

Nanostructured TiO₂ photocatalysts for the determination of organic pollutants

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ABSTRACT

Owing to the inherent advantages of nanostructured TiO₂ photocatalysts, including high photocatalytic activity, strong oxidation power, low cost, environmental benignity and excellent stability, TiO₂ photocatalysts have recently attracted extensive attention from scientific researchers, technology developers and investors for use in sensing applications. The TiO₂ sensors can be used for lab-based analyses, on-line and on-site determination of organic pollutants in wastewater. This work reviews the application of TiO₂ nanomaterials in photocatalytic and photoelectrocatalytic monitoring of aggregative organic parameters such as total organic carbon (TOC) and chemical oxygen demand (COD), as well as individual organic compounds in aqueous solution.

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1. Introduction

Titanium dioxide (TiO₂) nanomaterials have become a dominant photocatalyst since Fujishima and Honda's pioneering work in the photoelectrocatalytic oxidation of water in 1972 [1]. This is mainly due to TiO₂ nanomaterials possessing numerous important physicochemical properties and inherent advantages. These advantages include high efficiency, strong oxidation power, low cost, environmental benignity, and excellent chemical and photochemical stability. Consequently, tremendous efforts by the science and engineering community have been devoted to the synthesis of novel TiO₂ nanomaterials [2]. A number of excellent reviews regarding environmental remediation [3], solar energy conversion [4], energy storage [5], self-cleaning surfaces [5], and medical treatment [6] have been reported. Despite a large amount of published work and some successful commercialisation of nanostructured TiO₂ sensing technologies, there are few reviews on the sensing applications of nanostructured TiO₂.

The sensing applications of TiO₂ were first demonstrated by Fox and Tien [7] who used a Ti/TiO₂ electrode to detect aniline in a high performance liquid chromatography (HPLC) system in 1988. In 1990, Matthews et al. developed a flow through photocatalytic detector for the rapid determination of total organic carbon (TOC) using a TiO₂ immobilised coil reactor [8]. In 1996, Low et al. envisaged that the use of this cheap and robust photocatalyst for environmental monitoring would be increasingly common in the

future [9]. In 2000, Kim et al. proposed for the first time to utilise the photocatalytic degradation reaction of UV illuminated TiO₂ for the determination of chemical oxygen demand (COD) [10]. COD is one of the most important water quality parameters and is widely employed to assess the total organic pollution level, especially for heavily polluted industrial wastewaters [11]. These discoveries have led to increased research efforts to develop new generation nanostructured TiO₂ photocatalyst-based analytical methods for the determination of organic pollutants, including aggregative parameters TOC, COD and individual organic compounds.

TOC is considered the most relevant or "true" parameter for the global determination of organic pollution [12]. Two standard analytical methods, i.e., high temperature combustion and photo-oxidation methods, are commonly used for the determination of TOC in aqueous solutions. Both methods achieve the complete oxidation of organic compounds to carbon dioxide, which is subsequently measured by traditional chemical techniques such as infrared spectrometry, conductivity or flame ionization detection [8]. The combustion method demands high temperatures and expensive thermal catalysts. Furthermore, it is not ideal for the accurate measurement of low TOC concentrations (less than 1 µg mL⁻¹) due to injection volume limitations (100–200 µL). In contrast, the traditional photo-oxidation method is more suitable for the determination of lower TOC concentrations since much larger sample volumes can be injected into the analytical system. However, it commonly requires the use of much shorter wavelengths (180–260 nm, typically a mercury lamp) and the addition of peroxydisulphate. Attempts to develop TOC analysers mostly aim to improve existing standard methods, i.e., the combustion [13] and persulphate methods [14].

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Analytically, the COD value can be used to represent the total of all chemically degradable organic pollutants in water and wastewaters. Conventionally, COD is determined by a standard dichromate (Cr_2O_7^-) method [11]. The method estimates the oxygen demand via chemical degradation of organic compounds by strong oxidizing agents such as dichromate. The extent of degradation is determined by the amount of electrons transferred to the chemical oxidizing agent during chemical degradation, which is indirectly quantified by measuring dichromate depletion via titration or spectrophotometry. This standard dichromate method has a number of drawbacks. Firstly, it needs expensive (e.g., Ag_2SO_4), corrosive (e.g., concentrated H_2SO_4), and highly toxic (Hg(II) and Cr(VI)) reagents, in order to achieve complete degradation [11] resulting in secondary pollution. Secondly, even under such critical conditions, the complete oxidation of organic compounds still requires a 2–4 h reflux process under high temperature and pressure. Thirdly, the sensitivity of the standard method is approximately 10 mg/L, which is inadequate for many industrial environmental monitoring applications [15]. In attempts to improve sensitivity, reduce assay time and more importantly develop on-line/on-site COD monitoring technology, many alternative oxidation methods have been investigated. Among them, microwave-assisted oxidation [16] and ultrasound-assisted oxidation [12] have been proposed to accelerate the digestion reaction time of the standard COD method. Alternative oxidation reagents such as UV- O_3 oxidation [13] and cerium(IV) sulphate [14] were reported to address the secondary pollution generated by the standard dichromate COD method. Spectrometry, combined with statistical predictions, was applied to rapidly determine the COD concentration in wastewater [17]. Electrocatalytic oxidation [18] has been extensively researched for COD determination due to its simplicity, low cost, and great potential for incorporation into on-line/on-site instruments. These methods however, are still difficult to use on-line/onsite, in that the improved standard COD methods have high equipment and working environment requirements; spectrometric estimation has insufficient accuracy due to the dependence on matrix; and the electrochemical sensors often encounter great difficulties in achieving satisfactory accuracy, reproducibility and reliability due to insufficient oxidation abilities.

