

# Ti/TiO<sub>2</sub> nanotube array electrode as a new sensor to photoelectrocatalytic determination of ethylene glycol

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**Abstract.** The photoelectrocatalytic oxidation behaviour of ethylene glycol (EG) was studied in the present work using the TiO<sub>2</sub>-modified Ti foil (Ti/TiO<sub>2</sub>) electrode. The Ti/TiO<sub>2</sub> nanotube array (Ti-NTA) electrode was prepared by anodizing of the Ti foil in the HF aqueous solution (0.2% v/v). The anodization was conducted in the constant 30 V for 2 h, and then the as-prepared Ti-NTA electrode was calcinated at 50° C for 2 h. The surface morphology of Ti-NTA electrode was studied using scanning electron microscopy images. For EG determination, the photocurrent of EG (EG oxidation current in the UV irradiation) was assessed using the hydrodynamic photoamperometric method in the phosphate buffers. Ultimately, the optimum conditions of EG determination were studied in various pH values and applied bias potentials, and the pH = 3.0 and  $E = 1.0$  V (*vs.* reference electrode) were determined as the optimum conditions. It was found that the photocurrent of EG was linearly dependent on the concentration of EG in the range of  $3.0 \times 10^{-5}$  to  $0.88 \text{ mol l}^{-1}$ , and the detection limit of EG determination was found to be  $7.2 \times 10^{-6} \text{ mol l}^{-1}$  ( $3\sigma$ ).

**Keywords.** Photo-assisted electrocatalysis; Ti/TiO<sub>2</sub> nanotube array electrode; hydrodynamic amperometry; ethylene glycol.

## 1. Introduction

Most of the research works about TiO<sub>2</sub> are about degrading materials with this photocatalyst [1–4]. However, the photo-assisted electrocatalytic determination with this photocatalyst has not been studied so far. Only in a few articles the photo-assisted electrocatalytic, named as photoelectrocatalytic (PEC), determination has been studied with some other materials. For instance, the polyethylene blue-modified glassy carbon electrode was used to determine the sulphide in the flow injection [5]. The electropolymerized methylene blue was used for the determination of NADH in a flow injection system [6]. Also, Zhang *et al* [7] have determined the chemical oxygen demand (COD) in the wastewater using UV-LED-based photoelectrochemical cell. Zen *et al* [8] have prepared copper-plated screen-printed electrodes for oxidation of *o*-phenols. Formic acid was determined using the Ag–TiO<sub>2</sub>/ITO film [9]. Moreover, the Ti/TiO<sub>2</sub>/PbO<sub>2</sub> [10], and Ti/TiO<sub>2</sub> [11] electrodes were used for determination of the COD values and formaldehyde, respectively.

Besides, massive quantities of ethylene glycol (EG) are produced in the world each year. The industrial method for EG production involves hydrolysis of the corresponding alkylene oxide (epoxide) in excess water at high temperature and pressure [12]. EG is clear, colourless liquid with a syrup-like consistency. EG is used in the production of antifreeze, engine coolants, dyes, some types of inks and other chemicals. Given the widespread use of EG, the spill

could happen in many cases. EG breaks in the air in about 10 days, and breaks in the water or soil in a few weeks. It might enter into the environment through the discharging of EG-containing products, particularly at the airports, where it is used in the deicing agents for runways and airplanes. Hence, the determination of EG amount in the environment is needed. Some methods such as nanofiltration [13], GC [14] and electrochemical methods are used for this purpose.

In this study, the PEC oxidation method was applied to EG determination. In this method, determination of EG was performed using hydrodynamic photoamperometry by the Ti/TiO<sub>2</sub> nanotube array (Ti-NTA) electrode as photoanode.

