

*Full Paper*

## **A Photoelectrochemical Sensor for Methanol based on Its Oxidation at TiO<sub>2</sub> Thin Film Modified Ti Electrode**

**Ebrahim Zarei**

*Department of Basic Sciences, Farhangian University, Tehran, Iran*

\*Corresponding Author, Tel.: +98-11-33833114

E-Mail: [e.zarei@cfu.ac.ir](mailto:e.zarei@cfu.ac.ir)

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**Abstract-** In this research, the TiO<sub>2</sub> film layered titanium foil (Ti/TiO<sub>2</sub>) electrode was performed for photo-assisted electrocatalytic determination of methanol in aqueous solution. TiO<sub>2</sub> film was fabricated on the surface of titanium foil using anodizing this foil. The photoelectrochemical activity of methanol on the surface of the Ti/TiO<sub>2</sub> electrode was investigated by cyclic voltammetry and hydrodynamic photoamperometry techniques. Also, hydrodynamic photoamperometry method was employed for methanol determination and for obtaining the best response. Also, pH and bias voltage were optimized based on the photocurrent differences value in the absence and presence of methanol. It was showed that the electrode photocurrent was linearly related to the methanol concentration in the range of 0.070-0.46 mM. The limit of detection was led to be 7.5 μM (3σ).

**Keywords-** Photo-assisted electrocatalysis, Ti/TiO<sub>2</sub>, Determination, Methanol

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### **1. INTRODUCTION**

Most of research reports about applications of TiO<sub>2</sub> and some semiconductors as effective photocatalysts are related to their application for pollutants degradation [1-6]. Only in a few investigations, some target compounds have been determined using photoelectrocatalysis method. For instance, Wang et al. have determined α-fetoprotein antibodies using the TiO<sub>2</sub>/CdS modified indium tin oxide (ITO) [7]. Also, the Cu<sub>2</sub>O-loaded TiO<sub>2</sub> nanotube arrays [8], the Ti/TiO<sub>2</sub>/PbO<sub>2</sub> [9] and the nanoporous TiO<sub>2</sub> [10] electrodes have been applied for

detection of the chemical oxygen demand. Moreover, the ITO electrode modified with  $\text{WO}_3$ - $\text{TiO}_2$  for riboflavin and norepinephrine [11] have been used. He et al. [12] Zen et al. [13] have measured formic acid and o-phenols using the Ag- $\text{TiO}_2$ /ITO and copper-plated screen-printed electrodes respectively. Also, Wang et al. have used the dopamine coordinated nanoporous  $\text{TiO}_2$  film electrode for sensitive NADH determination [14]. Furthermore, Dilgin et al. have developed the application of photocatalysts but semiconductors, for example methylene blue and poly methylene blue for quantification of ascorbic acid [15] and NADH [16] respectively. Also, a nanoporous  $\text{TiO}_2$  array modified Ti electrode has been developed for photoelectrochemical determination of dopamine [17].

Methanol is used as a vital industrial solvent and crude substance for many processes. For instance, in the oil and gas industries methanol is in many cases applied to avoid gas hydrate formation during generation [18]. Methanol is harmful and can be deadly or exceptionally serious morbidity, probably leading to weakness blindness or renal inefficiency [19]. In addition to, methanol is one of the noticeable future fuels in fuel cells [20]. Also, the methanol detection is important in sugar cane and pectin ester content and pectin methyl esterase activity [21,22]. Thus, determination of its concentration is necessary. There are a few reports about the electrocatalytic determination of methanol [23-26]. Photoelectrochemical methanol oxidation has been investigated at the nanostructured  $\text{TiO}_2$  thin film electrodes such as highly ordered  $\text{TiO}_2$  nanotube array electrodes [27,28]. The methanol adsorption on  $\text{TiO}_2$  surface occurs via two paths. On the clean defective surface, the adsorbed methanol oxygen atom, fills the oxygen vacancy site [29]. The next path is considered the interactions between the methanol oxygen atoms and the coordinatively unsaturated Ti atoms at the surface [30]. In this work, the photoelectrocatalytic determination of methanol as a simple method for methanol quantification was employed using Ti/ $\text{TiO}_2$  plate electrode.

## 2. EXPERIMENTAL

### 2.1. Reagents and chemicals

Twice distilled water was applied as solvent for photoelectrochemical investigations. Methanol and titanium foils (0.25 mm thickness, 99.7% purity) were purchased from Merck and Sigma-Aldrich respectively. Hydrofluoric acid (99.5%, Fluka), and nitric acid (66%, Fluka) were used as received.  $\text{H}_3\text{PO}_4$  (99%, Fluka) and its salts were employed for fabrication of buffer solutions.