The nanostructured TiO_2 photocatalyst is a promising candidate for resolving the disadvantages of the aforementioned methods. It can be used in nanoparticle suspension and immobilised forms for rapid photocatalytic degradation reactions. When the TiO_2 photocatalysts are immobilised on a conducting substrate, the degradation efficiency can be significantly improved by the application of electrical potential and achieving photoelectrocatalytic effects [19]. This work aims to review the analytical application of nanostructured TiO_2 photocatalysts for the determination of organic pollutants according to the photocatalysts form (i.e., freestanding TiO_2 nanoparticulates and immobilised TiO_2), and photocatalytic system (i.e., photocatalysis and photoelectrocatalysis). It is expected that this review will have broad implications for future analytical applications using these functional nanomaterials.

2. Photocatalysis at TiO_2 nanoparticulates

It is well established that the photocatalytic oxidation process is initiated through the photogeneration of electron/hole pairs under UV illumination (see Fig. 1). Illumination of TiO_2 with a photon whose energy is equal to or greater than the band-gap energy (i.e., $E_g = 3.2 \text{ eV}$), will lead to the promotion of an electron from the valence band (VB) to the conduction band (CB) (Eq. (1)), resulting in free photoelectrons in the conduction band (e_{cb}^-) and photoholes in the valence band (h_{vb}^+)

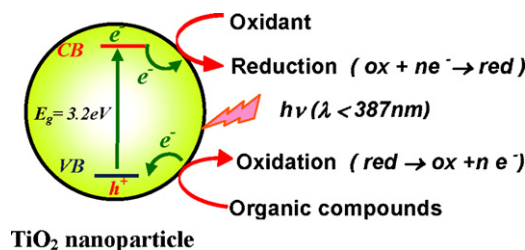
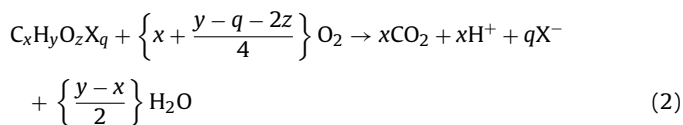


Fig. 1. Typical photocatalytic oxidation and reduction processes at a TiO_2 nanoparticle.

Owing to its powerful oxidation capability, +3.2 V generated under UV illumination at the TiO_2 surface, the photohole is able to mineralize almost all types of organic compounds in wastewaters. The overall chemical reaction equation using photocatalytic degradation is represented in Eq. (2) below [10]:



where X represents a halogen element. The oxidation number (n) in the complete oxidation process is equal to $4x + y - q - 2z$.

When the complete degradation of organic compounds is achieved as indicated in Eq. (2), O_2 and CO_2 are stoichiometrically consumed and produced, respectively. The amount of CO_2 produced can be used to detect TOC while the amount O_2 consumed can be used to determine COD.

2.1. Photocatalytic determination of total organic carbon (PcTOC) using TiO_2 nanoparticulates

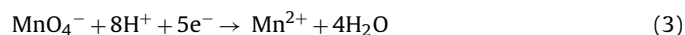
When the photocatalytic reaction is carried out directly in TiO_2 colloidal particle suspensions, the mass transport of organics from the bulk solution to the TiO_2 photocatalyst surface is greatly enhanced [20], which improves oxidation efficiency and reduces analytical time. Due to the high efficiency and low TiO_2 consumption in analytical processes, low cost, and nontoxic nature of TiO_2 , freestanding nanoparticulated TiO_2 catalysts, such as P25 TiO_2 powder, can be directly used as a reagent without being recycled in analytical processes. In PcTOC measurements, the amount of CO_2 produced is used to quantify the TOC value of the sample. Visco et al. reported a TOC sensing system that combined the photocatalytic oxidation detection principle with a CO_2 gas permeable membrane electrode as the CO_2 detector [21]. A series of online TOC analysers were commercialised based on this TOC detection principle by SGE International Pty Ltd (www.anatoc.com). In the analyses, the individual sample is mixed with a certain amount of nanocrystalline TiO_2 slurry and the CO_2 produced is analysed using a dual wavelength Non-Dispersive Infra-Red (NDIR) detector. These methods provide reliable analyses in the range of 50 ppb to 5000 ppm. In terms of the TiO_2 photocatalyst consumption, the cost per sample is negligible. Finally, the use of this analytical principle eliminates the hazardous chemicals and clumsy, expensive compressed gases used in traditional combustion based analytical methods [22].