## 2. Experimental

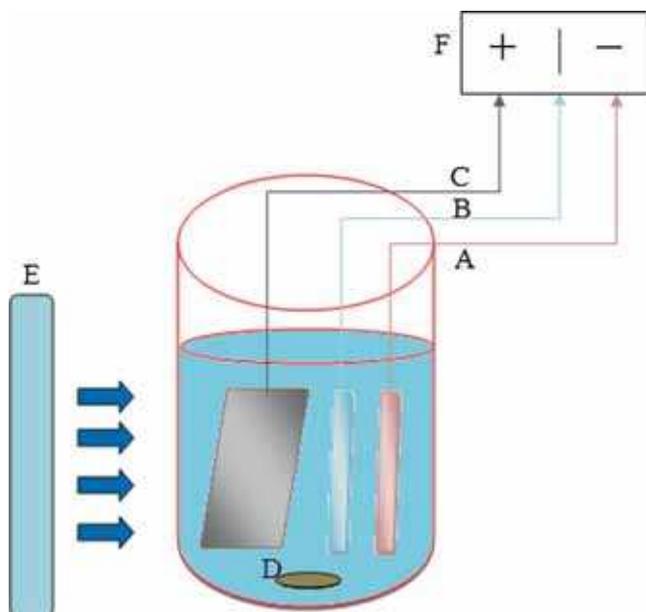
### 2.1 Materials and reagents

The solvent for electrochemical studies was doubly distilled water. EG from Merck was used as received. The titanium foils (thickness 0.25 mm, assay 99.7%) were purchased from Sigma-Aldrich. Buffer solutions were prepared with H<sub>3</sub>PO<sub>4</sub> and its sodium salts.

### 2.2 Fabrication of the Ti-NTA working electrode

A piece of Ti foil sheet (3.0 cm × 3.0 cm) was used as electrode substrates, which was firstly polished with different abrasive papers. Then, it was sonicated in the cold distilled water and chemically etched by immersion in the

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**Figure 1.** Schematic diagram of the reactor system, (A) auxiliary electrode, (B) reference electrode, (C) working electrode, (D) magnetic stirrer and (E) UV lamp.

HF/HNO<sub>3</sub>/H<sub>2</sub>O (1 : 4 : 5 v/v/v) mixed solution. Then, the Ti sheet was rinsed with acetone and deionized water. The treated Ti sheet was served as the anode and a Pt electrode was served as the cathode, and both of them were placed in a solution of 0.2% (v/v) hydrofluoric acid. The anodization was performed using a constant 30 V potential for 2 h. The freshly fabricated Ti-NTA electrode was then rinsed with distilled water and was dried in the air. Eventually, it was calcinated in a furnace at 500°C for 2 h [15].

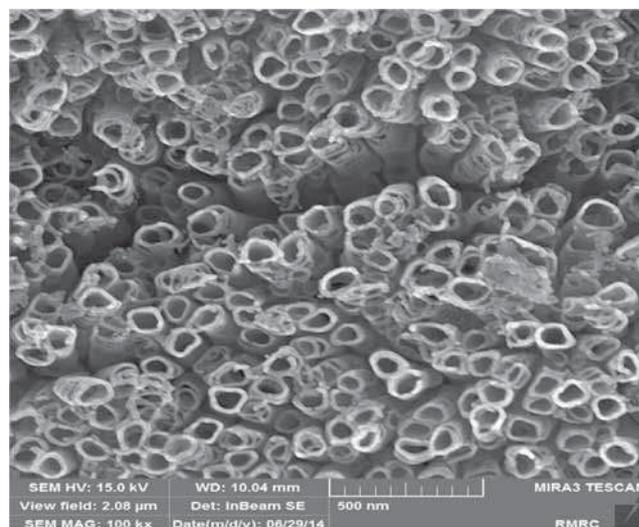
### 2.3 Instrumentation

The PEC oxidation experiments were carried out, as shown in figure 1, in a single quartz cylindrical photoreactor 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 to avoid environment illumination. An Ag|AgCl|KCl (3 M) and a platinum rod were used as the reference electrode and the auxiliary electrode, respectively. The photoelectrochemical experiments were carried out using a potentiostat/galvanostat ( $\mu$  Autolab Type III). A 4 W medium pressure mercury lamp with maximum UV irradiation was used for excitation of photoelectrode. A electrical power supply (MP, 6003, Taiwan) was used for preparation of the Ti-NTA working electrode.

