**A low cost universal photoelectrochemical detector for organic
compounds based on photoelectrocatalytic oxidation at a
nanostructured TiO₂ photoanode**

Lihong Li, Shanqing Zhang*, Huijun Zhao

**Environmental Futures Centre
and
Griffith School of Environment
Gold Coast Campus, Griffith University
QLD 4222, Australia**

***To whom Correspondence should be addressed:**

Dr. Shanqing Zhang

Telephone: +61-7-5552 8155

Fax: +61-7-5552 8067

Email: s.zhang@griffith.edu.au

Abstract

A photoelectrochemical detector (PECD) was developed for determination of organic compounds in flow injection analysis (FIA) and high performance liquid chromatography (HPLC) based on the extraordinary oxidation power of nanostructured TiO₂ photoanodes under UV illumination. The PECD is a simple, small, and compact photoelectrochemical cell consisting of low cost components such as a TiO₂ nanostructured photoanode and a UV-LED. Compared with conventional FIA and HPLC selective detectors, such as UV-Vis detector, electrochemical detector and fluorescent detector, the PECD has the advantage of being low cost, non-selective and sensitive. Using the FIA mode, the analytical principle of the PECD was demonstrated by detecting a large variety of organic compounds, such as sugars, amino acids, alcohol, straight chain carboxylic acids, and aromatic carboxylic acid. The PECD was subsequently coupled with a typical FIA and HPLC system for the determination of sugars. For the application in FIA, under the optimum experimental conditions, the linear ranges for glucose and sucrose were 25-600 μ M and 25-500 μ M, respectively, with the same detection limit of 10 μ M. When the PECD was coupled with a HPLC system, the linear range for both glucose and sucrose was 7.5-200 mM with the same detection limit of 1 mM under the optimal experimental conditions.

Keywords

TiO₂, photoelectrochemical detector, high performance liquid chromatography, nanostructure

1. Introduction

Flow injection analysis (FIA) and high performance liquid chromatography (HPLC) have become two of the most common analytical techniques in many fields, such as in pharmaceutical, environmental, forensic, clinical, food, flavour sciences and relative industries [1-4]. The availability of a large variety of detectors supports the applications of the FIA and HPLC. The detectors can be classified into specific or non-specific (i.e., universal) detectors [5]. Nowadays, the most common detectors, such as UV-Vis detectors, photodiode array detectors, amperometric electrochemical detectors, fluorescent detectors, are specific detectors, only giving response to the specific properties of the analytes. Mass spectroscopy (MS) detectors and reflective index detectors (RID) are more universal. But the MS detectors are extremely more expensive and are not sensitive to low molecular weight compounds [1] while RID commonly has unsatisfactory sensitivity [6]. Low cost and sensitive universal detectors are ideal for chromatographic application. In this regards, the flame ionization detector (FID) for gas chromatography (GC) is a good representative. The development of low cost and sensitive universal detectors is much needed to expand the applications of FIA and HPLC.

Since the discovery by Fujishima and Honda in 1972 of water cleavage using TiO_2 film photoanode under an anodic potential bias and UV illumination [7], considerable research efforts have been devoted to the development of high efficient TiO_2 film. In sensing applications, TiO_2 films have been widely studied as sensors for various gases, such as H_2 , O_2 , CO , NO_x , ethanol, acetone, liquefied petroleum gas, and toluene [8-10]. Additionally, combined with the immobilization of enzyme, TiO_2 based biosensor can be applied in determination of glucose with high sensitivity and fast response time [11]. It also has been reported that TiO_2 films can be used for different

ions sensing, including the pH sensing with TiO₂/SiO₂/Si structure [12], and mercury ions determination with the molecularly imprinted TiO₂ thin film [13].

The most significant attraction of using the TiO₂ photocatalyst is the strong oxidation power of the TiO₂ photoanode. It is well-established that the oxidation power is stemmed from the photohole generated under UV light. Because of this, a wide spectrum of organic compounds can be stoichiometrically mineralized (see Eq. 1).