2.2. Photocatalytic determination of chemical oxygen demand (PcCOD) using TiO_2 nanoparticulates

Similar to the PcTOC analysis, PcCOD measurements have been achieved in TiO_2 slurry systems. In the photocatalytic mineralization (Eq. (2)), oxygen acts as an electron acceptor during the mineralization reaction (see Fig. 1). As a reactant, O_2 consumed

in the reaction corresponds to the consumption of organic compounds, and therefore O_2 consumption is proportional to COD concentration. COD concentration can be determined by monitoring changes in O_2 concentration in TiO_2 nanoparticle suspended sample solutions using a disposable oxygen sensor [23]. The preliminary results suggested that, under UV irradiation, the decrease in dissolved O_2 concentration of the reaction media correlated well with the COD concentration of the sample using artificial and real water samples from lakes in Japan. The response time of the sensor was approximately 3 ± 4 min with a detection limit of 0.118 ppm. The linear range of the proposed method was between 1 and 10 ppm of COD.

A narrow linear range is the major and common drawback of the above PcCOD method. This can be attributed to the low oxidation percentage of the photocatalytic oxidation process, which possibly stems from insufficient photocatalytic activity, light intensity, and low O_2 solubility in the water solution (e.g., less than 8 ppm at 25 °C). Inadequate sensitivity of the oxygen probe may also play a role in the narrow linear range. These problems were addressed by replacing the O_2 electron acceptor with more oxidative electron acceptors, such as permanganate (MnO_4^-) [24] and cerium ions (Ce^{4+}) [25,26]. These electron acceptors can capture photoelectrons at the conduction band more effectively (see Eqs. (3) and (4)) leading to improved analytical performance as indicated in Table 1.



3. Photocatalysis at immobilised TiO_2

TiO_2 can be immobilised on many kinds of substrates, including titanium substrates, polymer substrates (e.g., polystyrene and polyethylene) stainless steel glazed ceramic tiles, and quartz for photocatalytic degradation reactions (Eq. (2)). The immobilisation of TiO_2 on the photochemical reactors removes the need to separate and recycle TiO_2 nanoparticles after the degradation reactions.

3.1. Photocatalytic determination of total organic carbon (PcTOC) using immobilised TiO_2

TOC can be determined using immobilised TiO_2 photocatalysts (see Eq. (2)). Matthews et al. pioneered the development of TOC online analysers using a TiO_2 immobilised coil reactor coupled with a conductivity meter as the CO_2 detector [8]. In their work, the TiO_2 photocatalyst was coated on the inside of a 7-m long borosilicate glass tubing spiral. The time for 99% oxidation of organic solutes to CO_2 was ca. 10 min or less. This method was suitable for the analysis of water containing 0.1–30 mg/L organic carbon and sample volumes of 1–40 mL. The main advantages are its simplicity, low cost, no need for TiO_2 addition and ease of operation. Such analytical methods have also been commercialised by Analyticon Instruments Corporation (www.analyticon.com).

3.2. Photocatalytic determination of chemical oxygen demand (PcCOD) using immobilised TiO_2

Using the photocatalytic reaction (Eq. (2)), a photocatalytic COD sensor was developed by combining TiO_2 beads photochemical column and an oxygen electrode [27]. The O_2 change resulting from the photocatalytic degradation of organic compounds was monitored by the oxygen electrode. This sensor responded linearly to the standard COD concentration of artificially treated wastewater in the range of 0.12–8 ppm. A complete analysis, including sampling and washing, took ca. 10 min. The sensor was stable for over 15 days and has successfully been utilised to determine COD in lake samples.

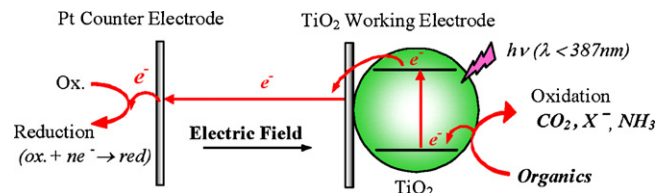
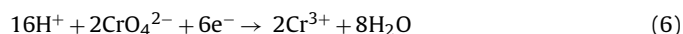
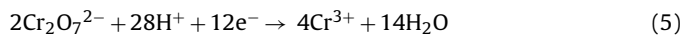


Fig. 2. A schematic diagram of the photoelectrocatalytic oxidation processes at a TiO_2 electrode and the simultaneous reduction at a Pt counter electrode.

In order to achieve continuous flow injection analysis of COD, dual oxygen electrodes [28] were used to monitor the O_2 concentration before and after the photocatalytic oxidation reaction. The O_2 concentration changes caused by the photocatalytic oxidation were strongly correlated with the standard COD values. The method has a detection limit of 1 ppm COD but has a very narrow linear range (ca. 10 ppm COD).

Karube's group advanced this concept by immobilising TiO_2 fine particles on a PTFE membrane on the tip of an oxygen probe [10]. These prepared COD sensors were used to detect COD values of artificial wastewater and real water samples from lakes in Japan. This method had a slightly increased linear range of ca. 20 ppm COD and was considered reliable in that the measured parameter was close to the theoretical COD value. The sensor had a detection limit of 0.25 ppm COD and showed long-term stability (RSD 5.7%, 30 days).

Overall, low O_2 solubility in water solutions continues to be the main cause of the narrow linear range of TiO_2 photocatalytic sensors. In order to address this problem, highly soluble oxidative electron acceptors such as dichromate ions ($Cr_2O_7^{2-}$, see Eqs. (5) and (6)) [29,30], permanganate ions (see Eq. (3)) [31,32] were incorporated into the photocatalytic oxidation system, leading to an extended linear range (Table 2).

