



## Performance of nano- and nonnano-catalytic electrodes for decontaminating municipal wastewater

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### ARTICLE INFO

#### Article history:

Received 24 January 2008

Received in revised form 20 June 2008

Accepted 20 June 2008

Available online 27 June 2008

#### Keywords:

Electrocatalyst

Electrochemical treatment

Nano

Municipal wastewater

### ABSTRACT

This research is intended to decompose organic substances in municipal wastewater with nano- and nonnano-scale electrocatalytic electrodes. As an anode, the nano-scale electrodes included lab-made TiO<sub>2</sub> and Cu<sub>2</sub>O electrodes; the nonnano-scale electrodes were a commercial TiO<sub>2</sub> and graphite plate. According to experimental results, the nano- and nonnano-scale catalytic electrodes can effectively remove the organic pollutants in the municipal wastewater. The perforated TiO<sub>2</sub> electrode is the best for eliminating the chemical oxygen demand (COD), and its efficiency is about 90% (COD decreases from 400 to 40 mg L<sup>-1</sup>). The conductivity of municipal wastewater and the electro-catalytic process will increase the pH and eventually remains in the neutral range. The conductivity of municipal wastewater can be lowered to some degrees. The most attractive discovery of electro-catalytic process is that the dissolved oxygen (DO) in the municipal wastewater can be increased by the TiO<sub>2</sub> electrode (nonnano-scale) around 4–6 mg L<sup>-1</sup>, but few DO is produced by the nano-scale electrocatalytic electrode.

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### 1. Introduction

Electrochemical techniques have been used to treat wastewater for decades. Many metal materials have been used as the anodes to treat different types of wastewater, and results are impressive [1–3]. In such electromechanical techniques, organic pollutants are primarily decomposed by direct oxidation. Yet, regarding cost effectiveness, electrochemical techniques are still unfeasible in comparison with traditional biological techniques. Hence, municipal wastewater is generally treated by biological techniques. So far, electrochemical techniques are usually used to treat pollutants that cannot be degraded by biological techniques. However, electrochemical process possesses promising remediation potentials if the promotion of electrode materials can facilitate the degradation efficiency of pollutants. The appearance of catalytic electrodes has been demonstrated that anodes manufactured by new materials present high possibility to treat wastewater [4].

In general, electrochemical techniques apply the electric field on the anode to oxidize the organic pollutants in wastewater. On contacting the anode, the organic pollutants can be oxidized to intermediate products (i.e., organic acids) which will be released

into water [5]. In theory, if there is ample time, the organic acids can be consecutively decomposed into CO<sub>2</sub> and H<sub>2</sub>O, and the chemical oxidation demand (COD) can be decreased so that the wastewater is qualified to be discharged. Nevertheless, since there are double layers on the anode surface and organic pollutants penetrate the double layers only by diffusion (molecular and convective); the rate of the direct decomposition is limited, which results in low degradation efficiency of electrochemical techniques. In addition to direct oxidation, the electrochemical reaction for decomposing the water molecules (i.e., water electrolysis) also consumes electricity. As the voltage of the electric field is increased, the decomposition of the water is increased; however, the treatment rate of organic pollutants may not increase proportionally. This extra electric consumption also limits the cost-effective application of electrochemical techniques. That is, the water decomposition will alter wastewater pH, cause the treatment difficulty, and increase the operation cost.

In contrast to tradition electrochemical process, catalytic electrodes can facilitate the decomposition of organic pollutants by producing strong oxidants (i.e., catalytic reactions) such as hydroxyl radicals (OH•). Even though the tradition electrochemical process can also produce oxidants (e.g., the reaction with chlorides in the wastewater) [6]; the catalytic electrodes can produce oxidants without chemicals addition. These oxidants may be distributed into the bulk solution and are capable of degrading

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organic pollutants dramatically, which is called “indirect decomposition”. This indirect decomposition may overcome the drawbacks of traditional electrochemical techniques (diffusion limitation of organic pollutants). As a result, the development of the electrochemical techniques has regained momentum. Up to date, catalytic electrodes have successfully been used to treat organic pollutants such as the surfactant and pesticides [7,8]. Even more,  $\text{TiO}_2$  has successfully been used to decompose *E. coli* in the wastewater [9].