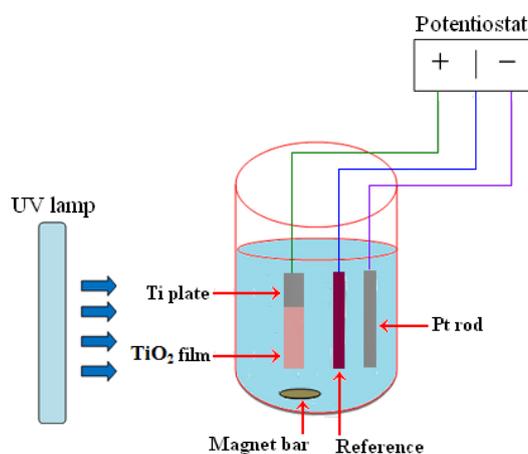
### 2.2. Apparatus

A bench-scale photoreactor instrument as appeared in Fig. 1 contained a cylindrical quartz cell with the size of 3.0 cm in diameter, 8.0 cm in height and 1.8 mm in thick was

utilized for carrying out photoelectrochemical tests. The reactor and the UV lamp were placed in a black box to avoid from extraneous radiation. The potentiostat ( $\mu$  Autolab Type III) was connected to the photoreactor containing three electrodes of Ti/TiO<sub>2</sub> electrode as anode, Pt wire electrode as cathode and an Ag/AgCl/KCl (3M) as reference electrode. These three electrodes were put in the center of the reactor in parallel. The photoactive surface of the anode (TiO<sub>2</sub>) was radiated by a 4 W medium pressure mercury lamp as UV light source. Scanning electron microscopy (SEM) (Philips Corp., XL30 model) was applied for investigating of the surface morphology of the TiO<sub>2</sub> modified graphite electrode.

### 2.3. Fabrication of working electrode

Ti sheet (3.0×3.0 cm<sup>2</sup>) was mechanically polished with 220# and 1500# abrasive papers respectively. Then, the Ti plate was wiped in an ultrasonic bath consisting distilled water, chemically etched by sinking aqueous solution containing HF/HNO<sub>3</sub>/H<sub>2</sub>O with the mixing volume ratio of 1:4:5 and cleaned thoroughly with acetone and deionized water. After that, the Ti sheet was anodized as anode in the presence of Pt rod as cathode using a two electrode system under constant bias voltage 20 V for 20 min in a solution of 0.2% (v/v) HF. In the last step, the Ti/TiO<sub>2</sub> electrode was then washed with distilled water, dried in air and calcinated in a furnace at 500 °C for 2 h.



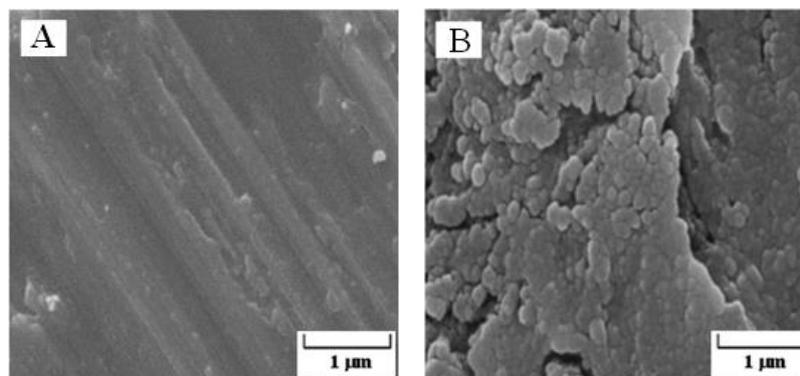
**Fig. 1.** Schematic diagram of the photoreactor system

## 3. RESULTS AND DISCUSSION

### 3.1. Surface morphology of the Ti/TiO<sub>2</sub> electrode

The Ti/TiO<sub>2</sub> electrode surface was studied using scanning electron microscopy (SEM) (Fig. 2). This Fig. presents the SEM photos of the unmodified and TiO<sub>2</sub> modified Ti electrodes. It can be indicated from Fig. 2B that TiO<sub>2</sub> coverage was formed and almost

distributed as a uniform texture on the surface of Ti substrate, howsoever some ups and downs were sometimes saw on the surface.