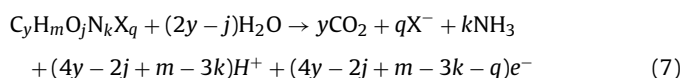


4. Photoelectrocatalysis at immobilised TiO_2

The immobilisation of nanostructured TiO_2 on conducting substrates results in nanostructured TiO_2 electrodes, which facilitates the application of potential bias and the measurement of electron transfer at the electrode surface. In comparison with the traditional photocatalytic system, the application of an electric field helps the separation of the electron and photohole at the TiO_2 surface and subsequently improves the photocatalytic oxidation performance, namely photoelectrocatalysis [33–37].

In the TiO_2 photoelectrocatalytic reaction system, the TiO_2 electrode is used as the working electrode, i.e., the photoanode. By applying an appropriate potential bias (i.e., electric field) to the working electrode (see Fig. 2), it becomes easier for the photoelectron to be transferred to the external circuit, rather than to the adsorbed O_2 [33]. The photoelectrons are subsequently forced to pass into the external circuit and delivered to the auxiliary electrode, where the reduction reaction takes place.

The general equation for mineralization at the TiO_2 photoanode can be summarised as follows [33]:



where the elements are represented by their atomic symbols and X represents a halogen atom. The stoichiometric ratio of elements in the organic compound is represented by the coefficients y, m, j, k and q. The electron transfer number (the same as oxidation number, n) in the complete oxidation process is equal to $4y - 2j + m - 3k - q$.

Table 1
Summary of the analytical applications of photocatalysis using TiO₂ nanoparticles.

Detection principle	Analysis time (min)	Limit of detection (mg/L)	Linear range (mg/L)	Catalyst	Refs
PcTOC	60	0.05	0.05–5000	TiO ₂ nano-particles	[21]
PcCOD, oxygen electrode	3 ± 4	0.118	1–10	TiO ₂ nano-particles	[23]
PcCOD, TiO ₂ –KMnO ₄	10	0.02	0.1–280	Fluorinated TiO ₂ nano-particles	[24]
PcCOD, TiO ₂ –cerium ions	2	0.4	1.0–12	P25 TiO ₂ nano-particles	[25]
PcCOD, TiO ₂ –cerium ions	n/a	0.9	0–100	P25 TiO ₂ nano-particles	[26]

Table 2
Summary of the analytical applications of the photocatalysis using immobilised TiO₂ systems.

Detection principle	Analysis time (min)	Limit of detection (mg/L)	Linear range (mg/L)	Catalyst	Refs
PcTOC conductivity detector	10	0.1	0.1–30	Immobilised TiO ₂ on coil reactor	[8]
PcCOD, oxygen electrode	3–5	0.25	0–20	Immobilised TiO ₂ on PTFE membrane	[10]
PcCOD oxygen electrode	10	0.12	0.12–8	TiO ₂ beads column	[27]
PcCOD dual oxygen electrodes	n/a	1	10	TiO ₂ beads column	[28]
PcCOD, TiO ₂ –dichromate	10	n/a	50–500	P25 TiO ₂ immobilised quartz reactor	[29]
PcCOD, TiO ₂ –dichromate	n/a	20	20–500	Nanocrystalline TiO ₂ film	[30]
PcCOD, TiO ₂ –KMnO ₄	10	n/a	0–260	Rotating TiO ₂ /Ti	[31]
PcCOD, TiO ₂ –KMnO ₄	20	0.1	0.3–10	ZnO/TiO ₂ nanocomposite film	[32]

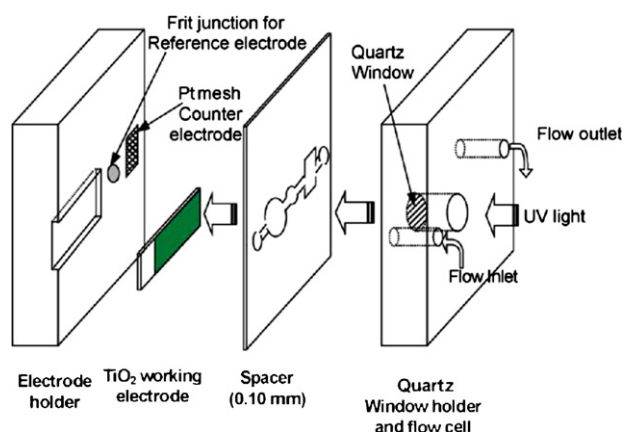


Fig. 3. Schematic diagram of the design of a thin-layer photoelectrochemical cell [33].

In the photoelectrocatalysis system, the photocurrent (or charge) can be monitored and provides a direct measure of the photo-oxidation reaction rate and the extent of oxidative degradation [19,35,38], which can be used as an analytical signal [19,34,35]. The determination of COD values based on the photoelectrocatalytic reaction (Eq. (7)) has been defined as PcCOD in the literature [33,34,39–43].

4.1. Photoelectrocatalytic determination of chemical oxygen demand (PcCOD)

Based on the mechanism of photoelectrocatalysis using nanocrystalline TiO₂ (Eq. (7)), Zhao et al. designed and developed the first generation PcCOD technology in a thin-layer photoelectrochemical cell based on the exhaustive degradation mode and using Xenon light as the UV light source (Fig. 3) [33,34]. The PcCOD technology however, have been further developed and can be classified into three categories according to the manner of detection: (a) absolute PcCOD that is based on exhaustive oxidation in stop-flow thin-layer cells [34]; (b) online PcCOD that is based on partial oxidation in continuous on-line thin layer cells [39]; and (c) PcCOD probes based on the in situ photoelectrocatalytic oxidation current [41].

