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Photoelectrocatalytic oxidation of formaldehyde using a Ti/TiO_2 foil electrode. Application for its novel and simple photoelectrochemical determination

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ABSTRACT

It was firstly described, that a TiO_2 film modified titanium foil electrode (Ti/TiO_2) shows an efficient photoelectrocatalytic activity towards formaldehyde oxidation in a phosphate buffer solution. Ti/TiO_2 foil electrode was prepared by anodizing Ti foil in aqueous solution. Also, this electrode was applied for the hydrodynamic photoamperometry measurement of formaldehyde in the optimum conditions (pH 7.0 as biological pH and bias potential 0.8 V vs. reference electrode). The photoelectrocatalytic oxidation photocurrent of the photoelectrode determined by photoamperometry method was linearly dependent on the formaldehyde concentration and the linearity range obtained was 6.70×10^{-4}–1.48×10^{-2} mol L^{-1}. Detection limit was found to be 3.09×10^{-4} mol L^{-1} (2σ).

1. Introduction

Photoelectrocatalytic determination of materials with a Ti/TiO_2 electrode has not been studied so far. However, many research reports about TiO_2 are related to its application for degradation of most kinds of organic pollutants, such as detergents, dyes, pesticides and herbicides, etc., under UV light irradiation [1–5]. Only in few articles, photoelectrocatalytic determination of some materials with electrodes except Ti/TiO_2 electrode has been investigated. Recently, tin oxide nanoparticle electrode for selective photoelectrochemical detection of DNA [6], TiO_2/CdS hybrid modified ITO for α-fetoprotein detection [7] and Ti/TiO_2/PbO_2 electrode to determine the chemical oxygen demand (COD) values [8] have been applied. Also, the modified carbon paste electrode was prepared by adsorption of methylene blue (MB) on zirconium phosphate [9] and muscovite [10] and these modified electrodes was successfully used for the photoelectrocatalytic oxidation of the ascorbic acid in a flow injection analysis (FIA) system. Moreover, Xu et al. reported that the dopamine coordinated nanoporous TiO_2 film electrode covered on an indium-tin oxide (ITO) electrode showed to be a new photoelectrochemical methodology for sensitive NADH determination [11]. Also, other research groups have been interested in the photoelectrocatalytic oxidation of NADH using a new polymeric phenothiazine modified graphite electrode [12], poly (toluidine blue O) modified glassy carbon electrode [13], poly-hematoxylin modified glassy carbon electrode [14], electropolymerized methylene blue modified glassy carbon electrode [15] and poly (neutral red) modified glassy carbon electrode [16] since the photoelectrocatalytic method has better sensitivity than the electrocatalytic method for the determination of NADH. S. Zhang et al. developed a photoelectrochemical detector for determination of glucose and sucrose in flow injection analysis (FIA) and high performance liquid chromatography (HPLC) based on the oxidation power of nanostructure TiO_2 coated onto the ITO substrate [17].

On the other hand, Formaldehyde is an extremely important industrial raw material due to its chemical activity, high purity and relative cheapness. At the moment, world production of this chemical is estimated to be in the range of 10 mt per year; half being utilized for the production of phenol-, urea- and melamine-formaldehyde resins which are widely used in the manufacturing of building plates, plywood and lacquer materials [18,19]. Formaldehyde is also used in chemical synthesis as an intermediate for the production of consumer goods as detergents, soaps, shampoos, and as a sterilizing agent in pharmacology and medicine. Thus, it is expected that millions of workers could have been exposed to formaldehyde. On the other hand, formaldehyde is a natural metabolite of living organisms. It can be found in fruits, vegetables, flesh [20] and biological fluids of human origin [18]. Therefore, simple and sensitive methods for determination of formaldehyde are needed for specific biotechnological processes, environmental control, medicine and even for drinking

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water and food analysis. For the first time, the present work developed the photoelectrocatalytic oxidation using Ti/TiO_2 foil electrode and application of this electrode for formaldehyde determination as a novel and simple method.