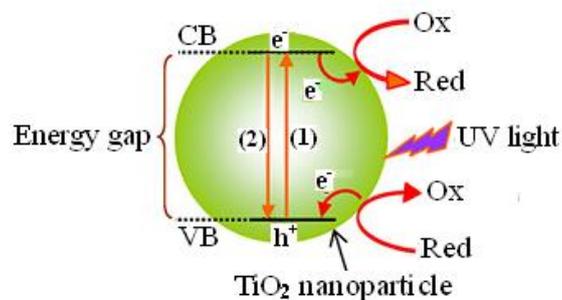


**Fig. 2.** SEM micrographs of (A) unmodified Ti and (B) TiO<sub>2</sub> modified Ti electrodes

### 3.2. Photoelectrochemical behavior of methanol on the Ti/TiO<sub>2</sub> electrode

In TiO<sub>2</sub>-based photocatalysis are generated a large number of electrons and holes under UV irradiation because of photo-excitation of electrons from the valence band (VB) to the conduction band (CB). UV light can ascend an electron from the valence band to the conduction band ( $e_{CB^-}$ ) creating a positively charged vacancy or hole ( $h_{VB^+}$ ) as observed in Fig. 3(1) [31]. The hydroxide radicals are generated according to on reaction between the holes ( $h^+$ ) as energetic oxidants and the water molecules or the hydroxyl ions. On the other hand, the recombination of electrons with unreacted holes or with adsorbed hydroxyl radicals are the main logics of photocatalysis efficiency decreasing as saw in Fig. 3(2).

The application of an anodic voltage to a Ti/TiO<sub>2</sub> electrode more gives a potential gradient inside the film to conduct the photogenerated holes and electrons in various positions effectually using photoelectrocatalysis. The photoelectrochemical responses of the Ti plate and Ti/TiO<sub>2</sub> electrodes on methanol oxidation were investigated by cyclic voltammetry.

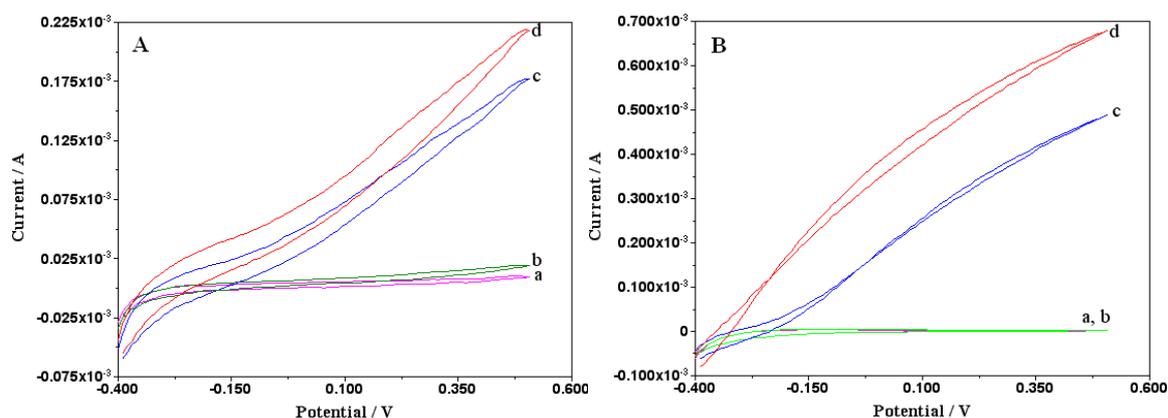


**Fig. 3.** Schematic photoexcitation of a semiconductor particle

For this aim, cyclic voltammetry tests were performed in the absence or presence of methanol at the surface of these in the darkness and under the UV light irradiation in pH 7.0 (Fig. 4). As it can be shown in Fig. 4A, the Ti foil generates a very small current in the darkness and the absence of methanol due to the impracticality of H<sub>2</sub>O and methanol oxidation at the Ti foil electrode surface (curves a and b respectively). However, under UV light illumination a remarkable value of currents at the electrode surface can be produced both in the absence and presence of methanol (curves c and d).

These results can be led to the photoelectrocatalytic processes of H<sub>2</sub>O and methanol oxidation. On the other hand, in the Ti/TiO<sub>2</sub> electrode case, according to Fig. 4B there is not any noteworthy current in the darkness and under the UV light irradiation in pH 7.0 like Ti plate (curves a and b). But, in the presence of the UV irradiation, the photocurrents amounts are around several times higher than that of the Ti foil electrode (curves c and d). This difference can be concerned to the electron-hole pairs production and consequently the increase of ability TiO<sub>2</sub> as a semiconductor related to Ti as a metal. Methanol as a whole scavenger by acquiring holes provides an easier pathway for oxidation and consequently would be efficient positively to electron-hole separation, which led to the more photocurrent.

