1 **A miniature photoelectrochemical sensorbased on organic**
2 **electrochemical transistor for sensitive determination of**
3 **chemical oxygen demand in wastewaters**

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Abstract

A three-electrode configuration is often required in the conventional photoelectrochemical measurements. Nevertheless, one common drawback is the reference electrode and the counter electrode used in the measurements, which has been proved to be an impediment for the miniaturization. In this study, a simple, cost-effective and miniature photoelectrochemical sensor based on high sensitive organic electrochemical transistor (OECT) is developed and used for the determination of chemical oxygen demand (COD) in wastewaters. The devices show detection limit down to 0.01 mg/L COD, which is two orders of magnitude better than that of the conventional photoelectrochemical method. The excellent sensing performance can be contributed to the novel sensing mechanism of OECT devices. That is, the devices are sensitive to the potential changes induced by the photoelectrochemical reaction on TiO₂ nanotube arrays gate electrodes. Real sample analyses are also carried out. The results demonstrate that the measured COD values using the OECT devices and the standard dichromate methods are in a good agreement. Since the proposed sensor is constructed on a miniature transistor, it is expected that the device shows a promising application on the integrated COD monitoring platform.

Keywords: Organic electrochemical transistor; Chemical oxygen demand (COD); Photoelectrochemical sensor; TiO₂ nanotube arrays;

1. Introduction

Chemical oxygen demand (COD) is defined as the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant (Association et al. 1915). It is one of the most widely used parameters for the water quality assessment and an important index for the control of operation of wastewater treatment plants (Brdjanovic et al. 2000, Dharmadhikari et al. 2005, Kim et al. 2002). Currently, a COD determination method based on the photoelectrochemical principle has attracted increasing attention (Li et al. 2006a, Li et al. 2006b, Li et al. 2012, Ma et al. 2011, Zheng et al. 2008). Its main principle is to utilize TiO_2 as photocatalyst to mineralize organic compounds. In the photoelectrochemical detection process, organic compounds in tested water are oxidized by the hydroxyl radicals ($\cdot\text{OH}$) produced on the TiO_2 working electrode, and generate electrical signals, which is proportional to COD values (Ma et al. 2011, Zhao et al. 2003). It has been shown that the photoelectrochemical method is a rapid and environmental friendly COD determination method (Zhang et al. 2009a, Zhang et al. 2009b, Zhang et al. 2009c, Zhao et al. 2004). However, one common drawback of the conventional photoelectrochemical analysis is the requisite of both the reference electrode and the counter electrode, which has been proved to be an impediment for the miniaturization. Moreover, the sensitivity of the conventional photoelectrochemical method is hard to improve due to the low photocatalytic degradation efficiency of TiO_2 .

Organic electrochemical transistors (OECTs—also known as conducting polymer transistors), first developed in 1984 by White et al. (White et al. 1984), are an important type of organic thin-film transistors. Its operation relies on electrochemical

doping/de-doping of an organic semiconductor film in contact with an electrolyte (Khodagholy et al. 2011, Mabeck and Malliaras 2006). The intimate contact between organic semiconductor and electrolyte makes the devices efficient ion-to-electron converters, and thus suitable for various sensing applications in aqueous environments (He et al. 2012, Khodagholy et al. 2013b, Liao et al. 2013, Liao et al. 2014, Liao et al. 2015b, Lin et al. 2011, Liu et al. 2008, Rivnay et al. 2013, Sessolo et al. 2014). For example, the detection limit to glucose could be as low as 5 nM, which is about three orders of magnitude better than that of the conventional electrochemical measurements (Tang et al. 2011b). The high sensitivity of the OECTs is also found in dopamine (Tang et al. 2011a), uric acid (Liao et al. 2015a), and epinephrine detection (Mak et al. 2015). The devices could even be used to monitor the low-amplitude electrophysiological signal, such as, brain activity (Khodagholy et al. 2013a), action potentials from cells (Yao et al. 2014), and human electrocardiographic (Campana et al. 2014).