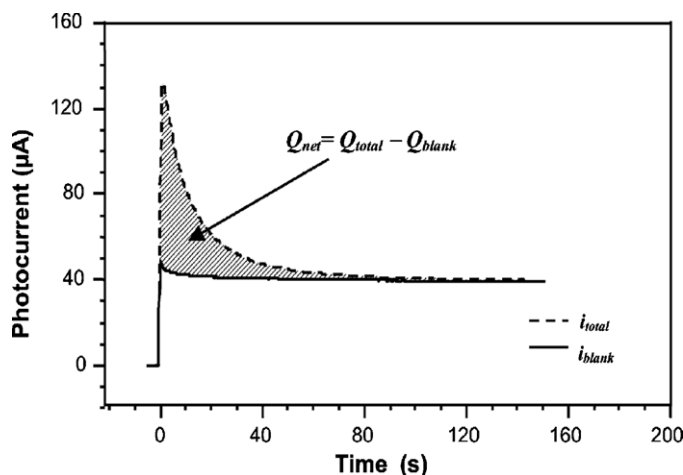


Fig. 4. Photocurrent responses of a blank solution (solid line) and a sample containing organic compounds (dashed line) in photoelectrochemical thin-layer cell [33].

4.1.1. Absolute PcCOD

In the absolute PcCOD method [33,34], the photoelectrocatalytic reaction at a TiO₂ photoanode is carried out in a thin-layer photoelectrochemical cell. The photoelectrocatalytic oxidation process is analogous to the digestion process in conventional COD analyses. The advantages of using the thin-layer photoelectrochemical cell are threefold: firstly, it can maximise the ratio of the photoanode area to solution volume, secondly, it can enhance the mass transport of the organic compounds to the photoanode surface, and thirdly, thin liquid layers can raise the light intensity illuminated on the photoanode surface by reducing the UV absorption by the sample media. The short analysis time of the PcCOD method is attributed to the use of thin layer cells.

A set of photocurrent responses at a TiO₂ photoanode in a thin-layer cell under UV illumination is shown in Fig. 4. The net charge Q_{net} (the shaded area in Fig. 4), generated from the photoelectrocatalytic oxidation of organics, can be obtained by subtracting Q_{blank} from Q_{total} . Faraday's law can be used to quantify the concentration by measuring the charge (see Eq. (8)) [34]:

$$Q_{net} = \int i_{net} dt = nFVC \quad (8)$$

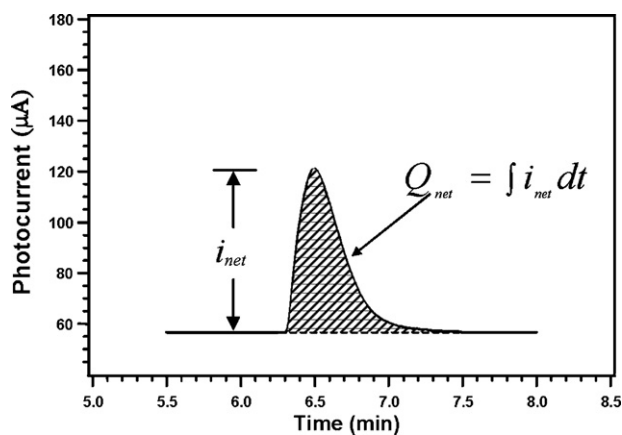


Fig. 5. Typical photocurrent responses in a continuous-flow online PeCOD measurement. The shaded area indicates the charge (i.e., Q_{net}), while the difference between the peak current and baseline background current is the net current (i_{net}).

where i_{net} is the net photocurrent generated from the photoelectrocatalytic oxidation of organics; F and V are the Faraday constant and the sample volume, respectively; C is the molar concentration of organics. For a given TiO_2 photoelectrocatalytic reaction system, the net charge value should increase linearly with organic concentration according to Eq. (8), which has been experimentally demonstrated [34].

Q_{net} is a direct measure of the total amount of transferred electrons that result from the complete degradation of all compounds in the sample. Since one O_2 molecule is equivalent to 4 transferred electrons, the measured Q_{net} value can be easily converted into an equivalent O_2 concentration (or oxygen demand). The equivalent COD value can therefore be represented as:

$$\text{COD (mg/LO}_2) = \frac{Q_{net}}{4FV} \times 32,000 \quad (9)$$

Based on this analytical principle, the PeCOD method is a direct and absolute method that requires no calibration. The effects of important experimental conditions such as light intensity, applied potential bias, supporting electrolyte concentration and oxygen concentration on analytical performance have been investigated and optimum experimental conditions obtained. An analytical linear range of 0–300 ppm COD with a practical detection limit of 0.2 ppm COD has been achieved [44]. The results demonstrate that the COD values measured using the PeCOD and the standard methods were in complete agreement.

