



Short communication

New application for the BiVO₄ photoanode: A photoelectroanalytical sensor for nitrite



Francisco Wirley Paulino Ribeiro^a, Fernando Cruz Moraes^a, Ernesto Chaves Pereira^a, Frank Marken^b, Lucia Helena Mascaro^{a,*}

^a Department of Chemistry, Federal University of Sao Carlos, Sao Carlos, Sao Paulo 13565-905, Brazil

^b Department of Chemistry, University of Bath, Bath BA2 7AY, United Kingdom

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ABSTRACT

A simple and sensitive photoelectrochemical sensor based on the bismuth vanadate (BiVO₄) photoanode coupled to visible light excitation was developed for nitrite detection. The BiVO₄ was prepared by hydrothermal methods and used as photoelectroactive sensor. Photoexcitation with visible light allows nitrite anions to act as highly efficient hole scavenger at low potential. The photocurrent response increases linearly with nitrite concentration in the solution. The proposed device operates in the range of detection (2.5 to 100.0 μmol L⁻¹), with limit of detection (1.5 μmol L⁻¹), and with good reproducibility (4.1%) for nitrite analysis.

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1. Introduction

Photoelectroanalysis is an emerging area of work where selectivity in surface reactions are exploited to give specific photocurrent responses with novel sensor device concepts that do not require additional energy resources. Photoelectrochemical devices have been exploited in solution for contemporaneous problems concerning energy and pollution since the first system for water splitting was demonstrated by Fujishima and Honda [1–4]. The studies mostly focused on development of semiconductor materials where the formation of electron–hole pair facilitates the redox reaction of solution species. Taking advantage of this photodriven principle some photoelectrochemical system has been reported also as a new tool in analytical chemistry [5–7] and in photoelectrochemical bioanalysis [8]. Photoelectrochemical sensors have been applied to analyses of a broad range of species of semiconductor materials [9–11]. Despite their interesting properties researches based on simple configurations of photoelectrochemical devices are scarce [12,13]. Bismuth vanadate (BiVO₄) has been considered a promising n-type semiconductor oxide material for application in clean energy generated by photoelectrochemical devices visible-light range [14]. This material shows as main advantages its nontoxicity, and chemical and electrochemical stability in aqueous solutions. It is also inexpensive, presenting a high photoelectrochemical

activity, and a small band-gap (~2.4 eV – monoclinic structure), which makes it suitable to be excited by visible light irradiation [14, 15]. A recent study for hydrogen production allied with oxidation of hydrazine demonstrated photocurrent response at Mo doped BiVO₄ electrode dependent of hydrazine concentration. The holes (h⁺) generated on Mo–BiVO₄ under visible light were able to oxidize the hydrazine [16]. Besides, to the best of our knowledge, there is no other report concerning the use of BiVO₄ as a photoelectrochemical sensor. Nitrite anions (NO₂⁻) have been considered a common inorganic environmental contaminant, which induces human health concerns [17–19]. This ion can react with amines to form carcinogenic nitrosamines in vivo and in excess in the blood can also react with hemoglobin leading to the formation of methemoglobin and suppressed oxygen transport [20]. Nitrite ions are known to have potentially harmful effects in spontaneous abortion, intrauterine growth restriction, birth defects, blue baby syndrome and gastric cancer [17,21]. According to the regulation for nitrite established by the United States Environmental Protection Agency (USEPA), the maximum contaminant level is 1.0 mg L⁻¹ in drinking water [19]. However, according the World Health Organization (WHO) the maximum limit is 3 mg L⁻¹ [22]. Several methods have been employed to determine nitrite, such as spectrophotometry [23], flow injection analysis [24], electrothermal molecular absorption spectrometry [25], colorimetric [26], fluorimetric [27], electrophoretic [28], chromatographic [29], and voltammetric [30]. Several electrochemical methods have been applied to nitrite analysis using direct oxidation on different electrode surfaces [21]. However, to the best of our knowledge, there is not any proposition of a photoelectrochemical method to

* Corresponding author. Tel.: +55 16 3361 8082.
E-mail address: lmascaro@ufscar.br (L.H. Mascaro).

detect nitrite in the literature. Therefore, the main purpose of this communication has been to apply BiVO_4 as a photoelectrochemical sensor for nitrite analysis based on a rapid, simple, accurate, and low-cost procedure.