Although details of organic pollutants decomposed by catalytic electrodes are not clear which is similar to the photocatalytic reaction, the  $\text{OH}^\bullet$  is also regarded as the major key role to transform the organic pollutants into harmless water and  $\text{CO}_2$  [10]. Based on this principle, there were various researches for treating different types of wastewater [11–13], and the COD and  $\text{NH}_4\text{-N}$  were decreased to some extent. As have uncovered by Rajkumar and Palanivelu's research [14], catalytic electrodes were used to decrease the TOC and COD in some specific wastewater and was suitable for treating high-concentration wastewater. Moreover, Feng et al. used electrocoagulation and electro-oxidation techniques to treat wastewater and reported that the efficiency of eliminating the T-N,  $\text{NH}_4\text{-N}$ , T-P and COD was 73%, 81%, 99% and 86%, respectively [15]. From the foregoing documents, it is learned that electrocatalyst techniques (catalytic electrodes application) can be widely used to eliminate the organic pollutants in wastewater.

Most of previous researches were focused on exploring impacts on the elimination rate of COD in some specific types of wastewater and the electricity efficiency by catalytic electrodes. Not much is addressed about the application to municipal wastewater and changes in other physical and chemical attributes such as pH, conductivity and dissolved oxygen (DO) although these are also important indexes of water quality. In this study, municipal wastewater was chosen as the remediation target; simultaneously, we not only tried to evaluate performance in decomposing the COD but also assess the pH, conductivity and DO of the municipal wastewater during operation of catalytic electrodes.

When electrode surfaces are manufactured in nano-scale, some characteristics can be promoted including the transfer speed of electrons, reactivity and diffusion in reaction [16–18]. As considering the nano-scale materials, their specific surface area will be increased, which results in high contacting rates and pollutants adsorption. Accordingly, nano-catalytic electrodes might contribute much higher treatment efficiencies than catalytic electrodes in regular sizes. Among many catalytic electrodes,  $\text{TiO}_2$ , a well-known photo-catalyst; many other oxides such as  $\text{ZnO}$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{WO}_3$ ,  $\text{SnO}_2$  and  $\text{ZrO}_2$ , sulfides such as  $\text{CdS}$  and  $\text{ZnS}$  can be regarded as catalytic electrodes. However,  $\text{TiO}_2$  has been the most common material because it is excellent in oxidation and reduction, chemically stable, non-toxic, and cheap. In this research, the other goal is to evaluate their COD degradation performance and physiochemical reactions in treating municipal wastewater by using nano- and nonnano-scale  $\text{TiO}_2$  electrodes. Overall, we tried to provide information about the nano- and nonnano-scale catalytic electrodes of treating the municipal wastewater.

## 2. Materials and methods

### 2.1. Electrocatalytic reactor

In this research, a reaction tank of which the size was 15 cm (diameter)  $\times$  7.5 cm (height) and contained 1.0L of municipal wastewater sample was used. A stainless steel plate served as the cathode. The used anodes included a graphite plate, a commercial  $\text{TiO}_2$  plate, a commercial perforated  $\text{TiO}_2$  plate (with punctured holes), a lab-made plate with nano-scale  $\text{Cu}_2\text{O}$  particles and a net-shaped plate with nano-scale  $\text{TiO}_2$  particles. The distance between

two electrodes was set at 7.0 cm. In addition to the net-shaped plate, the size of all electrodes was 11 cm (length)  $\times$  5 cm (width)  $\times$  0.5 cm (thickness). A CORNING Stirrer/Hot Plate was placed below the reaction tank and used to blend the water sample in a completely mixed status. A direct-current (DC) power supply was used to generate the electric field for the electrocatalytic system.

### 2.2. Preparation of the nano-scale cuprous oxide and $\text{TiO}_2$ electrode

The cuprous oxide electrode could be made by electroplating method [19]. A copper plate was placed at the anode as a sacrificed electrode. A stainless plate was placed at the cathode as a substrate material. The concentration of the electrolyte was  $\text{NaCl}$  of  $250\text{ g L}^{-1}$  and  $\text{NaOH}$  was used to adjust the pH of electrolyte at 8.0, 9.0, and 10.0. Each experiment was controlled at a constant current of 800 mA and conducted for 90 min. The preparation process of the lab-made  $\text{TiO}_2$  electrode will be addressed in other article, therefore, no statements here. In order to verify the nano-scale particles on the electrode surface and obtain the morphological information, the field emission scanning electron microscope (FE-SEM) was used to observe the superficial structures of the all anodes.