With these in mind, herein we report a novel and miniaturized OECT device using Pt nanoparticles modified TiO₂ nanotube arrays (Pt-NPs/TNTAs) as gate electrode for the photoelectrochemical determination of COD. In the proposed sensor, OECT-based transistor and Pt-NPs/TNTAs gate electrode are employed as the transducer and detecting element, respectively. The devices show low detection limit down to 0.01 mg/L COD, suggesting that the proposed method can also be applicable to slightly polluted water (ground water or underground water). For comparison, the analytical performances of the conventional photoelectrochemical measurement with the same Pt-NPs/TNTAs electrode are also evaluated. We find that the conventional photoelectrochemical method only shows a detection limit of 2 mg/L COD, further

indicating the advantage of the OECT devices in COD determination. Importantly, such OECT-based photoelectrochemical sensors combine the advantages of the organic thin-film transistors (e.g., cost-effective, miniaturization, sensitivity), and those of the conventional photoelectrochemical method (e.g., stability, accuracy, fast response), while eradicate the latter's drawbacks of the large and clumsy three-electrode system.

2. Experimental section

2.1. Device fabrication

-Figure 1-

Figure 1a shows the schematic diagram of an OECT-based photoelectrochemical sensor. The device was fabricated on a glass substrate (25 × 25 mm) onto which Cr/Au source and drain contacts were evaporated through a shadow mask. Subsequently, an active layer of PEDOT:PSS (thickness: 80 nm) was spin coated on the top of the glass substrate. Poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS) is prototypical semiconductor material that is commercially available and stable under a variety of conditions. The channel length and width of the devices were 0.2 mm and 6 mm, respectively. After annealing at 200 °C for 60 min in high purity N₂, a quartz tube was attached onto the device to contain the electrolyte. A Pt-NPs/TNTAs electrode was employed as gate to modulate the channel current by

116 applying a voltage between the gate electrode and the source. And a 3 W UV-LED
117 was placed against Pt-NPs/TNTAs gate electrode as the exciting light source.

118

119 2.2. Fabrication of Pt-NPs/TNTAs gate electrodes

120 The Pt-NPs/TNTAs electrodes were prepared by two steps. And the detailed
121 characterization of Pt-NPs/TNTAs can be found in our previous published work (Ref.
122 Liao et al. 2015b). Firstly, TNTAs were prepared by electrochemical
123 anodization. Titanium foils (0.2 mm thickness, 99.4% purity) were cut into small
124 rectangle pieces of 1 cm × 3 cm, which were then cleaned with acetone, ethanol and
125 deionized (DI) water, respectively. Anodization was performed in a two electrode
126 configuration with Ti foil as the working electrode and stainless steel foil as the
127 counter electrode. The samples were anodized at 25 V for 1 h and in the electrolyte
128 containing 0.27 mol/L NH₄F consisting of mixtures of DI water and glycerol
129 (1,2,3-propanetriol) prepared in volumetric ratio of 1:1. After anodization, the
130 samples were annealed at 450 °C for 3 h in high purity N₂. Secondly, in order to
131 improve the optical absorption properties and conductivity of the as-prepared TNTAs,
132 Pt nanoparticles (Pt-NPs) were deposited on TNTAs by ultrasound-assisted
133 electrodeposition method. A direct current power supply was used as the constant
134 current source. The as-prepared TNTAs were used as cathode, and stainless steel foil
135 as anode. The depositing bath was placed in the ultrasonic cell during the
136 electrodeposition process. The electrolyte consisted of mixture of H₂PtCl₆ (1g/L) and
137 H₃BO₃ (30g/L) solutions. The deposition time was set as 5 min.

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139 2.3. Photoelectrochemical measurements

140 The photoelectrochemical experiments were carried out at room temperature in a
141 cube quartz reactor (50×50×50 mm) using a three-electrode electrochemical
142 configuration: the Pt-NPs/TNTAs as working electrode, saturated Ag/AgCl (3 mol/L
143 KCl) as reference electrode, platinum foil as counter electrode. An electrochemical
144 workstation (Zanher Zennium) was used for application of potential bias, and
145 photocurrent signal recording. And a same 3 W UV-LED was used as excited light
146 source. In order to avoid the interference from ambient light, a dark box was used to
147 cover the photoelectrochemical apparatus during the experiments.