2. Experimental

The BiVO_4 photoanode was prepared by droplet of a mixture of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and NH_4VO_3 (Sigma-Aldrich) dissolved in polyethylene glycol (PEG300, Sigma-Aldrich) on FTO glass substrate ($10 \mu\text{L cm}^{-2}$). The procedure was repeated twice to prepare a reproducible electrode. Then, the as-deposited films were heated at 500°C for 1 h in furnace air [31]. The reference electrode was $\text{Ag}/\text{AgCl}/\text{KCl}_{\text{sat}}$, the auxiliary electrode was platinum, and BiVO_4/FTO as working electrode. The solutions of $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ and different concentrations of NaNO_2 (Sigma-Aldrich), 0.1 or 0.001 mol L^{-1} , (Sigma-Aldrich) were prepared using Millipore deionized water just prior to the measurements. All voltammetric measurements were carried out using a potentiostat (Autolab PGSTAT 302 N, Metrohm-Eco Chemie) using GPES software in a three-electrode conventional electrochemical cell. The photoelectrochemical data have been measured using a 50–500 W Xenon (Newport, 66902) calibrated to 100 mW cm^{-2} . The analytical approach was performed by standard additions of the $0.01 \text{ mol L}^{-1} \text{ NaNO}_2$ stock solution in the electrochemical cell containing $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ electrolyte solution, followed by chronoamperometry experiments at $+1.1 \text{ V}$ under front side on/off solar illumination ($\Delta t = 10 \text{ s}$) on BiVO_4/FTO photoanode.

3. Results and discussion

The photoresponse in BiVO_4 is strongly dependent of the crystalline phase it has been described that monoclinic is more appropriate to visible light harvesting [14]. Fig. 1 displays the typical BiVO_4 monoclinic phase diffraction peaks observed in X-ray data, with the most intense line around 29° (-121) [32]. The other characteristics of BiVO_4 photoanode films obtained were band-gap energy of 2.43 eV which has been measured using diffuse reflectance. Finally, SEM images (Fig. 1 inset) showed a porous structure with morphology consisting of wormlike particles with size around 300 nm . A transversal view presented that the BiVO_4 film has a thickness average at $4.81 \pm 0.21 \mu\text{m}$. The photoelectrochemical measurement performed by linear sweep voltammetry experiments with 20 mV s^{-1} in $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ at BiVO_4/FTO under front side solar simulated illumination exhibited a

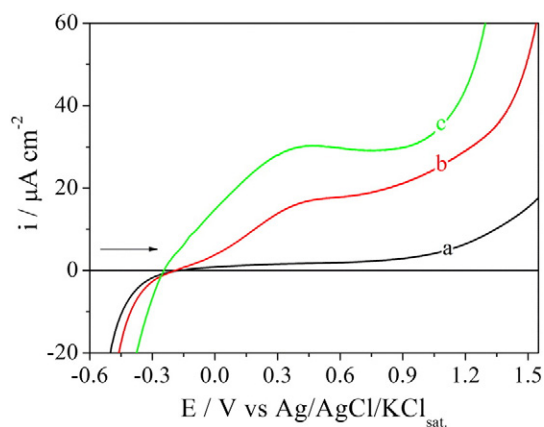


Fig. 2. Linear sweep voltammograms obtained for BiVO_4/FTO in $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ in the absence of nitrite (a), $1.0 \text{ mmol L}^{-1} \text{ NaNO}_2$ (b), $100 \text{ mmol L}^{-1} \text{ NaNO}_2$ (c) solar simulated illumination at front side with 20 mV s^{-1} .

small photocurrent at $+1.1 \text{ V}$ vs Ag/AgCl . Next, the photoelectrochemical measurements were performed in 0.1 mol L^{-1} of Na_2SO_4 and presence of different amounts of NaNO_2 . Fig. 2 shows the linear sweep voltammetric scan obtained using BiVO_4/FTO photoanode in $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ in the absence and presence of nitrite.

Under dark condition the voltammogram does not show any electrochemical process related to nitrite oxidation on the BiVO_4/FTO electrode. Despite nitrite can be electrochemically oxidized on different electrode surfaces, under dark the kinetics of charge transfer at BiVO_4 interface appears to be very slow, which explains the results obtained. This behavior is in agreement with Wang and co-workers, who proposed that the mechanism and nitrite oxidation kinetics exhibits a significant dependence on the nature of the electrode [33]. Strong interactions occur between nitrite ions and electrode surface occurring nitrite absorption. However, under illumination and in presence of nitrite, a fast increase of photocurrent is observed (about 20-fold increase compared with the response in $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$). It is also observed that a decrease in the onset potential occurs, which is a typical sign for the presence of a hole scavenger. Therefore, nitrite ions act as the hole scavenger reducing the recombination effect on the semiconductor surface resulting in the increase of the photocurrent.