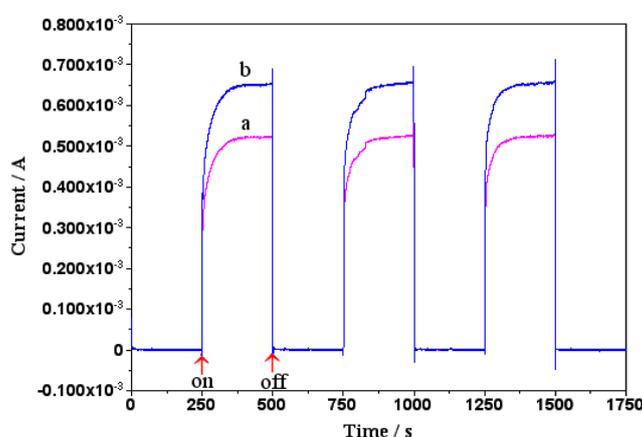
In addition to, for more assessing the photoelectrochemical behavior of the Ti/TiO<sub>2</sub> electrode and to prove its capability to photoelectrocatalysis oxidation of methanol, hydrodynamic amperometry was used in buffer solution in the presence and absence of methanol solution under UV illumination to study of photoelectrochemical response of the Ti/TiO<sub>2</sub> electrode (Fig. 5).



**Fig. 4.** Cyclic voltammograms of A) the Ti foil and B) the Ti/TiO<sub>2</sub> electrodes in the solution containing 0.46 mM methanol in the phosphate buffer solution (pH 7.0) at the scan rate of 10 mV s<sup>-1</sup>, (a) darkness and the absence of methanol, (b) darkness and the presence of methanol, (c) UV illumination and the absence of methanol and (d) UV illumination and the presence of methanol

As shown in this Fig., the climb and fall of the photocurrent responded well to the radiation

being turned on and off. The photocurrent goes ahead quickly after the illumination, and afterward the photocurrent accomplishes a steady state. This pattern of photocurrent can be profoundly recreated for on-off cycles of illumination. A known increase found in the photocurrent under radiation demonstrates that photogenerated electrons on the Ti/TiO<sub>2</sub> electrode can be sufficiently directed to the counter electrode using employed positive potential, which would be critical for avoiding of charge recombination. The presence of methanol in buffer solution causes a certainly easier mechanism for the exchange of the photogenerated holes in the Ti/TiO<sub>2</sub> electrode over the film/electrolyte interface against either adsorbed hydroxyl groups or water molecules. Consequently, the higher photocurrent produced in the absence of methanol than that of in the presence of methanol (curves a and b, respectively).



**Fig. 5.** Photocurrent-time response of the Ti/TiO<sub>2</sub> electrode at an applied potential of 0.5 V vs. reference electrode under on-off cycles of irradiation in phosphate buffer solution (pH 7.0); (a) in the absence and (b) the presence of 0.46 mM methanol

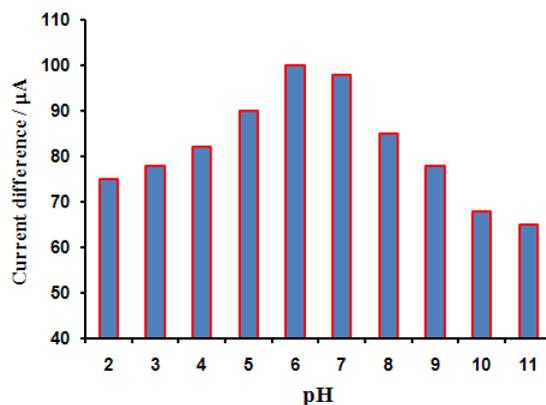
### 3.3. Effect of pH solution

The pH amount is a crucial factor in the photocatalytic and photoelectrocatalytic process, due to the pH amount of the solution will change the configuration of target material. On the other hand, hydroxyl groups on TiO<sub>2</sub> surface under different pH values, undergo the following reactions [32]:



The catalyst surface is positively altered when at pH value above just about 6, because the iso-electrical point of TiO<sub>2</sub> is at pH 4-6, henceforth, at more acidic pH, it is negatively charged [33]. Moreover, it should be noted that the change of pH has an important effect on modifying the position of the TiO<sub>2</sub> conduction band [34]. For this aim, the effect of pH value on the photocurrent differences in the absence and presence of 0.46 mM methanol was