The number of electrons captured in this process is the oxidation number ($n=4y-2j+m-3k-q$). When the electrochemistry technique is combined with photocatalysis, the oxidation power of the TiO₂ thin film can be dramatically enhanced. Electrochemical instrument such as potentiostat can not only provide electric field to suppress the recombination of photoelectron and photohole (and improve the oxidation efficiency further), but also measure the photocurrent generated from this process for quantitative analysis [14].

The photocatalytic oxidation property at the TiO₂ surface has been incorporated into detectors for application in HPLC [15]. Fox and Tien attempted to develop a flow-through photoelectrochemical detector for HPLC. UV illumination source was used to initiate a photoelectrocatalytic oxidation reaction to detect organic compounds. The detection limits for aniline, benzaldehyde and benzyl alcohol were 1.6 µg, 4.9 µg and 210 µg, respectively [15]. However, this detector has limited application due to the following factors. Firstly, this TiO₂ electrode can react with hydroxylic eluents such as water and methanol leading to extremely high background current [15], which limits its applications in reversed-phase HPLC. Secondly, this system has high building and maintenance cost due to the use of mercury lamp as the UV light source. Thirdly, the instability of the mercury lamp can commonly distort analytical signals

and result in noisy response. Brown *et al.* reported a photoelectrochemical detector for HPLC which was based on the TiO₂ wire electrode along a cylindrical electrochemical cell [16]. It could detect a variety of organic compounds including amines, aromatic alcohols, hydroquinones, aldehydes and furans, but could not sensitively detect sugars, aliphatic ketones and aliphatic esters due to the insufficient power of the TiO₂ electrode [16].

In this work, a photoelectrochemical detector (PECD) was developed to determine organic compounds universally for FIA and HPLC systems. This is based on the photoelectrocatalytic oxidation reaction of organic compounds at the TiO₂ nanostructured photoanode (see Eq. 1). A low cost, long-life and small UV-LED was used to provide UV illumination instead of expensive, instable and high running cost xenon lamp or mercury lamp [17-19]. To optimize the analytical performance of the detector, the effects of important experimental parameters such as applied potentials, light intensity, flow rate and injection volume, on the analytical signals were systematically investigated using pure organic compound in the FIA system. The analytical principle of this universal detector was demonstrated by measuring various types of organic compounds, and the analytical performance of the FIA-PECD was evaluated under the optimized experimental conditions. To illustrate the advantage of the PECD over the conventional HPLC detector (e.g. UV-Vis detector), the PECD was coupled with a HPLC system (i.e., HPLC-PECD) and used to determine the sugars separated by the HPLC reverse phase column.

2. Experimental

2.1 Chemicals and materials

The indium tin oxide (ITO) conducting glass slides ($8 \text{ } \Omega/\text{square}$) were supplied by Delta Technologies Ltd. Titanium butoxide (97%), nitric acid, isopropanol, carbowax 20 M, glucose, sucrose, fructose, tryptophan, glycine, threonine, propionic acid, butyric acid, maleic acid, oxalic acid, phthalic acid, sodium nitrate were purchased from Aldrich without further treatment prior to use. All other chemicals were of analytical grade and purchased from Aldrich unless otherwise stated. High-purity deionized water (Millipore Corp., $18 \text{ M}\Omega\cdot\text{cm}$) was used in the preparation of all solutions.