A similar behavior has been previously described for this material in the presence of other chemical species, such as sodium sulfite [34] and oxalic acid [31]. The interesting point is that the increase of nitrite concentration provides an increase of the photocurrent intensity. Therefore, this can be used as analytical signal for nitrite ion detection over BiVO_4/FTO electrodes. Previous studies have shown that the nitrite ion can be photocatalytically oxidized on other materials to produce nitrate ions [35,36]. Using those ideas, in Scheme 1 it is presented that the reaction of nitrite ions occurs on BiVO_4/FTO photoanode under visible light irradiation. The nitrite is oxidized by holes generated at the particle surface after the charge separation, thus avoiding the electron/hole recombination, resulting in an increase of the photocurrent as shown in chronoamperogram in Scheme 1. Furthermore, the kinetics of photoelectrochemical oxidation of nitrite is fast compared to water oxidation by the holes. This way, BiVO_4/FTO can be applied as sensor for nitrite ions.

In a second step, chronoamperometric experiments were performed in order to evaluate the photoelectrochemical response of the sensor as a function of nitrite ion concentration. In this study, the analytical response of the electrode was carried out in a fixed potential at $+1.1 \text{ V}$, under an on/off cycle of light irradiation. As displayed in inset of Fig. 3, sequential additions of NaNO_2 standards, concentrations varying from 2.5 to $100.0 \mu\text{mol L}^{-1}$ were used for construction of the calibration curve. All measurements were performed in a set of three on/off

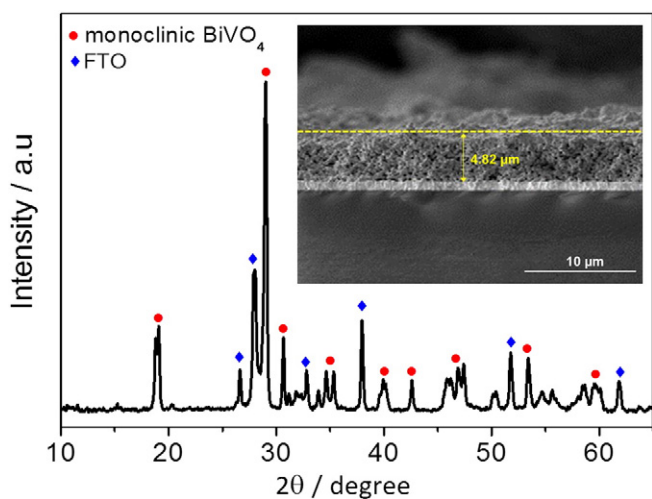
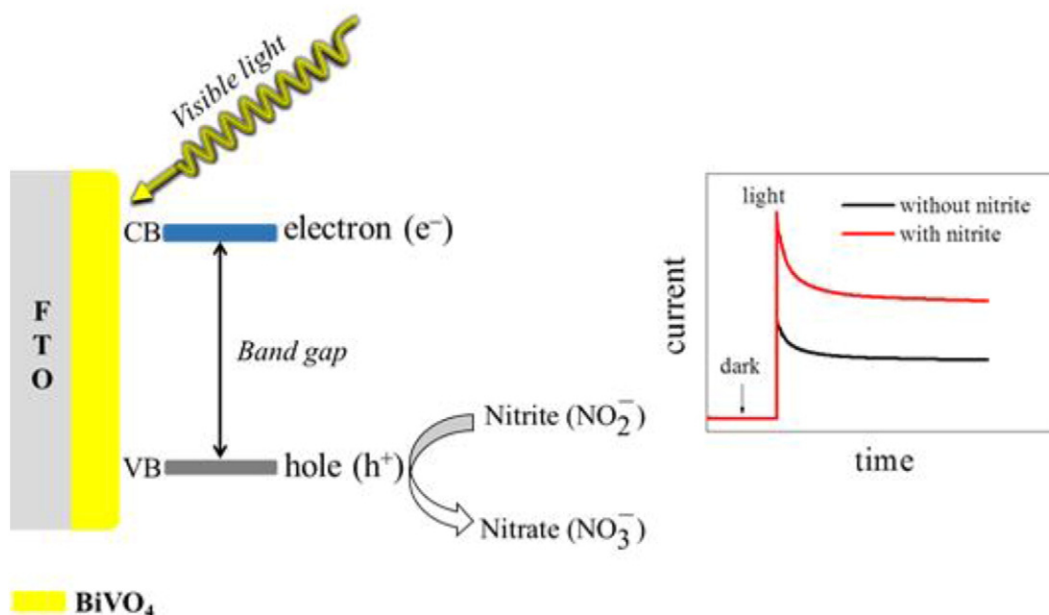


Fig. 1. XRD patterns of BiVO_4 film synthesized on FTO substrate. The peaks labeled with (●) and (◆) correspond to the monoclinic BiVO_4 phase and FTO substrate, respectively. Inset: SEM image of BiVO_4/FTO electrode cross section.



Scheme 1. The schematic representation of the reaction of nitrite on BiVO₄/FTO photoelectrode under visible light and the representative chronoamperogram showing the nitrite analysis at photoelectrochemical sensor.

cycles for each NO₂⁻ concentration levels, and the results were indicated as BiVO₄/FTO mean value of the current.