4.1.2. Online PeCOD

When the thin-layer PeCOD cell is incorporated with continuous FIA, the COD value can be measured online in two quantification manners, i.e., coulometric and amperometric methods. A typical photocurrent–time profile obtained in a continuous-flow online PeCOD measurement is shown in Fig. 5. The flat baseline (blank) photocurrent ($i_{baseline}$) observed from the carrier solution originates from water oxidation, while the peak response observed from the sample injection is the total current of two components, one originating from photoelectrocatalytic oxidation of organics (i_{net}) and the other from water oxidation (the blank photocurrent).

In the coulometric online method, the net charge, Q_{net} , originating from the oxidation of organic compounds can be obtained by the integration of the peak area between the total current (solid line) and baseline current (dash line), i.e., the shaded area indicated in Fig. 5. Eq. (10) can be used to directly quantify the COD value of a sample once Q_{net} is obtained since k , the slope, can be obtained by

calibration curve methods or standard addition calibration methods.

$$Q_{net} = k[\text{COD}] \quad (10)$$

In the amperometric online method, the net current, i_{net} is obtained by subtracting the background current from the peak current (Fig. 5). i_{net} is proportional to the concentration of the organic compounds and therefore COD concentration (see Eq. (11)):

$$i_{net} \propto [\text{COD}] \quad (11)$$

Zhang et al. developed the first coulometric online PeCOD analyser in a continuous flow mode [39]. In this method, the thin-layer photoelectrochemical detector based on photoelectrocatalytic oxidation can be considered a consumption type detector since part of the organic compounds in the sample are oxidized (i.e., consumed) at the TiO_2 photoanode. The thin-layer configuration is essential for achieving a large (electrode area)/(solution volume) ratio that ensures the rapid degradation of an injected sample. To assure Eq. (10), the organic compounds need to be indiscriminately oxidized by the high performance nanostructured TiO_2 photoanodes. Using the mixed-phase TiO_2 electrode, the coulometric online method was successfully applied to determine the COD of real samples from various industrial wastewaters [39]. The COD value of real samples determined by this method corresponded well with the standard dichromate method. An assay time of 1–5 min per sample could be readily achieved while a practical detection limit of 1 mg/L COD with a linear range of 1–100 mg/L was achieved under optimum conditions.

Chen et al. reported the amperometric online PeCOD method that achieved COD determination [45]. In their work, the TiO_2 photoanode was constructed by immobilising TiO_2 thin film on SnO_2/Sb glass and incorporating it into a continuous flow photoelectrochemical detector. Photocurrent was obtained and recorded under a positive bias potential of 0.4 V (vs. Ag/AgCl) and UV illumination of a 12 W quartz UV lamp. Under optimum conditions, the net current was calculated and a linear range of 0.5–235 mg/L COD of D-glucose was obtained. The COD values obtained from the amperometric online analysis of artificial wastewater corresponded well with those from the conventional dichromate method. Similarly, Jin and his co-authors used laser-assisted techniques to prepare Ti/ TiO_2 photoanodes [46] for online PeCOD measurements. The TiO_2 film consists of anatase TiO_2 nanoparticles and exhibits a superior photocatalytic activity. A linear range of 50–1000 mg/L and a detection limit of 15 mg/L ($S/N = 3$) has been realised using the amperometric online method.

4.1.3. PeCOD probe

PeCOD probes [41] were developed using a nanostructured mixed-phase TiO_2 photoanode (see Fig. 6). A UV-LED light source and a USB microelectrochemical station (see Fig. 7) were powered and controlled by a laptop computer, making the probe portable for onsite COD analyses. A set of photocurrent–time profiles obtained in the presence and absence of organic compounds at the TiO_2 photoanode in the bulk cell under UV illumination are presented in Fig. 7. The current increased rapidly and then decreased to a steady value. For the blank sample without any organic compounds, the steady photocurrent (i_{blank}) was generated from the oxidation of water, while the total photocurrent of steady state (i_{total}) for a sample containing organics resulted from the oxidation of water and organic compounds. Therefore, the net steady state photocurrent (i_{net}), generated from the oxidation of organics, can be obtained by subtracting the blank photocurrent (i_{blank}) from the total photocurrent (i_{total}) (see Eq. (12)).

$$i_{net} = i_{total} - i_{blank} \quad (12)$$

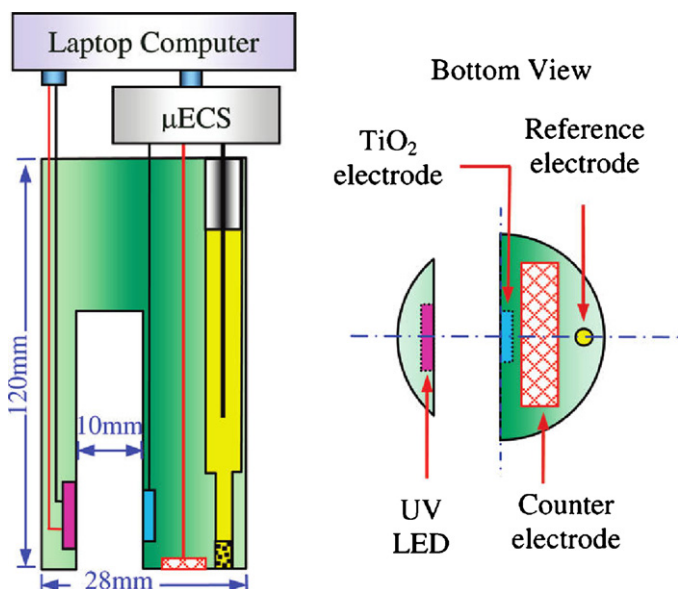


Fig. 6. Schematic diagram of the photoelectrochemical setup and PeCOD probe [41].