## 3. Results

### 3.1 Scanning electron microscopy (SEM) of the Ti-NTA electrode

Figure 2 shows SEM images of Ti-NTA electrode. It can be seen from this figure that the fabricated nanotube arrays is



**Figure 2.** SEM images of Ti-NTA electrodes.

distributed regularly. The inner diameter of nanotubes is less than 100 nm and the mean wall thickness of nanotubes is approximately 25 nm.

### 3.2 Photoelectrochemical behaviour of EG surface of Ti-NTA electrode

Advanced oxidation processes (AOPs) involve the generation of highly reactive hydroxyl radicals (HO<sup>•</sup>). Thus, AOPs have become as a promising wastewater treatment technology for degradation or oxidation of a wide range of organic contaminants. This is inspired by the potential application of TiO<sub>2</sub>-based photocatalysts for the total oxidation of organic compounds in contaminated air and wastewater. Upon UV illumination, the electrons (e<sup>-</sup>) are excited from the valence band (VB) to the conduction band (CB) of the Ti/TiO<sub>2</sub> semiconductor. This process generates the electron-hole pairs (scheme 1) [16].



The positive holes (h<sup>+</sup>) are powerful oxidants that oxidize the water molecules or the hydroxyl ions resulted to hydroxide radical:

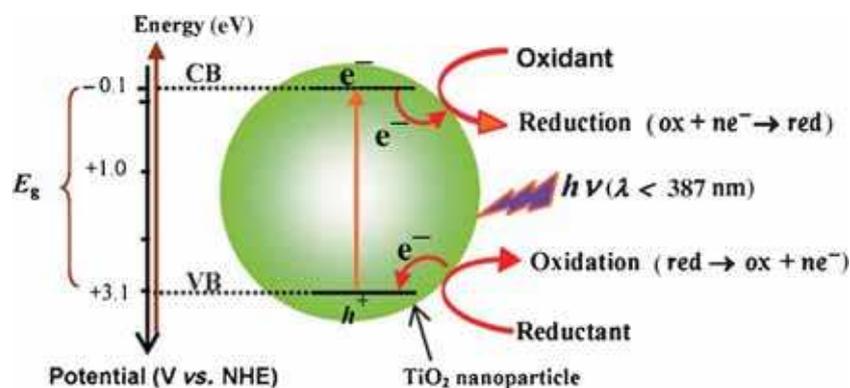


The hydroxide radicals are active oxidant, which react with the substrate (S) and oxidize it

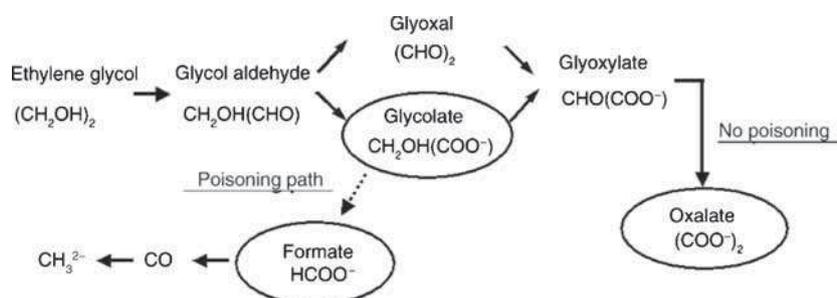


In addition, photogenerated electrons could pass to the semiconductor surface and react with the oxygen to produce some other weaker oxidants such as O<sub>2</sub><sup>-•</sup> (superoxide radical anion), HO<sub>2</sub><sup>•</sup> and H<sub>2</sub>O<sub>2</sub> by following reactions:





**Scheme 1.** Representative schematic diagram for energy band and mechanism of photoelectrocatalytic oxidation at the surface of the TiO<sub>2</sub> particle.