148 2.4. Device characterization

149 The OECT devices were characterized with a semiconductor parameter analyzer
150 (Keithley 4200). The devices were tested at a constant V_G ($V_G=0.4$ V) and V_{DS} ($V_{DS}=0.1$
151 V). Similar with three-electrode photoelectrochemical tests, the
152 experiments were also conducted in a dark box.

153 2.5 Detection of COD using conventional dichromate method

154 Real wastewater samples and the results of water quality analysis were obtained
155 from Hainan Environmental Monitoring Center, which is the state environmental
156 monitoring station in China. Prior to analysis, the wastewater samples were filtered to
157 remove the alga, bacteria and other particulates, and then stored at 4 °C in
158 refrigerator. The conventional dichromate method ($K_2Cr_2O_7$ method) was used to
159 measure COD value according to the National Standard of China (GB11914-89).

160

161 3. Results and discussion

162 3.1. Electrical measurements

163 OECTs operation relies on electrochemical doping/de-doping of an organic
164 semiconductor film in contact with an electrolyte (Khodagholy et al. 2011, Mabeck
165 and Malliaras 2006). As shown in Figure S1, when a positive gate voltage is applied,
166 the cations from the electrolyte are injected into the PEDOT:PSS film and dedope it,
167 thereby decreasing the drain current ($\text{PEDOT}^+:\text{PSS}^- + \text{M}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{PEDOT}^0 +$
168 $\text{M}^+:\text{PSS}^-$). But for the sensing applications, it is more convenient to measure the
169 channel current responses of the OECTs at fixed gate and drain voltages. Figure 2a
170 shows the drain-source current I_{DS} response of an OECT device to the intermittent UV
171 irradiation at a constant V_G ($V_G=0.4$ V) and V_{DS} ($V_{DS}=0.1$ V). As soon as I_{DS} of the
172 device reaches steady state in the dark, the light is quickly switched on, and a sharp
173 decrease of I_{DS} is observed. When the light is switched off, I_{DS} increases again.
174 However, the response and recovery of I_{DS} are relatively slow. The long response
175 time might be due to the slow process that the cations in the electrolyte are pushed into
176 the PEDOT:PSS channel, while the long recovery time might be due to the opposite
177 process that the cations in the PEDOT:PSS channel are released back to the
178 electrolyte (Berggren et al. 2008, Lin and Yan 2012). Several on/off cycles of
179 intermittent irradiation are repeated, and the I_{DS} response shows a good reproducibility.
180 This phenomenon is reminiscent of the photocurrent response in a conventional
181 three-electrode photoelectrochemical cell. As shown in Figure 2b, the Pt-NPs/TNTAs
182 electrode also shows a good reproducibility under the intermittent irradiation of an
183 UV-LED. With the same excitation light source and photoelectrode, the photocurrent
184 value is about several μA for the conventional photoelectrochemical measurement,

185 whereas the photocurrent value is about several hundred μA for the novel OECT
186 device ($I_{ph}, I_{ph} = |I_{DS,light} - I_{DS,dark}|$). In addition, several magnitude of enhancement in
187 photocurrent value is also observed when a 3W white LED was used as light source
188 (Figure S2, Supporting Information). The results above indicate that the OECT
189 devices are more sensitive to the gate potential changes induced by light illumination,
190 which can be ascribed to the signal amplification of the OECT-based transistors (Lin et
191 al. 2011).

192

193 -Figure 2-

194

195 It is worth noting that the current variation trend of the OECT devices to UV
196 irradiation is opposite to that of the conventional photoelectrochemical method. In the
197 conventional photoelectrochemical method, the rise and decay of the current
198 correspond to the illumination being switched on and off, respectively. In detail,
199 without illumination, no significant current is observed. Upon illumination of UV light,
200 the photocurrent promptly appears. When the illumination is interrupted, the current
201 rapidly falls to zero. From the viewpoint of the photoelectrochemistry of
202 semiconductors, the photocurrent is caused by the separation of photogenerated
203 electron-hole pairs at the semiconductor/electrolyte interface. Holes move to the
204 semiconductor surface, where they are trapped or captured by the reduced species in
205 the electrolyte, while the electrons are transported to the back contact (Hagfeldt et al.
206 1995, Wang et al. 2014, Yu et al. 2007). However, in the OECT devices, the rise and
207 decay of the channel current are opposite to those of the conventional
208 photoelectrochemical method. The reason may be due to the different working