### 2.3. Experiments of decomposing municipal wastewater

The wastewater sample was collected from the wastewater treatment plant at Chaoyang University of Technology. The COD of the municipal wastewater sample ranged from 350 to  $400\text{ mg L}^{-1}$ . The other characteristics of municipal wastewater such as pH, EC, and chloride concentration was 6.8–7.3,  $1650\ \mu\text{S cm}^{-1}$ , and  $52.03\text{ mg L}^{-1}$ , respectively. The concentration of heavy metals including Cd, Cu, Pb, and Zn was 0.0016, 0.0113, 0.0376, and  $0.0792\text{ mg L}^{-1}$ , respectively. As conducting experiments, different electrocatalytic electrodes were used to treat the municipal wastewater for 60 min. The major controlling factor was voltage gradients such as 1.0, 3.0, 5.0 and  $7.0\text{ V cm}^{-1}$ . During this electrochemical process, the COD, pH, conductivity, and DO were measured at each 5-min period of time. A pH meter (SUNTEX, SP-701), a conductivity meter (SUNTEX, SC-170), and a DO meter (YSI 550A) were used to monitor the value of pH, conductivity, and DO. To determine the COD of municipal wastewater, the closed-circuit titration (NIEA W5175.50B) was used. Afterwards, all experimental data were analyzed and discussed.

## 3. Results and discussion

### 3.1. Classification of nano-catalytic electrodes

In order to classify the nano-scale of used electrodes, the FE-SEM images of different electrodes (Figs. 1–3) were evaluated. Fig. 1 shows the FE-SEM image of  $\text{Cu}_2\text{O}$  electrode under pH 9 manufacturing condition as a typical sample. Actually, all FE-SEM images of  $\text{Cu}_2\text{O}$  electrodes can find nano-scale particles on the electrode surface under different pH manufacturing situations. In Fig. 1, one can observe that the cuprous oxide crystals pile on the substrate, the stainless steel plate, and a lot of nano-class particles (presented in red number on the picture) concentrate on the summit. It also can be seen that some nonnano-crystals surround these nanoparticles. This indicates the manufacture process of nano  $\text{Cu}_2\text{O}$  still needs some modifications. However, in comparison with electrodes at different pH conditions, more nano-class particles are made at pH 9 condition than others. Therefore, the  $\text{Cu}_2\text{O}$  electrode was made at pH 9 condition and used to treat the municipal wastewater. Fig. 2 shows the FE-SEM image of the commercial  $\text{TiO}_2$  electrode. According to this figure, the texture of the  $\text{TiO}_2$  electrode is quite tight and

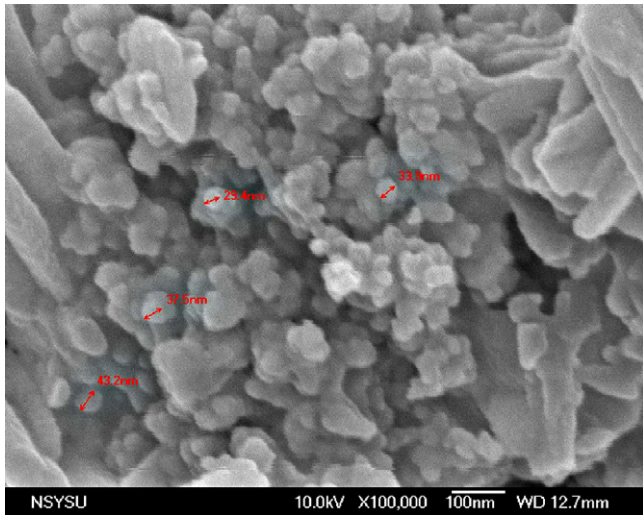


Fig. 1. The FE-SEM image of Cu<sub>2</sub>O electrode under pH 9 manufacturing condition.

includes a small number of pores. No nano-scale particles can be found on the electrode surface. In contrast to the commercial TiO<sub>2</sub> electrode, a net-shaped TiO<sub>2</sub> electrode made in the lab possesses nano-scale materials. The superficial structure of the nano-scale TiO<sub>2</sub> electrode is presented in Fig. 3a and b. Based on Fig. 3a and b, it can be found that nano-scale tips spread on the surface of the stainless net-shaped substrate in the form of columns. As a consequence, the Cu<sub>2</sub>O and net-shaped TiO<sub>2</sub> electrode can be classified as nano-catalytic electrodes.