2. Experimental

2.1. Materials

The solvent for electrochemical studies was doubly distilled water. The formaldehyde from Merck was used as received. Titanium foils (thickness 0.25 mm, assay 99.7%) was purchased from Sigma-Aldrich. Buffer solutions were prepared from NaOH and H_3PO_4 and its salts for pH range of 3.0 to 11.0.

2.2. Preparation of working electrode

A piece of raw Ti foil was cut into small rectangular pieces ($3.0 \times 3.0\ cm^2$) which were then polished with different abrasive papers, rinsed in an ultrasonic bath containing cold distilled water, chemically etched by immersion in $HF/HNO_3/H_2O$ (1:4:5 v/v/v) mixed solution [21] and finally rinsed with acetone and deionized water. The treated Ti sheet served as anode and a platinum rod served as cathode, and both were placed in a solution of 0.2 vol% hydrofluoric acid. Anodization was performed at a constant voltage of 20 V for 20 min. The freshly generated TiO_2 film electrode was then rinsed with distilled water and dried in the atmosphere. Finally it was calcinated in a muffle oven at 500 °C for 2 h.

2.3. Instrumentation

PEC degradation experiments were carried out as shown in Fig. 1 in a single photoreactor consisting of a quartz cylindrical cell (3.0 cm diameter × 8.0 cm height, 1.8 mm thick). The reactor and the UV lamp were placed in a black box in order to avoid extraneous illumination. A platinum rode as a counter electrode and an Ag|AgCl|KCl (3 mol L^{-1}) as reference electrode were used. Photoelectrochemical experiments were carried out using a potantiostat/galvanostat (μ Autolab Type III). A collimated light beam from 4 W medium pressure mercury lamp with a maximum UV irradiation peak was used for excitation of photoelectrode. A 20 V electrical power supply was adopted for preparation of working electrode.

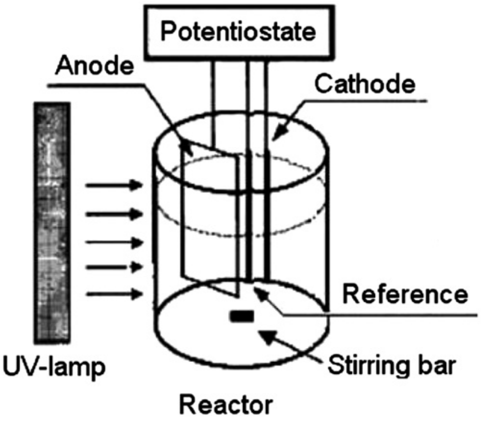

Fig. 1. Schematic diagram of the reactor system.

3. Results and discussions

3.1. Scanning electron microscopy (SEM) of Ti/TiO_2 electrode

Fig. 2 shows typical SEM images of the unmodified (A) and TiO_2 modified titanium electrodes (B). It can be seen from the micrograph that TiO_2 film was formed on the surface of titanium. The film coverage is almost uniform although some ups and downs were occasionally seen on the surface.

3.2. Photoelectrochemical behavior of formaldehyde at the surface of Ti/TiO_2 electrode

In photocatalysis process, when the TiO_2 nanoparticles in colloidal suspensions or deposited as a thin film on Ti was illuminated with UV light, a great number of electrons would be excited from the valence band (VB) to the conduction band (CB) by absorbing UV light quanta, leaving highly oxidative holes in VB (h^+_{VB}) and forming negative sites in CB (e^-_{CB}), as shown in Fig. 3A(1) and reaction (1) [22]:

$$TiO_2 + h\nu \rightarrow e^-_{CB} + h^+_{VB} \quad (1)$$

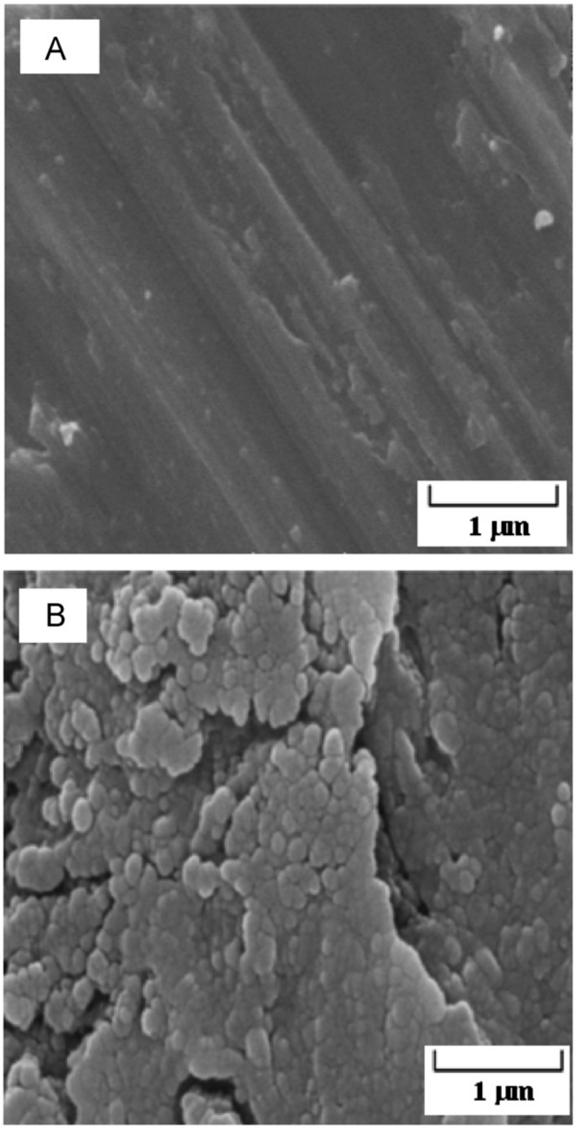

Fig. 2. SEM micrographs of unmodified titanium (A) and TiO_2 modified titanium (Ti/TiO_2) (B) electrodes.

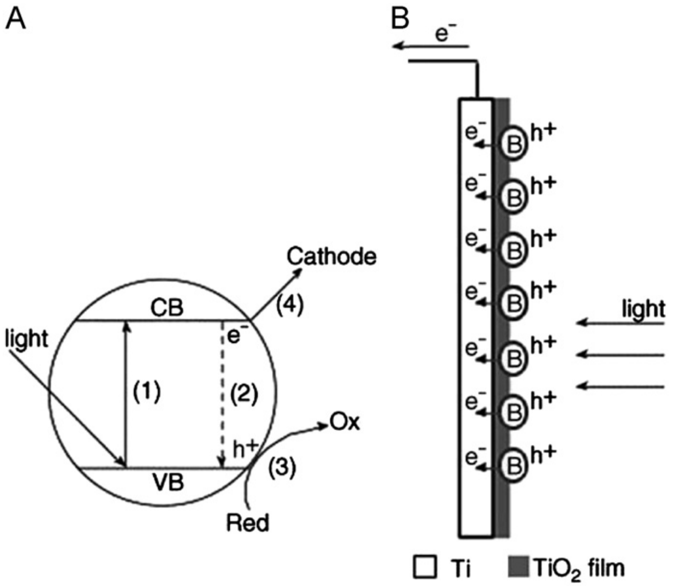

Fig. 3. Schematic representation of photocurrent generation from the microscopic (A) and macroscopic (B) views.