principle of the OECT devices, which will be discussed later. Interestingly, the gate-source current I_{GS} corresponds well to the illumination (Figure S3, Supporting Information), which is similar to that in the conventional photoelectrochemical method. From I_{GS} values we can easily distinguish two regimes in OECT operation since I_{GS} is usually used as a fingerprint of the regime of OECT operation (Lin and Lonergan 2006, Tarabella et al. 2010). Without UV irradiation, a negligible I_{GS} is observed. This is the non-Faradaic regime, in which no charge transfer reactions occur at the gate electrode. Under UV irradiation, a large steady-state I_{GS} is observed. This is the Faradaic regime, in which redox reactions (photocatalytic process) occur at the gate electrode.

3.2. Analytical principle

For an OECT device, the channel current I_{DS} is typically given by:

$$I_{DS} = \frac{q\mu p_0 t W}{L V_p} \left(V_p - V_G^{eff} + \frac{V_{DS}}{2} \right) V_{DS} \quad (|V_{DS}| \ll |V_p - V_G^{eff}|)$$

$$V_p = q p_0 t / c_i$$

$$V_G^{eff} = V_G + V_{offset} \quad (1)$$

where q is the electronic charge; μ is the hole mobility; p_0 is the initial hole density in the channel; t is the thickness of the organic semiconductor film; W and L are the channel width and length, respectively; c_i is the effective capacitance per unit area of the transistor; V_p is the pinch-off voltage; V_G^{eff} and V_{offset} are the effective gate voltage and the offset voltage at interfaces, respectively.

Without UV irradiation, the gate voltage applied on the OECT devices crosses two interfaces, including gate/electrolyte and electrolyte/channel interfaces (the solid line in Figure 1c). V_G can be given by:

$$V_G = V_{G-E} + V_{E-C} = \left(1 + \frac{C_{E-C}}{C_{G-E}}\right) V_{E-C} \quad (2)$$

where V_{G-E} and V_{E-C} are the voltages applied on the electrolyte/gate and electrolyte/channel interfaces, respectively; C_{G-E} and C_{E-C} are the capacitances of the two electric double layers near the gate and the channel, respectively.

When the UV light is switched on, the photocatalytic oxidation of organics at the gate electrode decreases the potential drop at the gate/electrolyte interface because of the generation of Faradic current. Thus, the voltage applied at the electrolyte/channel interface increases, as indicated by the dash line in Figure 1c. In other words, the transfer curves of the OECT devices will shift to the lower gate voltage after UV light is switched on (see Figure S4, Supporting Information). Assuming that the organics are stoichiometrically mineralized at the working electrode, the voltage applied on the gate/electrolyte interface is given by Nernst equation (Bard and Faulkner 2000):

$$V_{G-E} = -2.30 \frac{kT}{nq} \log C_m + A_1 \quad (3)$$

where k is Boltzmann constant; T is temperature; n is the electron transfer number of the individual organic compound; C_m is the molar concentration of organics in solution; A_1 is constant. Consequently, the voltage applied on the electrolyte/channel interface is:

$$V_{E-C} = V_G + 2.30 \frac{kT}{nq} \log C_m - A_1 \quad (4)$$

251 Thus, V_{E-C} increases with the increase of organics concentration and can
 252 directly change the channel current of the devices. Assuming that the channel
 253 current change is attributed to the change of the effective gate voltage of the
 254 OECT, we can read out the effective gate voltage V_G^{eff} corresponding to channel
 255 current from the transfer curve of the device in blank solution. According to
 256 Equations(2) and (4), V_G^{eff} is given by:

$$257 \quad V_G^{eff} = 2.30(1 + \frac{C_{E-C}}{C_{G-E}}) \frac{kT}{nq} \log C_m + A_1 \quad (5)$$

258 Using the electron transfer number of the organic compound, n , and the
 259 definition of COD, molar concentration (C_m) can be converted into COD
 260 concentration, $[COD] = 8000nC_m$. Then Equation (5) can be given by:

$$261 \quad V_G^{eff} = 2.30(1 + \frac{C_{E-C}}{C_{G-E}}) \frac{kT}{nq} \log [COD] + A_2 \quad (6)$$