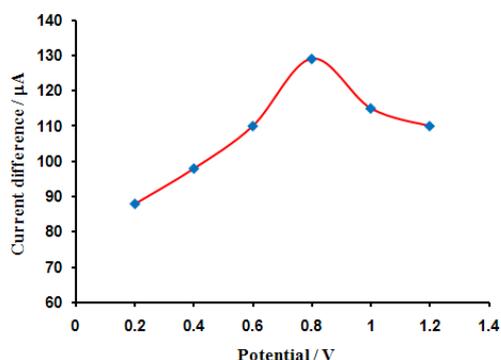
investigated in buffer solutions with pH 2 to 11 on the Ti/TiO<sub>2</sub> electrode biased at  $E=0.5$  V (Fig. 6). The results showed that at pH 6.0, the variation of photocurrents is maximum versus other pHs.



**Fig. 6.** Influence of pH values on the photocurrents differences of the Ti/TiO<sub>2</sub> electrode in the absence and presence of 0.46 mM methanol at the biased potential 0.5 V

### 3.4. Effect of Bias Potential

An electric field is produced by applying a potential gradient over the titanium dioxide film, which keeps photogenerated charges separated and forced the photogenerated holes and electrons to move in inverse directions. Subsequently, bias potential is a necessary element that impacts photoelectrocatalytic oxidation of methanol. For this purpose, the photocurrent differences of the Ti/TiO<sub>2</sub> electrode were measured in phosphate buffer solution (pH 6.0) using six amounts of bias potential 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2 V in the absence and presence of 0.46 mM methanol (Fig. 7). The obtained results presented that voltage 0.8 V was as the optimal voltage for methanol analysis. According to this phenomenon that more water can be oxidized by photogenerated holes, more increasing the employed voltage beyond 0.8 V results in a little decline in methanol oxidation [35].

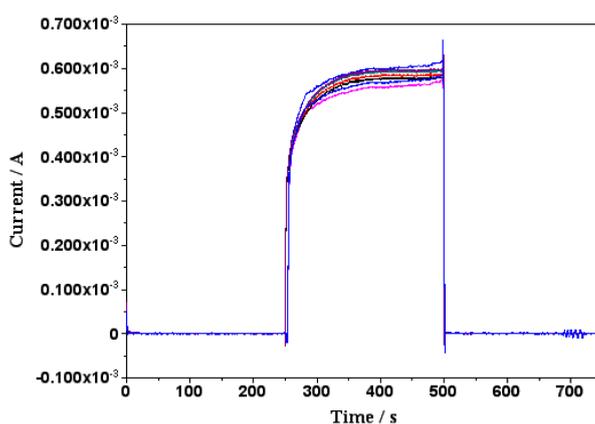


**Fig. 7.** Influence of different applied potentials values on the photocurrents differences of the Ti/TiO<sub>2</sub> electrode in the absence and presence of 0.46 mM methanol at pH 6.0

### 3.5. Repeatability, stability and interference studies

To evaluation and confirmation the repeatability of the Ti/TiO<sub>2</sub> electrode, seven repeatedly hydrodynamic photoamperometry was performed under the optimized conditions (Fig. 8). The relative standard deviation (RSD) was 2.57% for seven measurements. This result showed that the repeatability of the electrode is good. The stability of the electrode was estimated using monitoring of photocurrent after being stored at room temperature for two weeks. It was observed that, the photocurrent response preserved almost 94% of its initial amounts. These observations proved the suitable stability of the Ti/TiO<sub>2</sub> electrode.

For demonstrating the selectivity of the method on methanol determination, the effect of some conceivable interfering materials was tested under optimized cases. For this purpose, the standard for interference of each substance was considered at  $\pm 5.0\%$  in the resulted recovery for a solution consisting of 0.070 mM methanol, without any interfering. Table 1 proves that the Ti/TiO<sub>2</sub> electrode is selective for methanol in comparison with the examined interfering species.