### 3.2. COD removal efficiency of the commercial TiO<sub>2</sub> electrode

Fig. 4 shows the COD removal efficiency versus time under different voltage applications on the commercial TiO<sub>2</sub> electrode. It can be seen that the COD elimination efficiencies are low when the voltage gradients are controlled at 1.0 and 3.0V cm<sup>-1</sup>. Since catalytic electrodes decompose the organic pollutants by the direct and indirect oxidation, results indicate that neither could the TiO<sub>2</sub> anode directly oxidize the organic pollutants, nor could be excited to produce electron-hole pairs if the voltage gradients are too small. That is, there is few OH radical produced in the municipal wastewater so that the COD cannot be effectively eliminated. Some

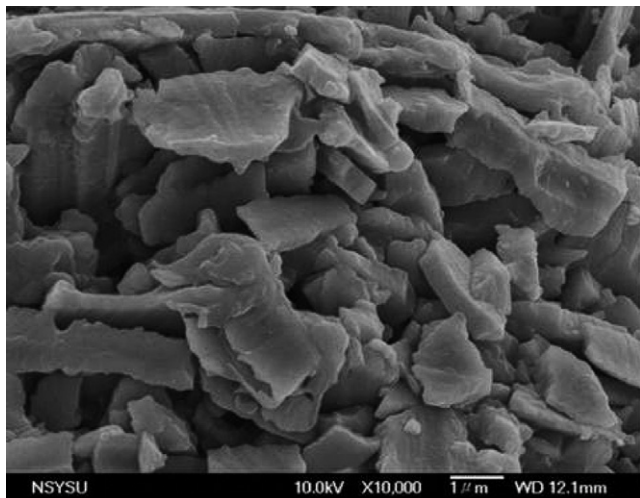


Fig. 2. The FE-SEM image of commercially available TiO<sub>2</sub> electrode.

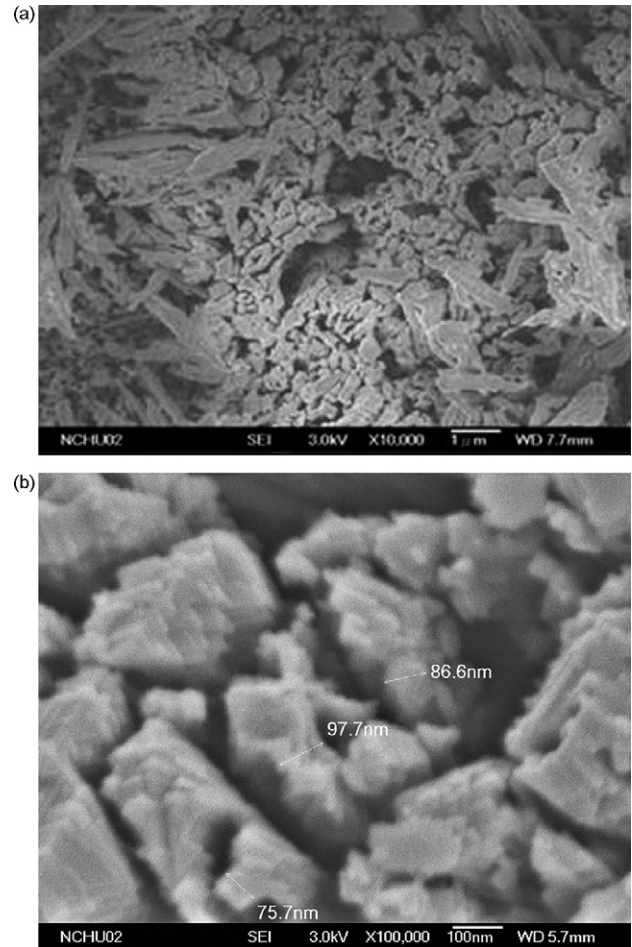


Fig. 3. (a) The FE-SEM image of nano-class TiO<sub>2</sub> electrode under 10,000× magnifications. (b) The FE-SEM image of nano-class TiO<sub>2</sub> electrode under 100,000× magnifications.