2.2 Preparation of TiO_2 colloid and TiO_2 photoanodes

The TiO_2 colloid was synthesized by the hydrolysis of titanium butoxide [20]. Briefly, 25 mL titanium butoxide with 8 mL isopropanol was added dropwise to 0.1 M nitric acid solution under vigorous stirring at room temperature. The slurry was kept in a water bath at $80 \text{ }^\circ\text{C}$, stirred and peptized for 10 h. The resultant colloid was hydrothermally treated at $200 \text{ }^\circ\text{C}$ for 12 h. The TiO_2 dry weight concentration of the colloid was adjusted to 6% (w/w) with water. Carbowax (1.8%, w/w) was added as a binder into the resultant colloid. The ITO glass slides were washed with acetone and then Milli-Q water to assure the cleanness. The TiO_2 colloid was dip-coated onto the ITO substrates ($15 \times 40 \text{ mm}$), dried in ambient environment and annealed at $450 \text{ }^\circ\text{C}$ for 0.5 h. After cooling, the substrates were dip-coated again, dried and annealed at $700 \text{ }^\circ\text{C}$ for 2 h.

2.3 Apparatus and methods

The PECD was a three-electrode thin layer cell with a quartz window for UV illumination (see Fig. 1). The TiO_2 photoanode, a saturated Ag/AgCl electrode and a

platinum mesh were used as the working electrode, reference electrode and counter electrode, respectively. The flow path and the photoelectrochemical reaction zone were confined by a spacer (see Fig. 1). The thickness of the spacer was 0.1 mm, and the diameter of the quartz lens was 5 mm. CS300 Electrochemical Workstation (Potentiostat CV-27 from Bioanalysis System, USA) coupled to a computer (DCNE, Dell Inc.) was used for application of potential bias and recording potential and current signals. Illumination was carried out using UV-LED (NCCU033, Nichia Corporation). The output UV light intensity was measured at 365 nm wavelength using a UV irradiance meter (UV-A Instruments of Beijing Normal University).

The HPLC system consisted of a Model LC1120 HPLC pump (GBC, Australia) and a Model 7725i injector (Rheodyne, USA). HPLC mobile phase (i.e. water) was degassed and filtered before use with 0.45 μm $\times$ 47 mm Nylon 66 membranes (Supelco, USA) and a solvent filtration kit (Synthware). The samples were degassed before injection. The sample was injected into a sample loop (20 μL) by a 100 μL Unimetrics syringe (Unimetrics, USA). The sample was filtered prior to injection with a 0.45- μm Millipore disposable filter (Millipore Corp., USA). The HPLC column utilized in this study was a Develosil 5 μ RP-Aqueous C30 250 $\times$ 4.6 mm i.d. stainless steel column (Phenomenex, USA) with a 10 $\times$ 4.0 mm i.d. guard column. In comparison of the analytical performance, a UV-Vis detector LC 1200 (GBC, Australia) was used.

In order to minimize the electric resistance of the thin layer cell, a NaNO_3 solution was used as supporting electrolyte at the thin layer photoelectrochemical reaction zone. In the FIA system, a 2.0 M NaNO_3 solution was used as the carrier and for preparing samples. For HPLC analysis, the solution eluted from the column was

mixed with 4.0 M NaNO₃ solution in a reaction coil before reaching the photoelectrochemical reaction zone.

(Fig. 1)

3. Results and discussion

3.1 Analytical principle

In this study, the photocurrent generated at the TiO₂ photoanode was measured at +0.3 V vs Ag/AgCl by the electrochemical workstation. When the UV-LED was not switched on, in the presence or absence of organic compounds, the electrochemical current was almost zero. This is because the photocatalytic oxidation of organic compounds (i.e., Eq. 1) and water was not activated.

When the UV-LED was switched on, the TiO₂ photoanode was under the constant illumination of 18 mW/cm² UV light of 365 nm. A constant photocurrent (i_{blank}) of ca. 15 μ A was observed for the blank solution (see Fig. 2). i_{blank} is resulted from the photoelectrocatalytic oxidation of water. When the sample containing organic compounds was injected and flowed through the thin layer cell, a typical chromatographic peak was observed (see Fig. 2). The current (i.e., i_{sample}) consists of two parts, one is the photoelectrocatalytic oxidation of water (i.e., the i_{blank}), and the other is the photoelectrocatalytic oxidation of organic compounds (i.e., i_{net}). Because the concentration of water is constant, the i_{blank} can be considered constant. i_{net} is therefore can be calculated by subtracting i_{blank} from i_{sample} , i.e.,

