry measurements show two linear regions: The first in the range of 30 – 100 µmol/L and the second in the range of 100 – 1000 µmol/L and a limit of detection of 0.16 µmol/L.

Keywords- Electrochemical sensors; Nitrite detection; Photocatalytic effect; Titanium oxide nanoparticles; Screen printed electrodes (SPE)

1 Introduction

Recently due to excessive use of fertilizer, more nitrogen compounds are converted to nitrate and hence go to soil to be absorbed by plants or to tickle away to ground water. A high amount of nitrate in drinking and ground water can cause problems on humans and on the ecosystem in general. Under the influence of certain intestinal bacteria, nitrate is developed into nitrite in the body. Nitrite oxidizes the hemoglobin and prevents the oxygen supply to the cells, which can end up deadly especially for infants (blue baby syndrome) by internal suffocation [1]. For those reasons, the World Health Organisation (WHO) has fixed the values of nitrate and nitrite concentrations in drinking water respectively 50 mg/l and 3 mg/l [2]. Unfortunately, the concentration of nitrate exceeded this limit in several countries [3].

Therefore, there is an urgent need for highly sensitive and accurate quantitative determination of nitrite. Nitrite detection techniques can be divided into several categories, such as spectroscopic [Fehler! Verweisquelle konnte nicht gefunden werden.], optical [5] and catalytic methods [6]. These methods have shown good results, but they still hard to process and require heavy and expensive equipment. To avoid these limitations, electrochemical methods are preferred due to the high performance in terms of sensitivity, selectivity, fast response in addition to the possibility of in-situ detection of nitrite ions.

Among electrochemical techniques, photo-electrochemical method presents a promising pathway for a sensitive and selective detection of nitrite, which combines the properties of the electrochemical and photocatalytic methods [7]. The most widely studied semiconductor photo catalyst for the photo-electrochemical detection is the titanium oxide TiO₂, which is well-known for its excellent photo-catalytic properties [8].

Therefore, in this work, a photo-electrochemical sensor based on a screen printed carbon electrodes (SPE) was used. The SPE is formed with three electrodes: working electrode (WE), counter electrode (CE) and reference electrode (RE). The WE of screen-printed electrodes was modified by drop casting of a TiO₂-sensitive layer over its surface. The functionalized layer was examined via scanning electron microscopy imaging and energy-dispersive-X-ray. Then, the functionalized electrode was tested to detect nitrite under UV irradiation of a UV lamp with a wavelength of 254 nm.

2 Material and methods

Standard nitrite solutions were prepared with sodium nitrite. Ferri/ferrocyanide redox probe solution was prepared with potassium ferrocyanide and potassium ferricyanide salts. Phosphate buffer solutions (PBS) were prepared with sodium phosphate (dibasic heptahydrate and monobasic monohydrate). All chemicals were purchased

from SigmaAldrich and used without additional purification.

A commercially available carbon screen printed electrodes (purchased from PalmSens BV, Houten, Netherlands) were used and functionalized with Titanium oxide P25 (TiO₂ P25) purchased from Sigma Aldrich. In order to control the quality of the functionalized layer, scanning electron microscopy imaging and energy-dispersive-X-ray were done using Nova NanoSEM 200 microscope.

In this work, all the electrochemical measurements were carried out at room temperature using a potentiostat PalmSens 3. Cyclic voltammetry (CV) measurements were performed for the functionalized electrodes in different pH of PBS solutions prepared by mixing sodium phosphate monobasic and sodium phosphate dibasic, which were purchased from Sigma Aldrich. The measurements were carried out in solution containing 10^{-3} mol of nitrite under UV light source using an ultraviolet lamp Pen-Ray Standard UV with a wavelength of 254 nm.

3 Results and Discussion

3.1 Electrode surface characterization by SEM and EDX

The investigation of the SPE surface morphology of the bare and the functionalized electrode were carried out using the scanning electron microscope (SEM). As shown in figure 1, the SEM image of the bare carbon electrode surface reveals the presence of irregular and randomly oriented microscopic defects, which can increase the effective surface of the electrode and increase the number of possible active sites to capture the nitrite ions.