Organics can then be directly oxidized by the hole or by heterogeneous hydroxyl radical formed from the following reaction between the photogenerated vacancy and adsorbed water:

$$h_{VB}^{+}+H_2O\rightarrow OH^{\bullet}+H^{+} \tag{2}$$

In addition, other weaker oxidizers (superoxide radical ion $O_2^{\bullet -}$, $HO_2^{\bullet}$ and H_2O_2) and more $OH^{\bullet}$ can be produced from the photoinjected electron by the following reactions [22]:

$$e_{CB}^{-}+O_2\rightarrow O_2^{\bullet -} \tag{3}$$

$$O_2^{\bullet -}+H^{+}\rightarrow HO_2^{\bullet} \tag{4}$$

$$2HO_2^{\bullet}\rightarrow H_2O_2+O_2 \tag{5}$$

$$H_2O_2+O_2^{\bullet -}\rightarrow OH^{\bullet}+OH^{-}+O_2 \tag{6}$$

The major loss in efficiency of photocatalysis is due to the recombination of electrons promoted to the valence band either with unreacted holes or with adsorbed hydroxyl radicals as observed in Fig. 3A(2) and the following reactions [23]:

$$e_{CB}^{-}+h_{VB}^{+}\rightarrow TiO_2+\text{heat} \tag{7}$$

$$e_{CB}^{-}+OH^{\bullet}\rightarrow OH^{-} \tag{8}$$

The electrochemical technology can provide much higher efficiency for organic material oxidation by means of photoelectrocatalysis. The efficiency of this process was improved by applying a suitable anodic potential to the circuit owing to the conducting titanium substrate. The application of an anodic bias to a Ti/TiO_2 electrode further provides a potential gradient within the film to drive away the photogenerated holes and electrons in different directions efficiently. The photogenerated holes could oxidize the organic compounds at the anode surface (Fig. 3A(3)), while the photogenerated electrons were transferred to the acceptor at the metallic cathode through the external electrical circuit (Fig. 3A(4)). The whole reaction process viewed on both microscopic (A) and macroscopic (B) scales was shown in Fig. 3.

In order to evaluate the photoelectrochemical activity of Ti/TiO_2 electrode and to confirm its ability for photoelectrocatalysis oxidation of formaldehyde, we performed cyclic voltammetry experiments in the dark and under UV light irradiation in the absence and presence of formaldehyde (Fig. 4). The tests were conducted in phosphate buffer solution (pH 7.0). As can be seen in Fig. 4, electrochemical oxidation current value of Ti/TiO_2 electrode in dark and in the absence of formaldehyde is very small (curve a). However, value of this current under irradiation increases very much (curve c). This indicates that photogenerated electrons on Ti/TiO_2 electrode could be effectively driven to the counter electrode by applied positive potential, which would be beneficial to electron–hole separation. Using the same conditions, we studied the photoelectrochemical behavior of Ti/TiO_2 electrode in the presence of formaldehyde (curves b and d). In dark, almost no difference between currents were observed in the absence and presence of formaldehyde which means that no electrochemical oxidation of formaldehyde at the surface of Ti/TiO_2 electrode occurred. But under UV illumination, a significant increase was showed in the presence of formaldehyde with respect to the absence of this material. The cause of these observations is that in buffer solution, the photogenerated holes in Ti/TiO_2 electrode oxidize either adsorbed water molecules or hydroxyl groups, while the presence of formaldehyde provides a much more facile pathway for the transfer of holes across the film/electrolyte interface, which results in the higher photocurrent.

Hydrodynamic amperometry was used to study the photoelectrochemical response of Ti/TiO_2 electrode, in buffer solution in the absence and presence formaldehyde with two various concentrations under UV irradiation. The results are shown in Fig. 5. It can be seen that the rise and fall of the photocurrent corresponded well to the illumination being switched on and off. The generation of photocurrent consisted of two steps. The first step of the photocurrent appears promptly after the illumination, and the second step of the photocurrent reaches a steady state. This pattern of photocurrent is highly reproducible for several on–off cycles of illumination. The results of hydrodynamic amperometry were consistent with observations of cyclic voltammetry. The current response on the Ti/TiO_2 electrode in dark is insignificant in the absence and presence of formaldehyde which means that no electrochemical oxidation occurred. Under illumination, a significant increase in the photocurrent is observed wherein the value of this increase is smaller in the absence of formaldehyde than that of presence of formaldehyde (curves a and b, respectively).