**Scheme 2.** Schematic diagram for supposed reaction pathway to EG oxidation and resulted products.



The recombination of electron-hole pairs or reaction between the photogenerated electrons and the hydroxyl radicals through the following pathways are the major reasons in the photocatalysis efficiency decreasing

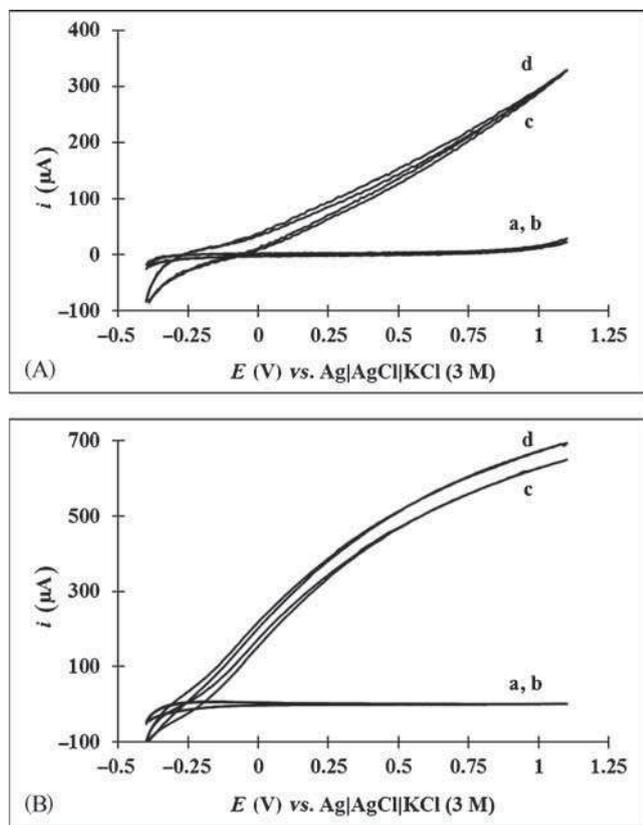


Applying a bias potential through the Ti-NTA working electrode decreases the recombination of the photogenerated electron-hole pairs (named the photoelectrocatalysis method). The application of the potential separates effectively these electron-hole pairs. In this method, separation of the photogenerated electron-hole pairs depends directly on the applied potential through the Ti-NTA electrode as working electrode. This applied potential drives the electrons to the auxiliary electrode and the holes remain at the surface of the Ti-NTA electrode. The photoelectrocatalysis method can provide much higher efficiency for organic material oxidation. Oxidation of EG at the surface of the Ti-NTA electrode and the amount of photocurrent  $i$  affected by pH, applied potential and EG concentration. Therefore, the effects of these factors were studied. Supposed reaction pathways are shown in scheme 2 [17]. As it is shown, final products could

be glycolate, oxalate and formate. Poisoning pathway refers to the adsorption of the species at the surface of the Ti-NTA electrode, which decreases the photocurrent with time.

The photoelectrochemical behaviour of the Ti foil and the Ti-NTA electrodes was evaluated using cyclic voltammetry (CV). For this purpose, the CV experiments were studied in the darkness and under the UV light irradiation at the surface of these electrodes in the phosphate buffer solution (pH 7.0). Besides, the effect of EG addition to the buffer solution, in the generation of photocurrent, was studied (figure 3). As it can be seen in figure 3Aa, in the darkness and in the only phosphate buffer, the Ti foil electrode surface produces a negligible current because of the impossibility of H<sub>2</sub>O oxidation at the surface of the Ti foil electrode. Also, the addition of EG to the buffer solution resulted to similar CV (figure 3Ab), which means the Ti foil cannot oxidize EG. On the contrary, under UV light illumination this electrode can produce high amount of currents either in the absence or presence of EG (figure 3Ac,d). This result can be attributed to the photoelectric phenomenon. The illumination energy of applied light is about 4.8 eV and the work function of the Ti is about 4.3 eV. Thus, our light can produce the photoelectrons at the surface of the Ti foil electrode.

In the Ti-NTA electrode case, as shown in figure 3B, in the darkness, similar results are observed in comparison with the Ti foil (figure 3Ba,b). Nevertheless, in the presence of the UV irradiation, the extents of the photocurrents are almost

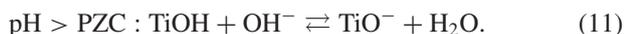
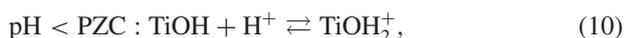


**Figure 3.** Cyclic voltammograms of (A) Ti foil electrode and (B) Ti-NTA electrode in the solution of 0.325 M EG in the phosphate buffer (pH = 7.0) containing 0.1 M Na<sub>2</sub>SO<sub>4</sub> as supporting electrolyte at the scan rate of 10 mV s<sup>-1</sup>, (a) darkness and the absence of EG, (b) darkness and the presence of EG, (c) UV irradiation and the absence of EG and (d) UV irradiation and the presence of EG.