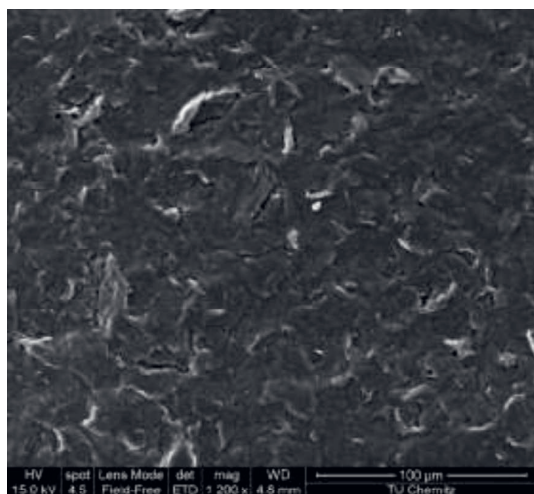


Figure 1: SEM image of the bare carbon electrode.

After functionalization with titanium oxide nanoparticles, a white layer has appeared on the surface of the working electrode as shown in figure 2.

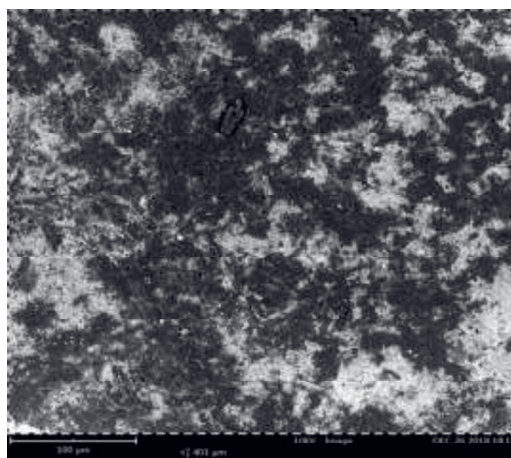


Figure 2: SEM image of the functionalized electrode

The evaluation of the chemical composition of the electrode surface was carried out using EDX technique. The EDX analysis of the bare electrode and TiO₂ functionalized electrodes is presented in table 1.

Table 1: Atomic composition of the working electrode material in % concentration

Element	Bare electrode	TiO ₂ -functionalized electrode
C	93.31	90.3
O	6.69	6.3
Ag	-	1.03
Ti	-	2.30

3.2 Electrochemical characterization of the electrodes

In this study, the electrochemical behaviour of the SPE and the kinetic transfer were investigated. The SPE was tested by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) in presence of the redox pair ferri/ferrocyanide [Fe(CN)₆]^{3-/4-} containing 0.1 M KCl as supporting electrolyte. The comparison between the cyclic voltammograms of the bare and the functionalized electrode shows a significant increase of the oxidation and reduction current peaks for the functionalized electrode as depicted in figure 3. This enhancement is related to the increases of the electro-active surface area of the electrode after the functionalization with the TiO₂ NPs.

In order to check the system reversibility, the difference between the oxidation and the reduction potential peaks $\Delta E = E_{pa} - E_{pc} = 250$ mV indicating that the system is quasi-reversible [9].

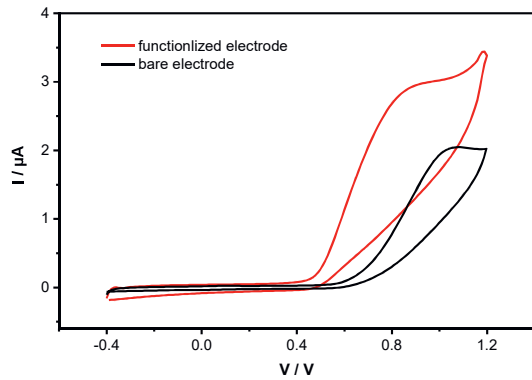


Figure 3: CVs of bare and functionalized electrodes in the presence of the redox pair ferri/ferrocyanide

The increase of the oxidation-reduction current peaks can be also referred to the reduction of the charge transfer resistance between the electrolyte and the electrode R_{ct} [10]. The reduction of R_{ct} value can be seen clearly through the EIS measurements in figure 4, where it is clear that the diameter of the semi-circle has been decreased after the functionalization with TiO_2 nanoparticles.

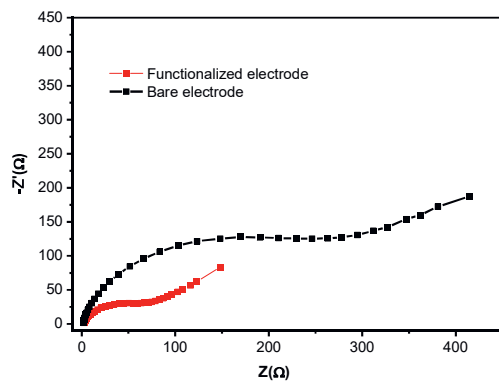


Figure 4: EIS of the bare and the functionalized electrode.