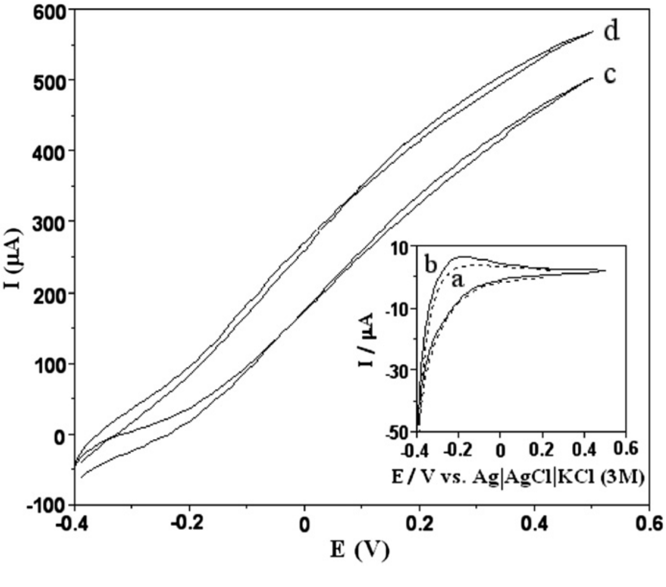

Fig. 4. Cyclic voltammograms of Ti/TiO_2 electrode in dark (a) in the absence and (b) in the presence of 99.90 mM formaldehyde, (c) and (d) as a and b+under UV irradiation respectively at a scan rate 10 mV s^{-1}.

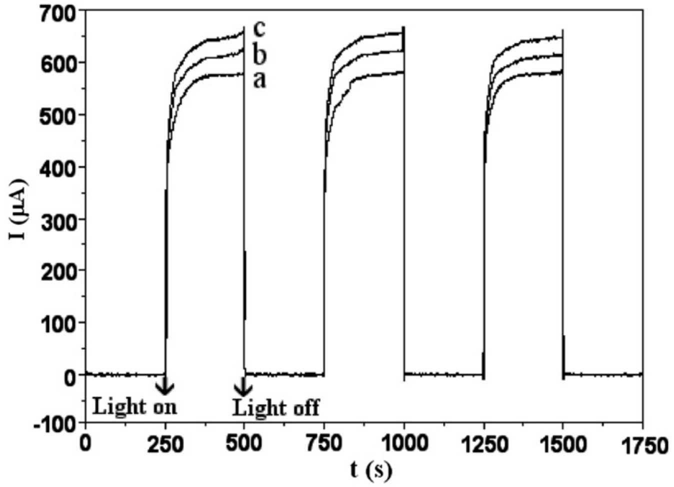

Fig. 5. Photocurrent of Ti/TiO_2 electrode for several on–off cycles of illumination at an applied potential of 0.6 V vs. reference electrode in (a) phosphate buffer solution (pH 7.0), (b) as a+7.00 mM formaldehyde and (c) as a+14.00 mM formaldehyde.

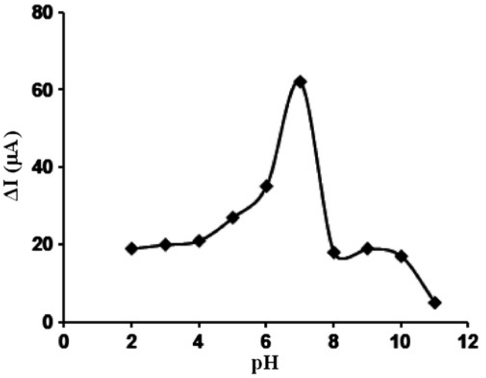

Fig. 6. Effect of pH value of solution on difference between phototocurrents Ti/TiO_2 electrode in the absence and the presence of 13.00 mM formaldehyde at bias potential 0.6 V vs. reference electrode.