262 The photocurrent measured from the solution containing organics is defined
 263 as i_{total} , and i_{blank} is measured from the blank supporting electrolyte solution. Thus
 264 the net steady-state photocurrent i_{net} , originated from the oxidation of the
 265 organics, can be obtained by subtracting i_{blank} from i_{total} in the presence of
 266 organics(Zhao et al. 2004)(see Figure 3).

$$267 \quad i_{net} = i_{total} - i_{blank} \quad (7)$$

268 Since the OECT devices work on constant V_G and V_{DS} , according to Equations
 269 (1), (5), (6) and (7), i_{net} can be given by:

$$270 \quad i_{net} = \frac{qp_0tW}{LV_p} V_{DS} \cdot \Delta V_G^{eff} \\ = \alpha \log C_m + A \quad (8)$$

$$\text{or} \quad = \alpha \log [COD] + A \quad (9)$$

where α and A are constant. As can be seen, the i_{net} is a linear response to the logarithm of COD value. Therefore it can be used to quantify the COD value of organic compounds.

-Figure 3-

3.3. Optimization of analytical signal

-Figure 4-

Prior to COD measurements, the analytical signal i_{ph} is optimized from light intensity, gate voltage, and supporting electrolyte concentration, respectively. As shown in Figure 4a, i_{ph} value is proportional to the light intensity. In spite of the fact that a larger i_{ph} value can be obtained when a higher power light source is used, from the points of energy consumption and device miniaturization, we still choose a low-power LED as light source in this work.

Figure 4b shows the effect of gate voltage on i_{ph} of OECTs. At the low gate voltage (<0.6 V), the i_{ph} value linearly increases with the increasing gate voltage. Further increase in the gate voltage, the i_{ph} value will become saturated. Therefore, a medium gate voltage $V_G = 0.4$ V is chosen during the experiments.

The channel current of the OECT devices is sensitive to the ionic strength in solution (Lin et al. 2010). Therefore, the effect of supporting electrolyte concentration on i_{ph} is investigated (Figure 4c). At fixed V_G and V_{DS} , with the Na^+ concentration increases to 0.3 M, the more Na^+ ions are injected into the PEDOT:PSS film and thus the increase of i_{ph} value is observed. Finally, the

296 i_{ph} will reach its saturation value at higher electrolyte concentrations since a
297 small channel area is used during the experiments. Therefore, 0.1 M NaH_2PO_4
298 is selected as the support electrolyte.

299

300 3.4. Validation of analytical principle

301 The applicability of the proposed detection principle is first examined
302 using synthetic samples prepared with pure organic compounds with known theoretical
303 COD value. According to their varying adsorptivity to the TiO_2 surface, glucose,
304 malonic acid (MA) and potassium hydrogen phthalate (KHP) are selected as the
305 representative organic compounds in this work (Han et al. 2009). As shown in Figure
306 5a, the rapidly raising photocurrent is obtained after switching on the light, and then
307 reaches steady state. A well-defined photocurrent response was obtained when 1 μM
308 KHP was added, while the conventional photoelectrochemical method had no obvious
309 current response until 100 μM KHP was added (Figure 5b). Other two organic
310 compounds (MA and glucose) are also investigated and exhibit similar photocurrent
311 response to those shown in Figure 5a (not shown here). The i_{net} can be further plotted
312 against the logarithm of concentrations of all the tested organic compounds shown in
313 Figure 5c, which implies Equation (8) is reasonable.

314 Since the electron transfer number n for the MA, glucose and KHP are 8, 24, and
315 30, respectively (Han et al. 2009, Zhang et al. 2014), the molar concentration (C_m) can
316 be converted into COD concentration, $[\text{COD}] = 8000nC_m$. Figure 5e shows the i_{net} as a
317 function of the theoretical COD values using Equation (9). The relationship
318 between current and the logarithm of the theoretical COD values is shown in the form of
319 the linear equation $y = 9.00 + 6.03 \log(x)$, where y represents the i_{net} obtained from the