In order to get further information about the reasons behind the reduction of the charge transfer resistance and to estimate the electro-active surface of the electrode before and after functionalization, the Randles-Sevcik equation (equation 1) was applied on the bare and the functionalized electrode [11].

$$I_p = 268600 n^{3/2} A D^{1/2} C v^{1/2} \quad (1)$$

Where I_p is the oxidation current in Amperes, n is the number of electrons transferred during the redox event, D is the standard diffusion coefficient in cm^2/s , C is the concentration of the redox pair in mol/cm^3 , v is the scan rate in V/S and A is the electro-active surface area in cm^2 .

The calculated electro-active surface areas show that before functionalization, the area was $0.0027 cm^2$ and this number has been increased around two times after the functionalization and it becomes $0.0055 cm^2$.

3.3 Nitrite detection

a) Effect of the functionalization with TiO_2 NPs

In order to investigate the effect of the functionalization of the electrode with TiO_2 NPs, cyclic voltammetry measurements were run on the bare and the functionalized electrode in a PBS solution containing a nitrite concentration of $10^{-3} M$. Figure 5 presents the two different CVs, it is clear from the voltammograms that the oxidation peak current has significantly increased after the functionalization of the electrode. We can refer this increase of the oxidation peak to the higher electro-active surface area of the functionalization electrode with TiO_2 NPs in comparison to the bare electrode [12].

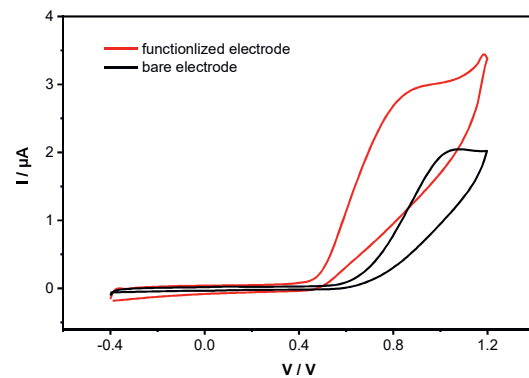


Figure 5: CVs of the bare and functionalized electrodes in $10^{-3} M$ of $NaNO_2$

b) Effect of pH and scan rate

The photo-catalytic reactions strongly depend on the pH value of the reaction solution because the surface charge properties of the semi-conductor can be influenced by the pH value. In acidic medium, TiO_2 surface becomes positively charged with the presence of H^+ ions ($TiOH_2^+$) which enhance the adsorption of nitrite ions (NO_2^-) to the electro-active sites of the photo-catalyst. Whereas in a basic medium the surface of the titanium oxide is negatively charged (TiO^-). In consequence, due to electrostatic repulsions, the adsorption of nitrite ions is unfavourable [13]. The effect of pH medium on the oxidation reaction was investigated by testing the sensor response in presence of $10^{-3} M$ of nitrite and at different pH (4.5, 5.7, 6.5 and 7.5). According to figure 6a, it is clear from the voltammograms that the suitable pH value that deliver the highest oxidation current is 5.7. To investigate the nature of the reaction, CV responses were recorded at different scan rates (0.3 – 0.9 V/S) on the functionalized electrode in a PBS solution pH = 5.7 in presence of $10^{-3} M$ of nitrite. The CV responses in figure 6b show a proportional increase of the oxidation current in correlation to the increase of the scan rate. The insert in figure 7 presents the linear fitting of the oxidation current as a function of the square root of the scan rate, which shows a linear rela-

tionship between them, with a correlation factor $R^2 = 0.997$. As a conclusion, the electrode exhibited a surface controlled process [10].