3.3. Factors influencing the photoelectrocatalytic oxidation of formaldehyde

3.3.1. pH solution

pH is a key factor that influences the photoelectrocatalytic oxidation of materials. Therefore, in this study the relationship between pH value and difference photocurrents of Ti/TiO_2 electrode in the absence and presence of formaldehyde, $\triangle I$, were investigated (Fig. 6). As shown in this Fig., formaldehyde photoelectrocatalytic oxidation kinetics are optimal at pH 7.0 compared with other pHs. pH influences the photoelectrocatalytic oxidation process in many ways, such as TiO_2 flat-band potential variation and changes in adsorption ability of the target compound on the TiO_2 film [24].

3.3.2. Bias potential

The bias potential is important in the process of photoelectrocatalytic oxidation of formaldehyde. Different photocurrents of Ti/TiO_2 electrode in the absence and presence of formaldehyde was studied for bias potential ranged between 0.2 and 1.4 (Fig. 7). The results showed that potential 0.8 V was as optimal as bias potential. The application of positive potential across the Ti/TiO_2 photoelectrode could produce a potential gradient inside the film that forced the photogenerated holes to move in opposite directions. Subsequently, the concentration of photogenerated holes (or hydroxyl radicals formed by subsequent oxidation of water) on the surface increased. Therefore, increase of bias potential results in increased photocurrent of Ti/TiO_2 photoelectrode both in the absence and presence of formaldehyde. However, what matters is difference between these photocurrents.

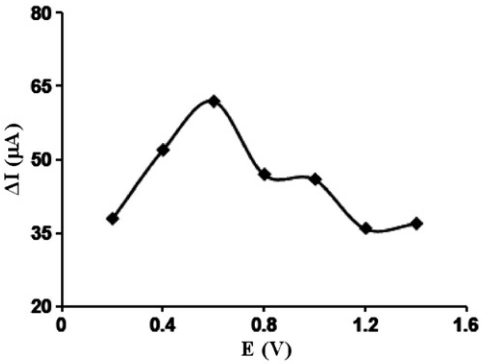

Fig. 7. Effect of bias potential on difference between phototocurrents Ti/TiO_2 electrode in the absence and the presence of 13.00 mM formaldehyde in phosphate buffer solution (pH 7.0).

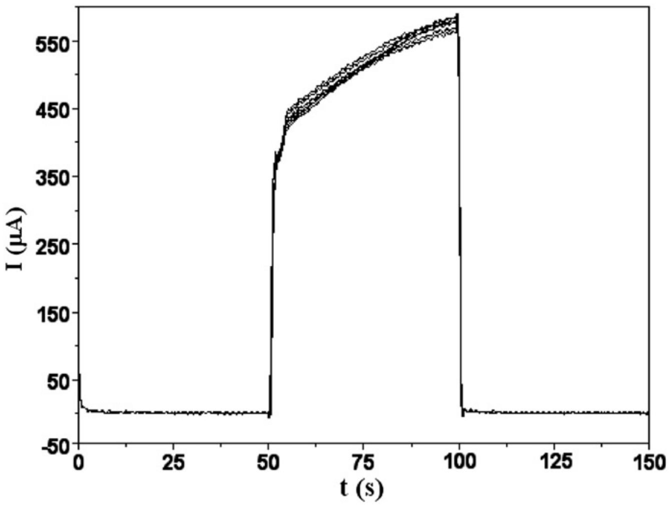

Fig. 8. Six successive hydrodynamic amperograms of Ti/TiO_2 electrode in the phosphate buffer solution (pH 7.0) at bias potential 0.6 V vs. reference electrode.