$$i_{net} = i_{sample} - i_{blank} \quad (2)$$

The charge (Q), generated from the oxidation of the organics, can be obtained by integration of i_{net} with time (see the shaded area in Fig. 2), i.e.,

$$Q = \int i_{net} dt \quad (3)$$

If the injected organic compound is completely mineralized according to Eq. 1, the theoretical charge ($Q_{theoretical}$) can be calculated using Faraday's law, i.e.,

$$Q_{theoretical} = nFVC \quad (4)$$

where n , F , V , and C are oxidation number, Faraday constant, reactor cell volume and molar concentration of the injected sample, respectively.

Because the sample solution flows through the thin layer cell continuously during the determination process, it can be expected that the organic compounds in the solution can be partially oxidized. The oxidation percentage (α) can be defined by Eq. 5, where Q is the amount of electrons captured during the detection process, and $Q_{theoretical}$ is the theoretical charge required for the complete oxidation of the injected sample.

$$\alpha = Q / Q_{theoretical} \quad (5)$$

The relationship between measured charge Q and analyte concentration C can be represented by Eq. 6 which was obtained by combining Eqs. 4 and Eq. 5.

$$Q = \alpha \cdot Q_{theoretical} = \alpha \cdot nFVC = kC \quad (6)$$

During the FIA and HPLC analysis, if the light intensity, applied potential, flow rate and injection volume are well controlled, α can be considered as a constant in a certain concentration range. If these conditions are achieved, the Q will be directly proportional to C as indicated in Eq. 6.

3.2. Optimization of the PECD

In the optimization experiments, the PECD was connected with a simple FIA system including a peristaltic pump and injector, which formed a FIA-PECD system.

3.2.1 Effect of potential bias

The recombination between photogenerated electrons and holes in semiconductor particles is one of major limiting factors for the photocatalytic oxidation process [21,

22]. If the photogenerated electrons are drawn from the semiconductor valence band, the efficiency of oxidation (i.e. reaction with holes) at the semiconductor-electrolyte interface will be improved and the sensitivity of the PECD will be improved as well [23]. The optimization of potential bias can improve the oxidation efficiency and ensure the maximum capture of photoelectron. The latter issue is essential for the detections since the analytical signal (Q) depends on the amount of electrons captured [14].

Fig. 3 shows the effect of applied potential bias on the measured charge Q . Q increased with the applied potential and then levelled off when the applied potential was over +0.1V. Within the applied potential range of -0.3 V to +0.1 V, the analytical responses increased because the increased applied potential was beneficial to the separation of photogenerated holes and electrons and the photoelectron removal process was the rate-limiting step in the photoelectrocatalytic oxidation process [14, 24, 25]. When the applied potential was more positive than +0.1 V vs Ag/AgCl, the photoelectron removal process was no longer the limiting step. Instead, the rate-limiting step in the photocatalytic oxidation process was the interfacial reactions [14], and the maximum electron capture was obtained, consequently, the amount of the captured electrons was insensitive to the applied potential. Therefore, in order to capture maximum electrons in the detections of different organic compounds while avoiding electrochemical reactions, the applied potential bias of +0.3 V vs Ag/AgCl was selected for the rest experiments.