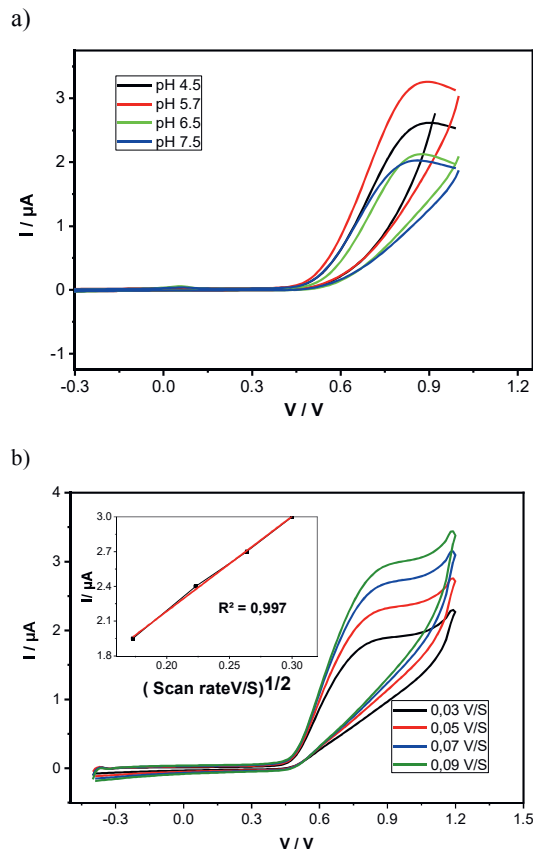


Figure 6 a) Response of the sensor in different pH values and b) CVs of 10^{-3} M of nitrite in different scan rate. Insert linear fitting of the oxidation current as a function of the square root of the scan rate.

c) Influence of UV irradiation on nitrite detection

In this part, the effect of the ultraviolet irradiation on the nitrite oxidation current peak was addressed. CV responses of the sensor were measured with three different nitrite concentrations ($5 \cdot 10^{-3}$, $6 \cdot 10^{-3}$, $7 \cdot 10^{-3}$) in PBS solution pH=5.7 with and without UV-irradiation. The irradiation of the TiO_2 surface with a UV light source 254 nm brings a sufficient energy to excite an electron from the valance band VB to the conductive band CB of the TiO_2 , which create a hole in the valance band and an electron in the conductive band of the TiO_2 . Photo-catalytic reactions are initiated by the photo-generated electrons (e^-) and holes (h^+) when the TiO_2 photo-catalyst is illuminated. The hole reacts with the adsorbed water or hydroxyl groups (OH^-) on the surface of the photo-catalyst to form hydroxyl radicals (OH^\bullet), which are, in general, accepted to be the reason for the initialization of the oxidation pathway [14]. As presented in figure 7, the UV irradiation has enhanced the oxidation peak around 20%.

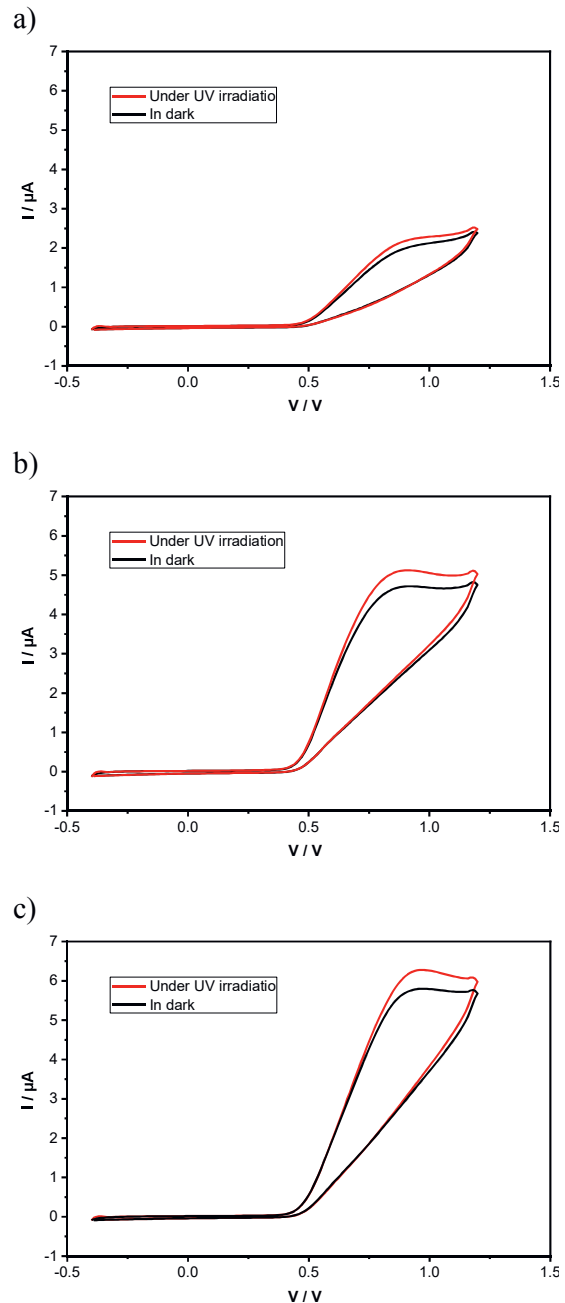


Figure 7 CVs response of different nitrite concentrations a) $5 \cdot 10^{-3}$, b) $6 \cdot 10^{-3}$ and c) $7 \cdot 10^{-3}$ mM