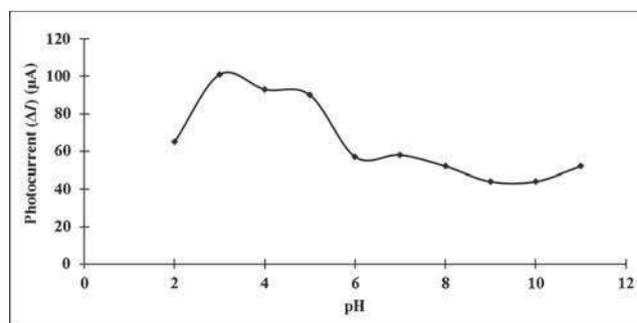
2-fold higher than the Ti foil electrode (figure 3Bc,d). From this figure, it can be concluded that because of the effective separation of the electron-hole pairs, the oxidation current of the Ti-NTA electrode is higher than the Ti foil electrode. The presence of EG (figure 3Ad) provides a much more facile pathway for the transfer of holes across the film/electrolyte boundary, and holes oxidize EG molecules, which resulted to the higher photocurrent.

### 3.3 Effective parameters on PEC oxidation of EG

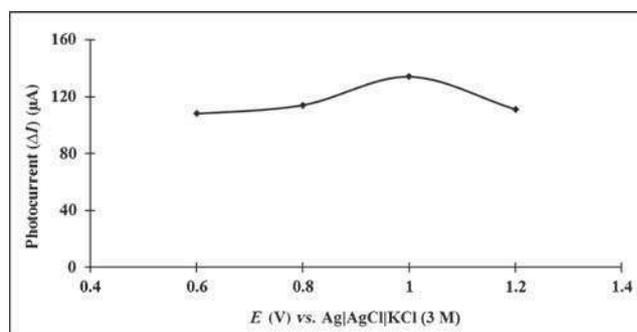
**3.3a Solution pH:** pH is a key factor that influences the PEC oxidation of materials. Under different pH conditions, the hydroxyl groups on the TiO<sub>2</sub> surface undergo the following equilibrium through Lewis acid-base reaction [18]:



The point of zero charge (PZC) of the TiO<sub>2</sub> is about pH = 6.8, so in the pH < PZC, the TiO<sub>2</sub> surface is positively charged and in the pH > PZC, the TiO<sub>2</sub> surface is negatively charged [19]. For PEC oxidation of compounds, their adsorption at



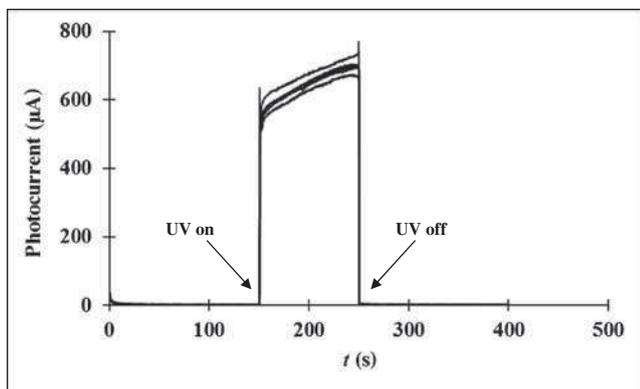
**Figure 4.** Effect of phosphate buffer pH on PEC oxidation of EG on surface of Ti-NTA electrode at bias potential of 0.6 V (vs. Ag|AgCl|KCl (3 M)) in solution of 0.325 M EG containing 0.1 M Na<sub>2</sub>SO<sub>4</sub> as supporting electrolyte.