(Fig. 3)

3.2.2 Effect of light intensity

Fig. 4 displays the effect of UV light intensity on the Q values. When the light intensity was less than 18 mW/cm^2 , there appeared to be a linear increase of Q with increased light intensity. This can be explained by the fact that at low light intensity, the increase of light intensity enhanced the production of photo holes and therefore oxidation percentage. In other words, higher ratio of organic compound was oxidized and subsequently led to higher Q value due to the increased light intensity. When the light intensity was over 18 mW/cm^2 , the Q value was relatively saturated. When the light intensity increased and exceeded to a threshold value (in this case 18 mW/cm^2), the sufficient supply of photoholes caused the depletion of the organics so much that the mass transport of the organics from the solution to the TiO_2 surface became an limiting factor. Therefore, further increases in light intensity did not produce obvious enhancement in the analytical responses [16]. Furthermore, too high intensity of UV light may produce air bubbles via the water splitting reaction, which will affect the analytical signal seriously. Therefore, the light intensity of 18 mW/cm^2 was selected in the rest experiments.

(Fig. 4)

3.2.3 Effect of flow rate

Flow rate plays an important role on the sensitivity of the PECED. The residence time of the sample at the photoelectrochemical zone changes upon the variation of the flow rate [26, 27]. Fig. 5a shows the Q - C relationships obtained under different flow rates. All the Q - C relationships in the tested flow rate range were linear, i.e., the Q values were directly proportional to the glucose concentrations C at a constant flow rate. Figure 5b indicates that the oxidation percentage was constant if the flow rate was controlled constant. This validates the analytical principle of the proposed analytical

method (Eq. (6)). Figure 5a also shows that the slopes of the Q - C calibration curves increased with the reduced flow rates. In other words, slow flow rates were in favour of high sensitivity. Slower flow rate led to longer contact time for the organics and TiO_2 ; therefore, higher oxidation percentage can be expected (see Figure 5b). Figure 5b shows that, for the samples with the same glucose concentration, a faster flow rate resulted in a lower oxidation percentage. In order to enhance the sensitivity of the detector, a slower flow rate was therefore preferred in the FIA system. However, too slow flow will lead to the problem of small sample throughout and peak-widening effect. Herein, the flow rate of 0.3 mL/min was selected as the optimum flow rate for the experiments in the FIA-PECD system.

(Fig. 5a and 5b)

3.2.4 Effect of injection volume

The dependence of the Q on the sample injection volume is shown in Fig. 6, which depicts the Q - C relationships for the injection volumes of 14, 64, 80 and 100 μL . For all the injection volumes, all the Q - C relationships were linear. It can be also seen that the slopes of the Q - C calibration curves in Fig. 6 became larger as the injection volume increased. It means that an augmentation of injection volume resulted in a higher sensitivity. That is because that a larger injection volume under a constant flow rate led to a longer contact between the organic compound and the TiO_2 surface, and hence a larger amount of organics was oxidized, then a higher Q was obtained. All these observation validates the detection principle regarding the sample volume (i.e., Eq. 6). It is therefore expected that the increase of the injection volume can boost the sensitivity of the PECD. However, a large injection volume may exceed the linear range of PECD and may be also out of the separation capacity of the HPLC column,

especially when the sample contains high concentration of organics. If the injection amount of organics is too large for the PECD, the oxidation percentage (α) will decrease and consequently the Eq. 6 is no longer valid. In other words, the obtained Q will not be proportional to C . In view of the aforementioned factors of the injection volume, relatively small injection volumes of 14 and 20 μL was selected for the experiments in the FIA-PECD and HPLC-PECD systems, respectively.

(Fig. 6)

3.3 The overall performance of the FIA-PECD

In order to demonstrate the PECD can be used to detect various types of organic compounds universally, the performance of the PECD was evaluated by testing different classes of organic compounds in the FIA system under the above optimized experimental conditions. The tested organic compounds included sugars, amino acids, straight chain carboxylic acids, aliphatic alcohol, and aromatic carboxylic acid (see Fig. 7). Figure 7 shows that the linear relationships were obtained between the measured charge Q and the molar concentration C for all the tested organic compounds. This validates the Eq. 6 where the Q is directly proportional to the molar concentration for different organic compounds, which suggests that this PECD is capable of being a universal detector for a wide spectrum of organic compounds.