catalytic materials, similar to TiO<sub>2</sub>, employed as the anode have been proved to produce OH radicals theoretically and practically [15,19,20]. The yield rate of OH radicals of TiO<sub>2</sub> has been determined in our lab and attempted to be published in other paper. However, the COD of the municipal wastewater tends to decrease dramatically when the voltage gradients are raised to 5.0 and 7.0V cm<sup>-1</sup>. Among experiments, the commercial TiO<sub>2</sub> electrode (with punc-

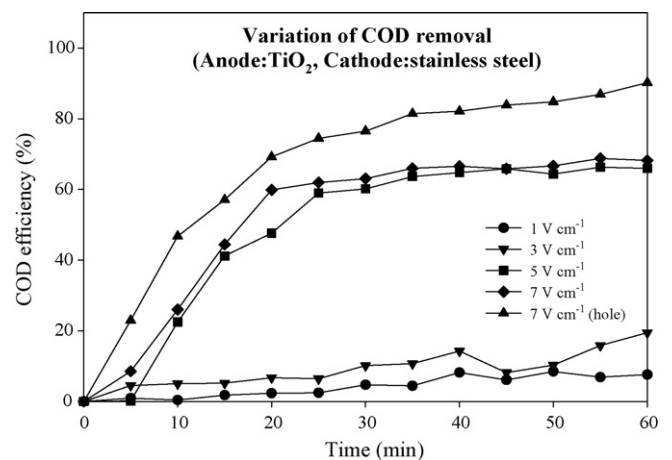


Fig. 4. The COD removal efficiency versus time under different voltage applications.



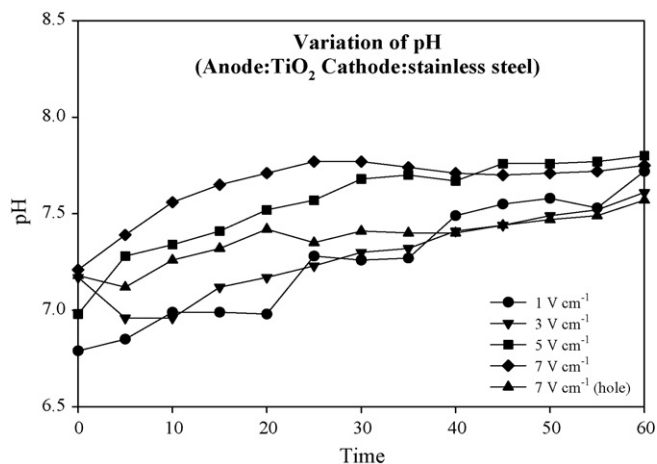


Fig. 5. The pH variation versus time under different voltage applications.

tured holes) effectively eliminates the COD from 400 to 40 mg L<sup>-1</sup> (the removal efficiency is as high as 90%). This reveals that the shape of electrode could be an important factor affecting the treatment efficiency. Additionally, the current efficiency under such operational condition was calculated to be around 20% based on the following equation [20].

$$CE(\%) = \frac{(COD_0 - COD_t)}{8It} FV \times 100 \quad (1)$$

where  $COD_0$  and  $COD_t$  are the chemical oxygen demands at times  $t = 0$  and  $t$ , respectively.  $I$  is the current (A),  $F$  is the Faraday constant (96.87 C mol<sup>-1</sup>),  $V$  is the volume of the solution (L) and 8 is the oxygen equivalent mass (g equiv<sup>-1</sup>).

It also can be seen that the decomposition takes place faster during the first 20 min than the rest of the duration at the voltage gradient of 5.0 or 7.0 V cm<sup>-1</sup>. This reaction kinetic indicates that the reaction rate of the electrocatalyst might be related to the diffusion rate, that is, the decomposition rate is related to the pollutants concentration in the municipal wastewater. In other words, organic pollutants will be decomposed mainly after entering the double layers of the electrode. One other reaction phenomenon is considered that there is no obvious difference between the COD removal efficiencies under 5.0 and 7.0 V cm<sup>-1</sup> treatments. In theory, the amount of the OH radical should be proportionally increased with increasing the external electric field. The more OH radical can decompose more organic pollutants in the municipal wastewater, which is inconsistent with experimental data. This could be attributed to that most of the radicals exist on the surface of the electrode and slowly spread into the municipal wastewater. Accordingly, the reaction rate is still limited by the diffusion reaction of organic pollutants significantly.