d) Nitrite detection using square wave voltammetry (SWV) technique

The response of the sensor upon different nitrite concentration was recorded using the square wave voltammetry technique in a PBS solution pH=5,7 under ultraviolet irradiation. Figure 8 presents the recorded SWV of different concentration of nitrite.

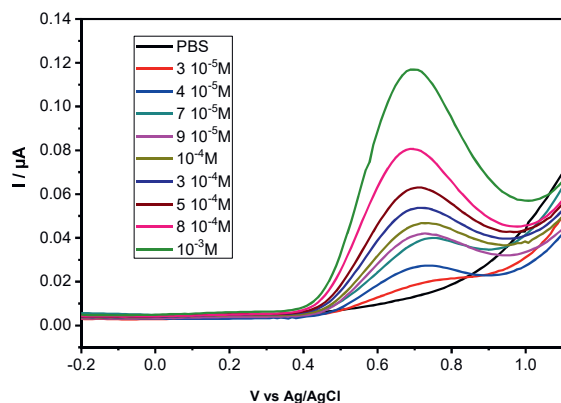


Figure 7: SWV recorded upon different concentration of nitrite

Figure 9 presents the linear fitting of the oxidation peak currents as a function of nitrite concentration, the linear fitting shows that the sensor present two linearity zones, the first for low concentrations 30 – 100 μmol with a correlation factor $R^2 = 0.99$, and the second for the high concentrations 100 – 1000 μmol with a correlation factor $R^2 = 0.98$. The limit of detection of the sensor was calculated using the formula in equation 2 [11]

$$\text{LOD} = 3 \times \delta / m \quad (2)$$

Where δ is the stander deviation and m is the slop of the calibrations curve. This calculation gave a limit of detection LOD around 0.16 μmol .

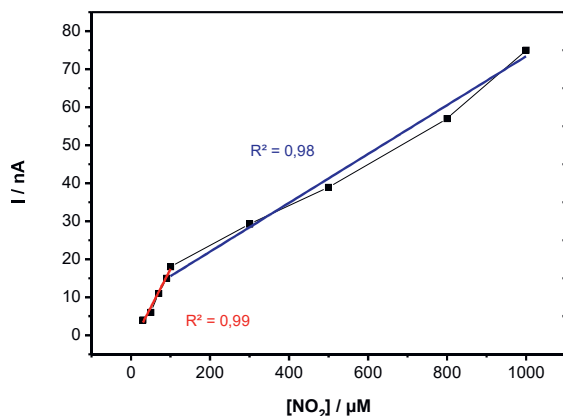


Figure 9 Linear fitting of the oxidation peak as a function of nitrite concentration.

4 Conclusion

In this paper, we have enhanced the performance of photo-electrochemical sensor via functionalization of SPE with TiO_2 NPs and selection of the suitable working conditions. The TiO_2 /SPE sensor shows a good electrochemical behaviour in comparison with the bare electrode. The functionalization of the sensor with TiO_2 NPs increases the electro-active surface area and the oxidation current

under the UV irradiation. The presented sensor exhibits a LOD 0.16 μmol , which satisfy the requirement of the WHO. Further investigations can be done in the future such as the interference test and a real test on drinking water.

Acknowledgement

This work was carried out with the support of the Nitramon project (project no. 100339427) funded by the Sächsische Aufbaubank (SAB) and the European Social Fund (ESF) and the project Electrochemical Sensors for Environmental Applications (ESEA) (project no. 249305) funded by DAAD. Authors acknowledge the support of Aleksandr Oshchepkov (within the project Nitramon) from Technische Universität Chemnitz, Chemical depart, group of Supramolecular Chemistry for solutions preparation and discussions. A.A.-H. and O. K. acknowledge the financial support within the project InnoTeam-SimplySafe (contr. nr.100331073) funded by the Sächsische Aufbaubank (SAB) and the European Social Fund (ESF).

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