(Fig. 7)

Under the optimized conditions, glucose and sucrose were used as the representative organic compounds to evaluate the analytical performance of the PECD because they are not commonly detected by the most often-used HPLC detector (i.e. UV-Vis detector). Fig. 8 displays the typical well-defined and reproducible analytical signals

for the injections of the samples containing 100, 300 and 500 μM glucose. The relative standard deviations (RSD%) of six replicate injections of 100 μM glucose and sucrose were 3.20% and 3.23%, respectively. The linear ranges for determination of glucose and sucrose were 25-600 μM and 25-500 μM , respectively, with the detection limit of 10 μM for both sugars.

(Fig. 8)

3.4 Determination of sugars with the HPLC-PECD system

The PECD was introduced for the determination of sugars to demonstrate its feasibility and compatibility with HPLC system. According to the results from the FIA-PECD system makes the PECD to be the detector for HPLC possible, i.e., HPLC-PECD.

Most of the experimental conditions from the FIA-PECD system can be employed directly to the HPLC-PECD system, e.g., the applied potential bias and the light intensity. Some of the experimental conditions, such as flow rate need to be optimized specially for HPLC system. In particular, a flow rate of 1.1 mL/min for the 4.0 M NaNO_3 supporting electrolyte used in the HPLC-PECD was faster than that of 0.3 mL/min in the FIA-PECD system. It was observed that the photocurrent was lower and a lot noisier at a slow flow rate (e.g. 0.3 mL/min) than that at a faster flow rate (e.g. 1.1 mL/min) in the HPLC-PECD system. This might be due to the advantages brought by the fast flow rate. The faster flow rate is beneficial for better mixing effect for the HPLC eluted solution and 4M NaNO_3 supporting electrolyte in the mixing coil. Also the fast flow rate provides higher pressure within the PECD and therefore better contact for the solution and the TiO_2 surface. Consequently, more stable and higher

i_{blank} was obtained. In order to obtain better quality of the analytical signals, the flow rate of 1.1 mL/min was selected for the HPLC-PECD system.

Fig. 9 displays the typical response for sugars obtained from the HPLC-PECD system. According to the retention time analysis of the single pure compound, the retention time of glucose was shorter than that of sucrose under the same experimental conditions. Thus, for the analysis of the mixture sample in Fig. 9, the first peak was glucose while the second peak belonged to sucrose. Fig. 10 gives the calibration curves for glucose and sucrose using the PECD. It can be seen that the linear relationships between Q and C were obtained in the range of 7.5-200 mM for both glucose and sucrose. In addition, the detection limit for both glucose and sucrose was 1 mM, and the RSD% of six replicate injections of 40 mM glucose was 4.56%.

(Fig. 9 and Fig. 10)

Under the same HPLC experimental conditions, UV-Vis detector (at 190 nm) [28, 29] was used to detect the sugar mixture samples for comparison. The linear ranges for glucose and sucrose at UV-Vis detector were 7.5-60 mM and 7.5 - 40 mM for glucose and sucrose, respectively. This suggests that PECD had wider linear range than the UV-Vis detector. Moreover, the detection limits for both glucose and sucrose for the UV-Vis detector were 3 mM which were less sensitive than that of the PECD.

4. Conclusion

A low cost and efficient PECD for FIA and HPLC was developed. The analytical principle was validated by quantitative determination of a variety of organic compounds including sugars, amino acids, straight chain carboxylic acids, aliphatic alcohol, and aromatic carboxylic acid using FIA. The PECD was successfully coupled

with the HPLC for determining sugars. Compared with the UV-Vis detection method, PECD achieved a higher sensitivity and larger linear range for determination of glucose and sucrose. With the further optimization of the cell design and improvement of the TiO₂ photoanode, the performance of the PECD can be improved and it can be expected that the PECD can be commercially available in the near future.