### 3.3. pH and conductivity of the commercial TiO<sub>2</sub> electrode

Figs. 5 and 6 present the pH variation and conductivity removal versus time under different voltage applications on the commercial TiO<sub>2</sub> electrode, respectively. Referred to Fig. 5, it can be noticed that the pH slowly increases during 1.0 and 3.0 V cm<sup>-1</sup> voltage operations. Because few OH radicals occur under such low voltage operation (referring to Section 3.2), this implies that the hydrolysis reaction (water molecule split into H<sup>+</sup> and OH<sup>-</sup>) is still one of the major reactions in this system. In contrast, the pH values of municipal wastewater under the relatively high voltage operations (5.0 and 7.0 V cm<sup>-1</sup>) are higher than those under low voltages. This presents that the commercial TiO<sub>2</sub> electrode indeed produces

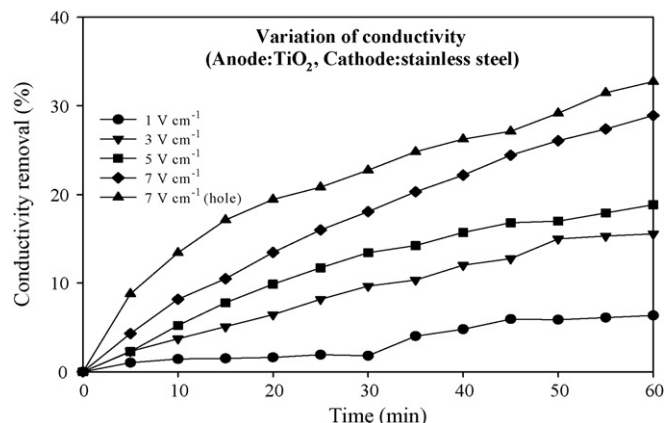


Fig. 6. The conductivity removal versus time under different voltage applications.

OH radicals, which results in higher pH values. Nevertheless, the municipal wastewater remains pH neutral ranges (from 7.5 to 8.0) during electro-catalytic treatments.

Referring to Fig. 6, it can be found that the conductivity elimination efficiency is in proportion to the voltage gradient. The original conductivity of the municipal wastewater is about 1650  $\mu\text{S cm}^{-1}$ . Except at 1.0 V cm<sup>-1</sup> (the conductivity elimination efficiency is about 6.4%), the conductivity elimination efficiency is remarkable 16%, 19% and 29% at other voltage gradients at 3.0, 5.0 and 7.0 V cm<sup>-1</sup> operation, respectively. Since some ions in the municipal wastewater could be reduced on the electrode surface, the conductivity of the municipal wastewater could be decreased. The conductivity of the municipal wastewater is mostly attributed to sodium chloride and sodium ions that cannot be electroplated on the cathode plate, the conductivity of the municipal wastewater remains to be of relatively high degree. It can be noticed that the TiO<sub>2</sub> electrode with punctured holes still results in the desirable treatment performance (decreased to 32%) when the voltage gradient is set at 7.0 V cm<sup>-1</sup>.

### 3.4. COD removal efficiency of different electrodes

Referring to Fig. 7, there are shown COD removal efficiencies with different electrodes used as the anode while the stainless plate is served as the cathode at the voltage gradient of 7.0 V cm<sup>-1</sup>. It should be noticed that all electrodes possess the same surface area except the electrode with nano-TiO<sub>2</sub>. In Fig. 7, it can be found that the COD removal efficiency is higher with the commercial TiO<sub>2</sub>

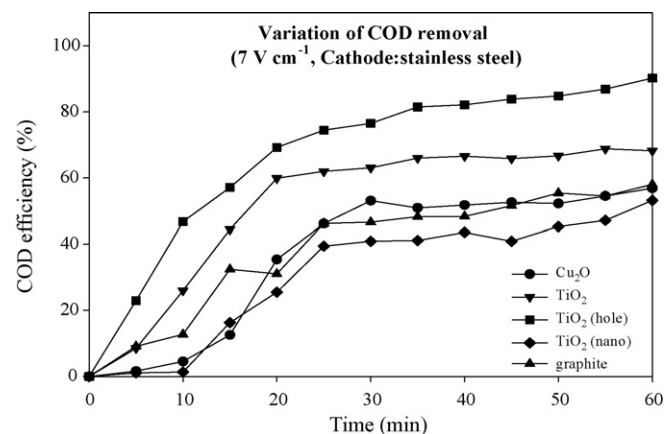


Fig. 7. The COD removal efficiency with different types of electrodes.