organics oxidation, and x represents the COD values of the organics. The detection limit is estimated to be 0.01 mg/L COD ($S/N=3$). For comparison, the conventional photoelectrochemical method by using Pt-NPs/TNTAs as the working electrode is also investigated. As shown in Figure 5d, the obtained i_{net} values are directly proportional to the molar concentration of all tested organic compounds. Subsequently, the i_{net} values are also plotted against the theoretical COD values shown in Figure 5f. As expected, the results show that all the organic compounds investigated are fitted into a linear line $y=0.26+0.01x$. The different mathematical expressions to COD values between the OECT devices and conventional photoelectrochemical method further prove the different working mechanism between the two detection methods. The detection limit of the conventional photoelectrochemical method is estimated to be 2 mg/L COD ($S/N=3$). Obviously, the detection limit of the OECT device to the COD determination is two orders of magnitude lower than that by the conventional photoelectrochemical method using the same Pt-NPs/TNTAs electrode. However, from Figure 5e, it seems that OECT devices may not be accurate to detect organic compounds with high concentrations. We speculate that the KHP and MA may have more complicated molecular structures, which make them are hard to be decomposed by photocatalysis. But we cannot confirm this conclusion based on the existing data, and more research is needed in our future work.

In order to further clarify the measuring accuracy of the OECT devices, the Pearson correlation coefficient is used as an indicator of the intensity of the association between the predicted COD values measured by the OECT devices and the theoretical COD values. When Pearson coefficient r lies between 0.8 and 1.0, it

implies that there is a strong correlation between these two variables. Figure S5 shows the correlation between the COD values obtained by the both methods. It is found that Pearson coefficient $r=0.991$ for the OECT devices, indicating that the devices are suitable to measure COD values of wastewater. In addition, through comparing the detection limit of the proposed OECT devices with other COD sensors reported before (Table S1, Supporting Information), we find that the proposed OECT devices are also more sensitive for COD sensing than many other COD sensors reported before. The excellent sensing performance can be attributed to the fact that the OECT devices are sensitive to the potential changes occurring on the gate electrodes given by Equation (6) even when faradic currents are too low to be detected.

3.5. Effects of the water components

-Figure 6-

Since Chloride ion is the common interference which affects the COD measurement with standard $K_2Cr_2O_7$ method. So it is necessary to investigate the effect of Cl^- concentration on COD determination performance of the OECT devices (Figure 6a). It is found that within the concentration range of Cl^- from 0 to 2000 mg/L, i_{net} is stable, which indicates that the COD value obtained by the OECT device is independent of the Cl^- interference.

Figure 6b shows the effect of sample solution pH on the COD determination performance. No significant changes in i_{net} are observed when the solution pH is varied

366 from 5 to 9. However, unstable i_{net} is observed under both strong acid and alkali
367 conditions. Therefore, an optimum pH range from 5 to 9 is suggested for the
368 OECT devices.

369

370 3.6. Real sample analysis

371

372 -Table 1-

373

374 The analysis of real samples is also carried out. The COD values of water
375 samples are analyzed by the standard $K_2Cr_2O_7$ method, the conventional
376 photoelectrochemical method and the proposed OECT devices, respectively. Prior to
377 analysis, the wastewater samples were filtered to remove the alga, bacteria and other
378 particulates. The results obtained by the three methods are summarized in Table 1. The
379 relative standard deviation (*RSD*) of the OECT devices is below 5%, which is lower
380 than that of the conventional photoelectrochemical method, indicating that
381 the reproducibility of the OECT devices is better than that of the conventional
382 photoelectrochemical method. Moreover, all the relative errors calculated from the
383 COD values measured by the OECT devices and the standard $K_2Cr_2O_7$ method are
384 within $\pm 6\%$, demonstrating that the proposed method shows excellent correspondence
385 with the $K_2Cr_2O_7$ method and can be successfully applied in practice. Additionally,
386 comparing the relative errors obtained from the different methods, the lower errors
387 further indicating the advantage of the OECT devices.

388 In order to investigate the long-term stability of the devices, the photocurrent
389 responses to 100 μ M KHP with theoretical COD value of 24 mg/L were measured
390 over a 10-days period. The *RSD* is 4.6%, indicating that the OECT devices have good
391 stability.