To build up the analytical curve, the currents were sampled exactly in the middle of the cycles, and the current values, presented as Δi , are the values of the current obtained by NO₂⁻ standard additions subtracted from the electrolyte in the absence of nitrite ions (black curve in the Fig. 3 inset). The analytical response shown in Fig. 3 has a linear relationship, in the concentration range studied, in accord with the following equation: Δi ($\mu\text{A cm}^{-2}$) = 0.18 ($\mu\text{A cm}^{-2}$) + 0.053 ($\mu\text{A cm}^{-2}/\mu\text{mol L}^{-1}$) [NO₂⁻] ($\mu\text{mol L}^{-1}$) with a correlation coefficient of 0.998 ($n = 6$). The limit of detection (LOD) obtained was 1.5 $\mu\text{mol L}^{-1}$ (0.07 mg L⁻¹) determined using a $3\sigma/\text{slope}$ ratio, in which σ is the standard deviation of the intercept. The repeatability precision of the BiVO₄/FTO sensor was measured using six experiments. Prior to each

experiment, the electrode surfaces were rinsed thoroughly with double-distilled water. Then, addition of 45.0 $\mu\text{mol L}^{-1}$ of nitrate ion solution in 0.1 mol L⁻¹ Na₂SO₄ was performed for BiVO₄/FTO. The RSD was calculated as 4.1%. According to the regulation for nitrite established by the USEPA the maximum contaminant level is 1.0 mg L⁻¹ in drinking water [19]. In addition, the WHO has set the maximum limit at 3.0 mg L⁻¹ [22]. Based on this information, the detection limit obtained by the BiVO₄/FTO photoelectrochemical sensor is low enough for determination of nitrite ions in drinking water, proving that this electrochemical device is suitable to be used in environmental analysis. The LOD value achieved by BiVO₄/FTO photoelectrochemical sensor was lower than results obtained by the use of direct electrochemical sensor for nitrite published recently using carbon paste electrode decorated with silver particles (3.0 $\mu\text{mol L}^{-1}$) [30], and zirconium-based porphyrin metal-organic framework (2.1 $\mu\text{mol L}^{-1}$) [38]. A LOD of 0.4 $\mu\text{mol L}^{-1}$ was observed in bare glassy carbon electrode using chronoamperometry but LOD increased to 300 $\mu\text{mol L}^{-1}$ employing cyclic voltammetry [37]. The important point for this electrochemical methodology is that a new approach for nitrite detection has been shown in this work using pure BiVO₄. This facile strategy extends the application of this semiconductor for monitoring of nitrite besides water splitting and waste degradation.

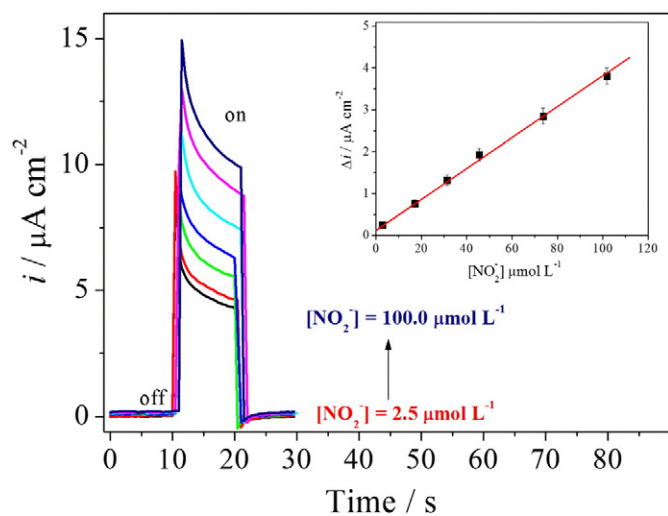


Fig. 3. Linear relationship between Δi and NO₂⁻ concentrations. Inset: Chronoamperograms for BiVO₄/FTO photoelectrochemical sensor recorded at +1.1 V, in 0.1 mol L⁻¹ Na₂SO₄ on with standard additions of nitrite in a concentration range varying from 2.5 to 100 $\mu\text{mol L}^{-1}$.

4. Conclusion

A new photoelectrochemical nitrite sensor has been developed based on the BiVO₄/FTO photoanode semiconductor prepared with PEG300 green solvent. The detection process was based on the principle that nitrite acts as a hole scavenger reducing the electron/hole recombination after the charge separation under visible light, resulting in the increase of photocurrent. The photoelectrochemical procedure was suitable for nitrite analysis with good electroanalytical performance having satisfactory linearity, sensitivity, repeatability and limit of detection. This is the first time that a photoelectrochemical device was applied for nitrite detection and furthermore, the first report concerning the use of pure BiVO₄ used as a photosensor. Further development of this process into a battery-free device is possible.

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