electrodes, perforated or not, than with the graphite and  $\text{Cu}_2\text{O}$  plates. However, the COD removal efficiency is lowest with the nano- $\text{TiO}_2$  electrode. The COD removal efficiencies are 90% with the perforated  $\text{TiO}_2$  plate, 62% with the  $\text{TiO}_2$  plate, 55% with the graphite and  $\text{Cu}_2\text{O}$  plates, and 53% with the nano- $\text{TiO}_2$  net. For all treatments by different electrodes, the COD removal efficiencies increase faster in the first 30 min than in the last 30 min. This implies that the diffusion mechanism still plays a significant role during the electrocatalytic decontamination. The higher COD removal efficiency with  $\text{TiO}_2$  can indirectly prove that organic pollutants are decomposed by OH radicals in addition to direct oxidation reactions on the electrode surface. As a consequence, the electro-catalytic process performs better COD removal than the regular electrolytic process. For the consideration of the nano- $\text{TiO}_2$  net, which results in the lowest COD removal efficiency among the electrodes; it may be attributed to its smallest electrode surface area. The small surface not only limits the current density but also the contacting possibility of organic pollutants. The impacts on the electricity efficiency of the COD removal efficiency need further studies.

### 3.5. pH and conductivity of different electrodes

Fig. 8 shows a pH trend of the municipal wastewater where various electrodes are used as the anode at the voltage gradient of  $7.0\text{ V cm}^{-1}$ . A general trend is found that the pH rises slowly except the graphite electrode. The pH rises especially fast where the nano-scale  $\text{TiO}_2$  net is used as the anode. It is speculated that the semiconductors,  $\text{TiO}_2$  and  $\text{Cu}_2\text{O}$ , produce electron-hole pairs, which react with water and produce a large amount of unstable hydroxyl radicals to cause pH rising. That is, the best electrocatalyst might be the nano-scale net-shaped  $\text{TiO}_2$  electrode. The reason why the COD removal efficiency of nano-scale  $\text{TiO}_2$  electrode is rather low can be attributed to its smaller surface area. For graphite plate, it is not a semiconductor (i.e., no hydroxyl radicals), which results in the relatively low pH. In the electrochemical process, the neutral pH can be maintained between 7 and 8.5.

Fig. 9 presents a conductivity trend of the municipal wastewater where various electrodes are used as the anode at the voltage gradient of  $7.0\text{ V cm}^{-1}$ . It is found that the conductivity decrease with operation time. In eliminating the conductivity, the nano-scale  $\text{TiO}_2$  net is better than other types of electrodes. The nano-scale  $\text{TiO}_2$  net,  $\text{TiO}_2$  plates, and graphite plate eliminates 42%, 28%, and 14% of the conductivity, respectively.

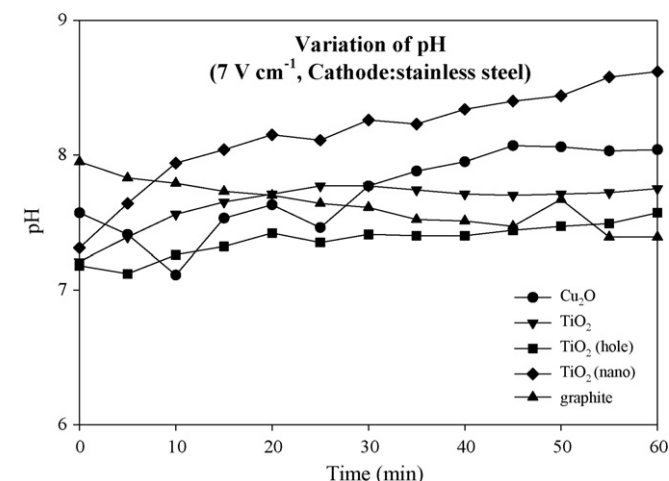


Fig. 8. The pH variation with different types of electrodes.