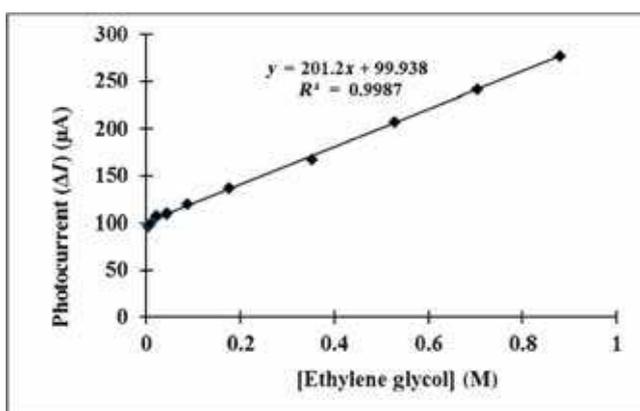
**Figure 5.** Effect of applied bias potential (vs. Ag|AgCl|KCl (3 M)) on PEC oxidation of EG on surface of Ti-NTA electrode at pH = 3.0 in solution of 0.325 M EG containing 0.1 M Na<sub>2</sub>SO<sub>4</sub> as supporting electrolyte.

the surface of the Ti-NTA electrode is necessary. In addition, pH influences the adsorption ability of the target compound on the TiO<sub>2</sub> film [20]. Also, the change of pH has an important effect on modifying the position of the TiO<sub>2</sub> conduction band (60 mV per pH unit) [21]. Given this variation of conduction band of the TiO<sub>2</sub>, the oxidizing ability of the photogenerated holes is raised, and the production of hydroxyl radicals is facilitated due to oxidation of water (or hydroxide ions) by photogenerated holes. Therefore, the effect of the solution pH value on the photocurrent differences in the presence and absence of EG ( $\Delta I$ ) was investigated (figure 4). From this figure, it is clear that at pH = 3.00 maximum photocurrent is produced by oxidation of EG at the surface of the Ti-NTA photoelectrode.

**3.3b Bias potential:** It is mentioned previously that anodic bias potential has an important role in the separation of the photogenerated electron-hole pairs, and increases the photocurrent amount. Therefore, various amounts of the potentials were applied through the Ti-NTA photoelectrode, while the UV irradiation was illuminated the Ti-NTA photoelectrode. The results of produced photocurrents ( $\Delta I$ ) are shown in figure 5 for potential range of 0.6–1.2 V vs. Ag|AgCl|KCl (3 M) as the reference electrode. As it is



**Figure 6.** Six successive hydrodynamic amperograms of Ti-NTA electrode in the phosphate buffer solution (pH 7.0) at bias potential of 0.6 V (vs. Ag|AgCl|KCl (3 M)).



**Figure 7.** Plot of photocurrent as a function of various EG concentrations.

shown, the  $E = 1.0$  V is optimum potential in the studied potential range.

**3.3c Repeatability of Ti-NTA photoelectrode response:** Repeatability evaluation of the Ti-NTA photoelectrode was performed using six repeatedly hydrodynamic amperometry in the phosphate buffer (pH = 7.0). As it can be seen in figure 6, repeatability of the Ti-NTA photoelectrode is good and negligible differences between these experiments can be observed and relative standard deviation (RSD) = 5.18% is calculated from these measurements.

**3.3d PEC determination of EG:** A linear relation between the photocurrent and the concentration of EG at the surface of the Ti-NTA photoelectrode was observed during the PEC oxidation of EG (figure 7). It was found that the detection limit of determination was  $7.2 \times 10^{-6}$  mol l<sup>-1</sup> ( $3\sigma$ ), and the linear range was  $3.0 \times 10^{-5}$  to 0.88 mol l<sup>-1</sup>.

## 4. Conclusions

In this paper, a new and simple amperometric sensor was developed for the determination of EG based on PEC oxidation of EG at the surface of the Ti-NTA photoelectrode. The Ti-NTA photoelectrode can be prepared simply and rapidly by anodizing of the Ti foil in the HF aqueous solution. Moreover, the optimum pH and applied bias potential were evaluated. This sensor showed satisfactory results with good detection limit at the optimum condition for the determination of EG.

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