4. Reproducibility and stability of Ti/TiO_2 electrode

To prove the reproducibility of Ti/TiO_2 electrode, hydrodynamic amperometry experiments were repeatedly performed six times as shown in Fig. 8 with this electrode in phosphate buffer solution (pH 7.0). As it can be seen, Ti/TiO_2 electrode has good reproducibility. The stability of this electrode was also investigated. After the electrode was stored for approximately for two weeks only a small decrease of current sensitivity, about 6%, was observed, which can be attributed to the good stability of Ti/TiO_2 electrode.

5. Interference study

Interference study was carried out with several chemical substances prior to the application of the proposed method to determine formaldehyde. The potential interfering substances were chosen from some substances commonly found with formaldehyde. The tolerance limit is defined as the maximum concentration of the interfering substance that causes relative error less than 5% for the determination of 13.00 mM formaldehyde. The results showed that 20-fold quantities of glucose, fructose and sucrose and 40-fold quantities of K^+, Na^+, Mg^{2+}, Ca^{2+}, Cl^-, F^-, HCO_3^- and SO_4^{2-} had no interference on formaldehyde determination. However, ascorbic acid had major interference for determination of formaldehyde at the surface of Ti/TiO_2 electrode. Interference from ascorbic acid can be minimized by using the ascorbic oxidase enzyme which exhibits high selectivity to the oxidation of ascorbic acid, if necessary.

Table 2
Photoelectrocatalytic determination of formaldehyde in the phosphate buffer (pH 7.0) withTi/TiO_2 electrode.

Labled[a]	Proposed method		Official method		t_{exp}	F_{exp}
	Found[a,b]	Recovery (%)	Found[a,b]	Recovery (%)		
13.32	12.81	96.17	12.46	93.54	1.38	1.56

[a] Unit based on mol L^{-1}.
[b] Average of three replicate determinations.

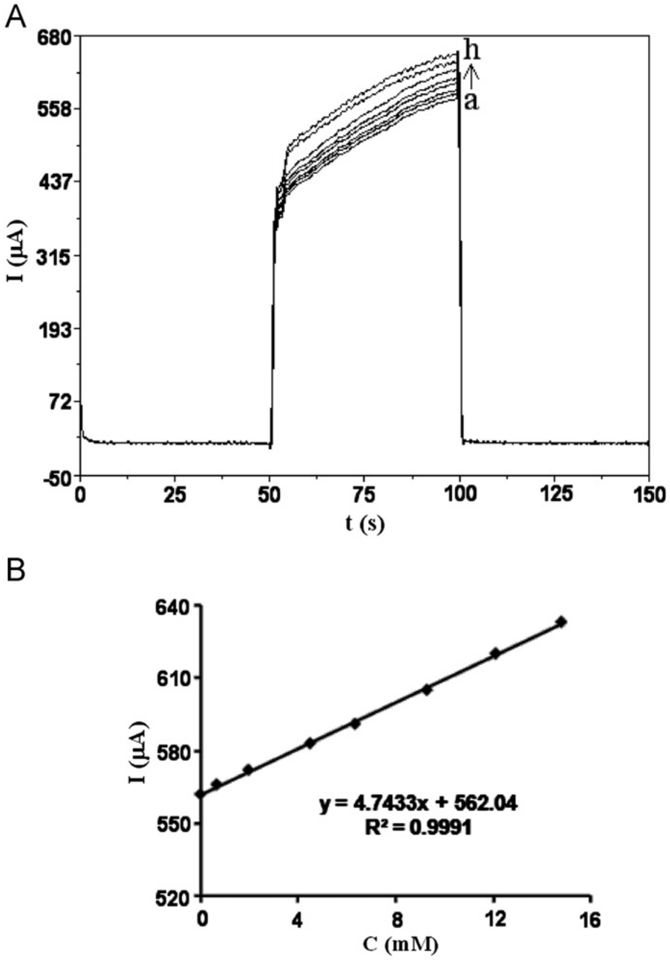

Fig. 9. (A) Hydrodynamic amperometry Ti/TiO_2 electrode in the phosphate buffer solution (pH 7.0) and at bias potential 0.8 V vs. reference electrode in the presence of various formaldehyde concentrations: (a) 0.00, (b) 0.67, (c) 1.97, (d) 4.50, (e) 6.34, (f) 9.29, (g) 12.11 and (h) 14.80 mM. (B) Plot of photocurrent as a function of formaldehyde concentration.