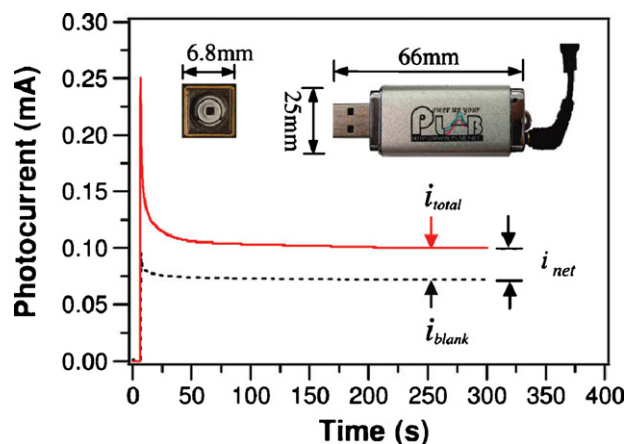


Fig. 7. Typical photocurrent response of a 0.1 M NaNO_3 blank solution (i_{blank} , dashed line) and a 0.1 M NaNO_3 solution containing organic compounds (i_{total} , solid line). i_{net} is the difference between the two steady state currents. The insert shows the images and dimensions of the UV-LED (left) and the μECS microelectrochemical system (right) [41].

According to theoretical analyses and experimental verification under optimised conditions, it can be concluded that i_{net} is directly proportional to COD concentration. A practical detection limit of 0.2 mg/L of O_2 and a linear range of 0–120 mg/L of O_2 have been achieved. The analytical method using the portable PeCOD probe has the advantages of being rapid, low cost, robust, user friendly and environmentally friendly. It has been successfully applied to determine COD values of synthetic and real samples from various industries with excellent agreement with the standard method.

4.2. Advances in photoanodes for sensing

In order to further improve the analytical performance and application range of TiO_2 photoanodes, numerous approaches have been used to fabricate new generation TiO_2 photoanodes. The applications of various photoanodes for the PeCOD application are summarised in Table 3.

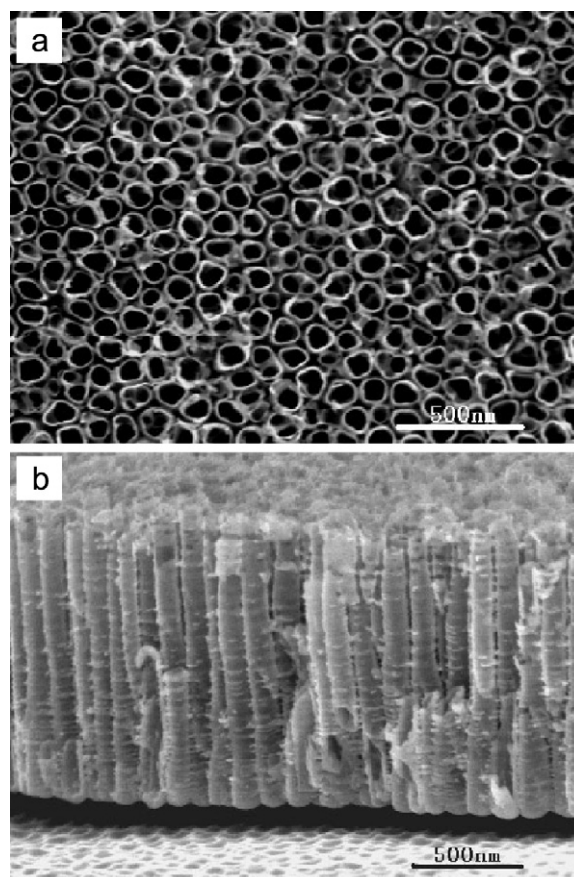


Fig. 8. The SEM morphology (a) and cross-section (b) of a typical TiO_2 nanotube array used for the PeCOD sensing [43].

4.2.1. TiO_2 nanotube arrays photoanodes

Zhou's group fabricated highly ordered TiO_2 nanotube arrays (TNAs) (see Fig. 8) for the absolute PeCOD detector [42,43]. High photocatalytic activity was observed for the TNA photoanodes due to the high surface area, efficient electron transfer, and the formation of Schottky-type contacts between the TiO_2 nanotubes and Ti metal. This enabled COD determination with a wider dynamic working range of 0–700 mg/L in comparison with the original PeCOD technology.

Zhou et al. [47] constructed a rotating TiO_2/Ti photoanode for PeCOD measurement. Their photoelectrochemical cell consisted of the rotating photoanode and a rectangular quartz cell. Two types of digestion processes were used: PeCOD-thin and PeCOD-bulk. The mass transport and UV illumination at the upper half of the photoanode was boosted and termed "PeCOD-thin". The mass transport at the lower half of the photoanode was also enhanced using the rotating photoanode, and termed "PeCOD-bulk". Due to the dual functions of these special arrangements (called PeCOD combined), a wide analytical linear range of 2.7–11,500 mg/L was obtained during an approximate 5–110 min assay time period. The proposed method was further validated by real sample analyses.