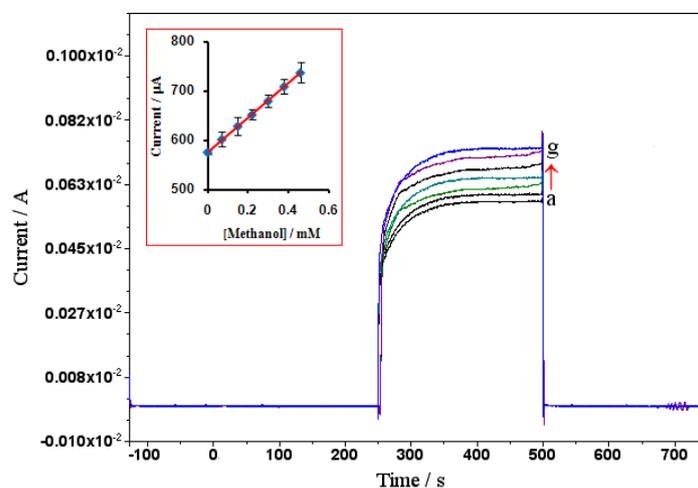
**Fig. 8.** Seven consequent hydrodynamic amperograms of the Ti/TiO<sub>2</sub> electrode under optimized conditions (pH 6.0 and bias potential 0.8 V)

**Table 1.** Tolerance level of some interfering species for methanol determination

Interfering substance	Interfering substance/methanol	Recovery (%)
Na <sup>+</sup>	50	98
Mg <sup>2+</sup>	42	97
NH <sub>4</sub> <sup>+</sup>	43	96
HCO <sub>3</sub> <sup>-</sup>	46	96
SO <sub>4</sub> <sup>2-</sup>	38	101
Cl <sup>-</sup>	35	102
F <sup>-</sup>	42	98
Glucose	18	102
Sucrose	15	103
Formaldehyde	7	104

### 3.6. Analytical application of the Ti/TiO<sub>2</sub> electrode

It was previously mentioned, the photocurrent value of the Ti/TiO<sub>2</sub> electrode increase in the presence of methanol. Therefore, photoelectrocatalytic oxidation of methanol can be effective method for detection of methanol concentration (Fig. 9).



**Fig. 9.** The obtained hydrodynamic amperograms of the Ti/TiO<sub>2</sub> electrode in the phosphate buffer solution (pH 6.0) and at bias potential 0.8 V vs. reference electrode in the presence of various methanol concentrations: (a) 0.00, (b) 0.07, (c) 0.15, (d) 0.22, (e) 0.30, (f) 0.38 and (g) 0.46 mM. Inset: Plot of photocurrent relative to methanol concentration

**Table 2.** Comparison of some electrochemical sensors for methanol determination

Electrode	Method	LDR ( $\mu\text{M}$ )	LOD ( $\mu\text{M}$ )	Ref.
Carbon paste <sup>a</sup>	Electrocatalysis-amperometry	60-220	8.21	[23]
Cu <sup>b</sup>	Electrocatalysis-amperometry	100-1500	100	[24]
Glassy carbon <sup>c</sup>	Electrocatalysis-cyclic voltammetry	10000-90000	97.66	[25]
Glassy carbon <sup>d</sup>	Electrocatalysis-amperometry	200-5000	10	[26]
Ti/TiO <sub>2</sub>	Photoelectrocatalysis-amperometry	70-460	7.5	This study

<sup>a</sup>Carbon paste electrode modified with silver chloride

<sup>b</sup>Cu electrode modified with copper oxides

<sup>c</sup>Glassy carbon electrode modified with nickel-manganese salen complexes encapsulated in mesoporous zeolite A

<sup>d</sup>Glassy carbon electrode modified with chitosan-immobilized nickel(II) and the antibiotic cefixime

It was observed that there are a linear correlation between the photocurrent amount and the methanol concentration in the range of 0.070-0.46 mM with correlation coefficient of

0.99. Also, the detection limit was obtained 7.5  $\mu\text{M}$  ( $3\sigma$ ) (inset of Fig. 9). Therefore, the photoelectrocatalytic oxidation of methanol can readily be employed for the determination of methanol. The comparison of several parameters of methanol about some modified electrodes is summarized in Table 2. It can be resulted from Table that these parameters value is contrastive with qualities reported by other research groups for electrocatalytic oxidation of methanol at the surface of other electrodes [23-26].

#### 4. CONCLUSION

In this paper, the photoelectrochemical behavior of methanol was studied by cyclic voltammetry and hydrodynamic amperometry methods. In these experiments, methanol as a scavenger caused increasing the photocurrent value of the Ti/TiO<sub>2</sub> electrode. According to present information, there is not any report about methanol determination using photoelectrocatalysis. Therefore, it was developed photoelectrocatalytic determination of methanol using the Ti/TiO<sub>2</sub> electrode fabricated by anodizing Ti foil in aqueous solution as a new and simple methanol sensor. The electrode showed promising results with suitable detection limit.

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