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References

- [1] B. Zhang, X. Li, B. Yan, Advances in HPLC detection - towards universal detection, *Anal. Bioanal. Chem.* 390 (2008) 299-301.
- [2] T.A. Ivandini, B.V. Sarada, C. Terashima, T.N. Rao, D.A. Tryk, H. Ishiguro, Y. Kubota, A. Fujishima, Electrochemical detection of tricyclic antidepressant drugs by HPLC using highly boron-doped diamond electrodes, *J. Electroanal. Chem.* 521 (2002) 117-126.
- [3] T.N. Rao, B.V. Sarada, D.A. Tryk, A. Fujishima, Electroanalytical study of sulfa drugs at diamond electrodes and their determination by HPLC with amperometric detection, *J. Electroanal. Chem.* 491 (2000) 175-181.
- [4] M. Trojanowicz, *Flow injection analysis: instrumentation and applications*, 1st ed., World Scientific Publishing Co. Pte. Ltd., Singapore, 2000.
- [5] D.A. Skoog, F.J. Holler, T.A. Nieman, *Principles of instrumental analysis*, 5th ed., Thomson Learning, CA, USA, 1998.
- [6] K. Stulík, V. Pacáková, Electrochemical detection techniques in high-performance liquid chromatography, *J. Electroanal. Chem.* 129 (1981) 1-24.
- [7] A. Fujishima, K. Honda, Electrochemical photolysis of water at a semiconductor electrode, *Nature (London)* 238 (1972) 37-38.
- [8] X. Chen, S.S. Mao, Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications, *Chem. Rev.* 107 (2007) 2891-2959.
- [9] D. Mardare, N. Iftimie, D. Luca, TiO₂ thin films as sensing gas materials, *J. Non-Cryst. Solids* 354 (2008) 4396-4400.
- [10] M.-H. Seo, M. Yuasa, T. Kida, J.-S. Huh, N. Yamazoe, K. Shimano, Detection of organic gases using TiO₂ nanotube-based gas sensors, *Procedia Chem.* 1 (2009) 192-195.
- [11] M.M. Rahman, A.J.S. Ahammad, J.-H. Jin, S.J. Ahn, J.-J. Lee, A comprehensive review of glucose biosensors based on nanostructured metal-oxides, *Sensors* 10 (2010) 4855-4886.
- [12] P.-K. Shin, The pH-sensing and light-induced drift properties of titanium dioxide thin films deposited by MOCVD, *Appl. Surf. Sci.* 214 (2003) 214-221.
- [13] Z. Liu, S. Huan, J. Jiang, G. Shen, R. Yu, Molecularly imprinted TiO₂ thin film using stable ground-state complex as template as applied to selective electrochemical determination of mercury, *Talanta* 68 (2006) 1120-1125.
- [14] S. Zhang, D. Jiang, H. Zhao, Development of chemical oxygen demand on-line monitoring system based on a photoelectrochemical degradation principle, *Environ. Sci. Technol.* 40 (2006) 2363-2368.
- [15] M.A. Fox, T.P. Tien, Photoelectrochemical detector for high-pressure liquid chromatography, *Anal. Chem.* 60 (1988) 2278-2282.
- [16] G.N. Brown, J.W. Birks, C.A. Koval, Development and characterization of a titanium dioxide-based semiconductor photoelectrochemical detector, *Anal. Chem.* 64 (1992) 427-434.
- [17] R.W. Cole, J.N. Turner, Light-emitting diodes are better illumination sources for biological microscopy than conventional sources, *Microsc. Microanal.* 14 (2008) 243-250.
- [18] M. Belz, F.A. Klein, H.S. Eckhardt, K.-F. Klein, D. Dinges, K.T.V. Grattan, Optical detection techniques and light delivery with UV LEDs and optical fibres, *J. Phys.: Conf. Ser.* 85 (2007) 012034.
- [19] N.S. Kenning, B.A. Ficek, C.C. Hoppe, A.B. Scranton, Spatial and temporal evolution of the photoinitiation rate for thick polymer systems illuminated by