392 4. Conclusions

393 In summary, a highly sensitive photoelectrochemical sensor is developed by
394 using an OECT device with a Pt-NPs/TNTAs gate electrode. The sensing mechanism
395 can be contributed to the photoelectrochemical reaction of organic compounds on the
396 gate electrode, which leads to the change of effective gate voltage applied on the
397 transistor. The OECT devices show low detection limit of 0.01 mg/L COD, which is
398 two orders of magnitude better than that of the conventional photoelectrochemical
399 method using the same Pt-NPs/TNTAs electrode. The validity of the OECT devices
400 for COD analysis has also been demonstrated by correlating the COD values of
401 several types of real samples obtained from the OECT devices and the standard
402 dichromate methods. Importantly, such OECT-based sensors combine the advantages
403 of the organic thin-film transistors (e.g., cost-effective, miniaturization, sensitivity),
404 and those of the conventional photoelectrochemical method (e.g., stability, accuracy,
405 fast response), while eradicate the latter's drawbacks of the large and clumsy
406 three-electrode system. Therefore, it is expected that the OECT-based
407 photoelectrochemical sensors are potential candidates for COD onsite measurement.

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421

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625 **Table 1. Comparison of COD values of various wastewater samples obtained by different methods.**

Sample	K ₂ Cr ₂ O ₇ method	OECT device			Conventional photoelectrochemical method		
		Mean	<i>RSD</i> (%)	Relative error	Mean	<i>RSD</i> (%)	Relative error
		(mg/L)	(n=5)	(%)	(mg/L)	(n=5)	(%)
Municipal wastewater treatment plant							
influent	264.5	278.5	4.84	5.29	273.5	3.58	3.40
effluent	39.2	38.3	3.26	-2.30	41.6	4.82	6.12
Pulp and paper mill wastewater							
influent	1514.3	1457.5	3.19	-3.75	1484.5	2.44	-1.97
effluent	53.5	54.5	2.75	1.87	55.7	5.83	4.11
Petrochemical wastewater							
influent	166.8	171.7	4.22	2.93	176.4	5.66	5.75
effluent	38.1	39.0	3.85	2.36	39.8	3.14	4.46

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Figure 1. (a) Schematic diagram of an OEECT-based photoelectrochemical sensor, and FESEM images of Pt-NPs/TNTAs. (b) Photocatalytic reaction on the Pt-NPs/TNTAs electrode. (c) Sketch of the potential distribution between the gate electrode and the channel in the absence and presence of UV light irradiation. EDL is the abbreviation for “electric double layer”.

Figure 2. (a) I_{DS} vs. time curve of an OECT device in 0.1 M NaH_2PO_4 solution at repeated on/off cycles of a 3 W UV-LED UV illumination. (b) Photocurrent vs. time curve tested in a conventional photoelectrochemical cell at the same conditions. The applied potential is 0.4 V vs. Ag/AgCl.

Figure 3. Typical photocurrent response of a 0.1 M NaH₂PO₄ blank solution (i_{blank} , black line) and a 0.1 M NaH₂PO₄ solution containing organic compounds (i_{total} , red line). i_{net} was the difference of the two the steady state currents.

Figure 4. Optimization of the OEECT-based photoelectrochemical sensors: effects of (a) light intensity, (b) gate voltage, and (c) supporting electrolyte concentration on i_{ph} .

Figure 5. Typical photocurrent responses to various KHP concentrations tested in (a) an OECT device and (b) conventional photoelectrochemical cell using the same Pt-NPs/TNTAs as gate electrode and working electrode, respectively. The insets in (a) and (b) show the digital images of the OECT device and photoelectrochemical cell, respectively. Relationships between i_{net} and the molar concentrations of the different organic compounds: (c) obtained from the OECT device; (d) obtained from the conventional photoelectrochemical method. The calibration curve of i_{net} and COD values of the model samples: (e) obtained from the OECT device; (f) obtained from the conventional photoelectrochemical method.

Figure 6. Effect of (a) Cl^- concentration and (b) solution pH on the photoelectrochemical detection of 100 μM KHP on OECT devices. The insets in (a) and (b) are the corresponding plots of i_{net} ($i_{\text{net}} = i_{\text{total}} - i_{\text{blank}}$).

Graphic abstract