4.2.2. Carbon nanotubes/ TiO_2 photoanode

Carbon nanotubes (CNTs) have been considered one of the most popular functional materials in recent years. Using the advantages of CNTs, such as the large surface area, extraordinary electrical conductivity, robust mechanical strength and thermal stability, CNTs/ TiO_2 composite materials have been employed for sensing devices [48]. As shown in Fig. 9, the carbon nanotubes have been successfully incorporated with the TiO_2 nanoparticulates [49]. With

Table 3
Summary of the analytical performance of PeCOD technologies.

Detection principle	Analysis time (min)	Limit of detection (mg/L)	Linear range (mg/L)	Photoanodes	Refs
Absolute PeCOD, thin-layer	<5	0.2	0.2–360	Mixed-phase TiO ₂ /ITO	[33]
Absolute PeCOD, thin-layer	1–5	0.2	0–200	Mixed-phase TiO ₂ /ITO	[34]
On line PeCOD, thin-layer flow cell	1–5	1.0	1–100	Mixed-phase TiO ₂ /ITO	[39]
PeCOD, probe	1–5	0.2	0–120	Mixed-phase TiO ₂ /ITO	[41]
Absolute PeCOD, thin-layer cell	1–5	n/a	0–850	TiO ₂ nanotube array/Ti	[42]
Absolute PeCOD, thin-layer cell	1–10	n/a	0–700	TiO ₂ nanotube array/Ti	[43]
Absolute PeCOD, thin-layer	1–5	0.2	0–300	Mixed-phase TiO ₂ /ITO	[44]
Online PeCOD, thin-layer flow cell	ca. 2	15.0	50–1000	Nanocrystalline TiO ₂ /Ti	[46]
PeCOD-combined, combined cell	5–110	2.7	2.7–11,500	Rotating TiO ₂ /Ti photoanode	[47]

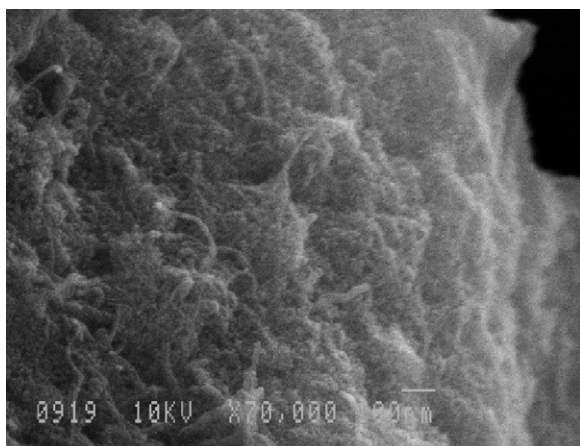


Fig. 9. Cross-section SEM images of the CNTs/TiO₂ photoanode after calcination processes [49].

the enhanced photocatalytic activity from the CNTs, the CNTs/TiO₂ photoanodes are capable of oxidizing and detecting various organic compounds (e.g., glucose, potassium hydrogen phthalate, and phenol) in aqueous solutions in a photoelectrochemical bulk cell.

4.2.3. TiO₂/boron-doped diamond photoanode

Boron-doped diamond (BDD) is one of the most promising advanced electrode materials in the field of electroanalysis with many advantageous characteristics including very low background currents, a wide working potential window, resilient mechanical strength, robust resistance against corrosion (even being anodic polarised in acidic solutions) and long term durability and stability [50–52]. The boron doping makes this p-type semiconductor as electrically conductive as common conductors at room temperature [53]. It is well established that TiO₂ nanoparticles exhibit n-type semiconductor properties. Thus, the incorporation of n-type TiO₂ with p-type BDD could lead to the formation of a p–n heterojunction, which can act as an internal electrostatic potential in the space charge region to facilitate efficient separation of the photo-induced electrons and holes [54]. Based on these advantages, TiO₂/BDD electrodes have been fabricated and successfully used to detect a wide spectrum of organic compounds in aqueous solution using a steady state current method [55].

5. Conclusions

Utilising the extraordinary photocatalytic oxidation power of nanostructured TiO₂ under UV illumination, the TiO₂ photocatalyst can be considered a universal sensing component for a wide spectrum of organic compounds. It is capable of determining aggregative organic compounds, such as TOC and COD, and individual organic compounds. The determination of COD based on the TiO₂ photoelectrocatalytic oxidation principles has been

attracting increasing attention and resulted in commercially available PeCOD technologies. The capacity of TiO₂ photoanodes can be further enhanced via the following approaches:

- (i) Construction of novel, robust, and highly efficient nanostructured TiO₂ photoanodes using modern materials synthesis technologies, such as liquid phase hydrothermal reactions, vapour phase hydrothermal reactions, anodic oxidation technology, template synthesis and electrochemical deposition technology, conductor and semiconductor doping technology.
- (ii) Making TiO₂ photoanodes the core component for achieving online and on-site determination of a wide spectrum of organic pollutants by combining emerging modern technologies, in particular, modern electronic technology (such as UV-LED as a low power consumption and high optical output light source), microelectronic lithography for sensor array construction, micromachining for lab-on-chip fabrication, micro-fabrication and computing technology for automation.
- (iii) Widening the applicability of the photoanodes by maximising the oxidation percentage of environmentally significant and persistent organic compounds, such as nitrogen-containing aromatic compounds.

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