- polychromatic light: selection of efficient photoinitiators for LED or mercury lamps, *Polym. Int.* 57 (2008) 1134-1140.
- [20] C. Barbé, J. , F. Arendse, P. Comte, M. Jirousek, F. Lenzmann, V. Shklover, M. Grätzel, Nanocrystalline titanium oxide electrodes for photovoltaic applications, *J. Am. Ceram. Soc.* 80 (1997) 3157-3171.
 - [21] J. Lin, R. Zong, M. Zhou, Y. Zhu, Photoelectric catalytic degradation of methylene blue by C60-modified TiO₂ nanotube array, *Appl. Catal., B* 89 (2009) 425-431.
 - [22] A.L. Linsebigler, G. Lu, J.T. Yates, Photocatalysis on TiO₂ surfaces: principles, mechanisms, and selected results, *Chem. Rev.* 95 (1995) 735-758.
 - [23] K. Vinodgopal, S. Hotchandani, P.V. Kamat, Electrochemically assisted photocatalysis: titania particulate film electrodes for photocatalytic degradation of 4-chlorophenol, *J. Phys. Chem.* 97 (1993) 9040-9044.
 - [24] X. Zhao, Y. Zhu, Synergetic degradation of Rhodamine B at a porous ZnWO₄ film electrode by combined electro-oxidation and photocatalysis, *Environ. Sci. Technol.* 40 (2006) 3367-3372.
 - [25] R.J. Candal, W.A. Zeltner, M.A. Anderson, Effects of pH and applied potential on photocurrent and oxidation rate of saline solutions of formic acid in a photoelectrocatalytic reactor, *Environ. Sci. Technol.* 34 (2000) 3443-3451.
 - [26] X.-g. Hao, H.-h. Li, Z.-l. Zhang, C.-m. Fan, S.-b. Liu, Y.-p. Sun, Modeling and experimentation of a novel labyrinth bubble photoreactor for degradation of organic pollutant, *Chem. Eng. Res. Des.* 87 (2009) 1604-1611.
 - [27] R.A. Damodar, T. Swaminathan, Performance evaluation of a continuous flow immobilized rotating tube photocatalytic reactor (IRTPR) immobilized with TiO₂ catalyst for azo dye degradation, *Chem. Eng. J.* 144 (2008) 59-66.
 - [28] H. Binder, Separation of monosaccharides by high-performance liquid chromatography: comparison of ultraviolet and refractive index detection, *J. Chromatogr., A* 189 (1980) 414-420.
 - [29] P.E. Shaw, C.W.W. III, Separation of fructose, glucose and sucrose in fruit by high performance liquid chromatography using UV detection at 190 nm, *J. Sci. Food Agric.* 34 (1983) 109-112.

Figures Captions

- Fig. 1** Schematic diagram of the PECD.
- Fig. 2** The measurement of the charge, Q , generated from the oxidation of the organic compound at the PECD.
- Fig. 3** Effect of the potential bias on the measured charge of 200 μM glucose at the PECD.
- Fig. 4** Effect of UV light intensity on the measured charge of 200 μM glucose at the PECD.
- Fig. 5** (a) Effect of flow rate on the Q - C relationship; (b) Effect of flow rate on the oxidation percentage at different concentration of glucose at the PECD.
- Fig. 6** Effect of injection volume on the Q - C relationship at the PECD.
- Fig. 7** Determination of different organic compounds at the PECD.
- Fig. 8** Responses of the glucose samples (100, 300 and 500 μM) obtained from the FIA-PECD.
- Fig. 9** Typical responses of a sugar mixture obtained from the HPLC-PECD system. Mobile phase of the HPLC is water with a flow rate of 0.5 mL/min and an injection volume of 20 μL Peak 1. glucose (60 mM); Peak 2. sucrose (30 mM).
- Fig. 10** Calibration curves of the glucose and sucrose obtained from the HPLC-PECD system.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

(a)

(b)

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10