6. Photoelectrocayalytic determination of formaldehyde

Photoelectrocatalytic oxidation current of formaldehyde at the surface of Ti/TiO_2 was linearly dependent on the formaldehyde concentration. The calibration plot was linear in the range of 6.70×10^{-4}–1.48×10^{-2} mol L^{-1} with correlation coefficient of 0.9991. The detection limit was as 3.09×10^{-4} mol L^{-1} (Fig. 9A and B). Since the acceptable detection limit according to the standards of Occupation Safety and Health Administration (OSHA), varies from 0.1 to 1 mM formaldehyde [25,26], therefore, the detection limit of this method is suitable for the determination of formaldehyde. The comparison of several parameters of formaldehyde at some modified electrodes is listed in Table 1. It can be seen from the table that these parameters values are comparable with values reported by other research groups for the electrocatalytic oxidation of formaldehyde on the surface of chemically modified electrodes by other mediators [27–29].

7. Photoelectrocayalytic determination of formaldehyde in formalin

In order to demonstrate the capability of Ti/TiO_2 electrode towards the catalytic oxidation of formaldehyde, we examined this ability in amperometric determination of formaldehyde in formalin. The determination of formaldehyde was carried out by the standard addition method. The data obtained for analysis formaldehyde by this method have been illustrated for several times in Table 2. Also, in order to investigate the proposed method the same sample was analyzed using iodometric titration method in acidic solution as an official method [30]. The results have been summarized in Table 2. As it can be seen, the results obtained from the two methods are in good agreement and confirm the reliability of the proposed method. A statistical test (*F*-test) was used to confirm the precision of the proposed method. As it can be seen, *F*-test results bear a noticeable difference from the critical value (19.00) in four degrees of freedom and 95% of confidence. Moreover, a statistical *t*-test

Table 1
Comparison some of the analytical parameters of the different modified electrodes for formaldehyde determination.

Electrode	Method	LDR (mM)	LOD (mM)	Ref.
PTOE[a]	Electrocatalysis–chronoamperometry	2.5–17.7	0.015	[27]
CNFGNPGE[b]	Electrocatalysis–amperometry	0.01–0.1	–	[28]
AOXISFET[c]	Potentiometry	5–200	–	[29]
Ti/TiO_2	Photoelectrocatalysis–amperometry	0.67–14.8	0.31	This work

[a] Palladium modified TiO_2 electrode.
[b] Cathodic electrodeposition paints modified with $Os(bpy)_2Cl$ complexes-NAD^+–formaldehyde dehydrogenase-glutathione-nafion architecture modified platinized graphite electrode.
[c] Highly or partially purified alcohol oxidase immobilized on the ion sensitive field effect transistor.

was performed to evaluate the accuracy of the proposed method. The results suggested that there is no evidence of systematic difference between the results obtained by either of the methods. Four degrees of freedom and 95% of confidence as well as the critical *t*-value (2.78) were used to support the conclusions of this test.

8. Conclusions

In this paper, for the first time we have developed a new and simple formaldehyde sensor based on photoelectrocatalytic determination using Ti/TiO_2 electrode prepared by anodizing Ti foil in aqueous solution. The sensor showed promising determination of formaldehyde with good detection limit. The Ti/TiO_2 electrode can be prepared simply and successfully used as an amperometric sensor for formaldehyde determination in real sample with suitable precision and accuracy.

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