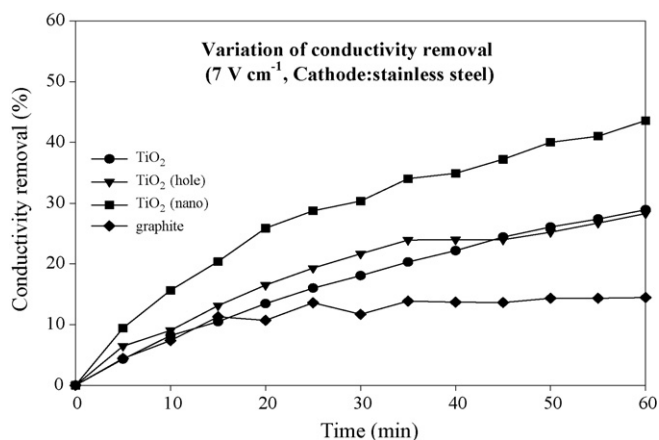


Fig. 9. The conductivity removal with different types of electrodes.

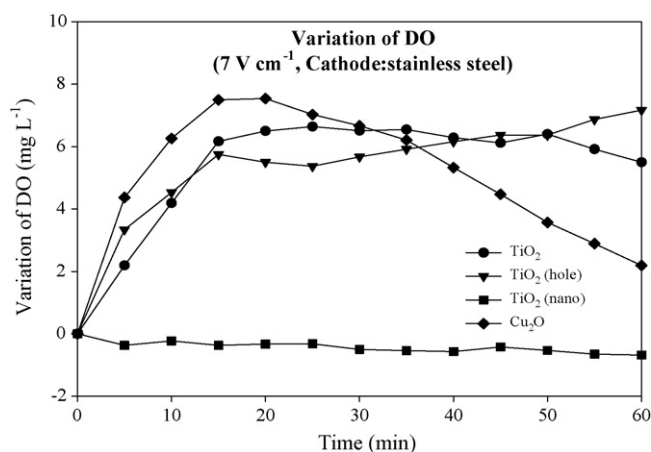


Fig. 10. The DO variation with different types of electrodes.

### 3.6. DO variation of different electrodes

Fig. 10 shows a DO trend with different electrodes application. The DO increases tremendously during the electro-catalytic process except nano-scale  $\text{TiO}_2$  net. Most of the increase occurs in the first 15 min and then stops increasing. For the commercial  $\text{TiO}_2$ , the DO increases to  $6\text{ mg L}^{-1}$  and maintains stably during 60-min treatment. Where the  $\text{Cu}_2\text{O}$  electrode is used, the DO increases to  $8\text{ mg L}^{-1}$  after 20-min treatment and decreases gradually. This phenomenon may result from the increasing temperature of the municipal wastewater because the DO solubility will decrease with increasing temperature. Where the nano-scale  $\text{TiO}_2$  net is used, the DO does not considerably increase. The speculation is that the oxygen produced by the water electrolysis cannot only be consumed by the electro-catalytic process (produce hydroxyl radicals) but also adsorbed into the nano-scale matrix (gas can be stored in the nano-scale materials). At the voltage gradient of  $5.0\text{ V cm}^{-1}$  (data not shown), the perforated  $\text{TiO}_2$  electrode also increases the DO to  $6\text{ mg L}^{-1}$ . This result implies that the factor of voltage gradients become insignificant as the DO concentration achieve saturation. In addition, the  $\text{TiO}_2$  without holes just increases the DO to  $4\text{ mg L}^{-1}$ . This presents the geometric structure indeed can affect the electro-catalytic process to some degree.

## 4. Conclusion

Based on experimental results, some conclusions can be drawn:

1. The nano- and nonnano-scale catalytic electrodes can effectively remove the organic pollutants in the municipal wastewater. The COD removal is not significant when the voltage gradient is too low such as 1.0 and 3.0 V cm<sup>-1</sup>. However, the COD removal is considerably enhanced when the voltage gradient is 5.0 or 7.0 V cm<sup>-1</sup>. The perforated TiO<sub>2</sub> electrode is the best for eliminating the COD, and its efficiency is about 90% (COD decreases from 400 to 40 mg L<sup>-1</sup>).
2. The electro-catalytic process will increase the pH and eventually stops regardless of nano- and nonnano-scale catalytic electrodes, however, the pH remains in the neutral range.
3. The conductivity of municipal wastewater can be lowered to some degrees and the efficiency in lowering the conductivity is proportional to the voltage gradient.
4. The electro-catalytic process may increase the DO in the municipal wastewater, which is beneficial to ecosystem. The DO in the municipal wastewater can be increased by the TiO<sub>2</sub> electrode (nonnano-scale) around 4–6 mg L<sup>-1</sup>, but few DO is produced by the nano-scale electrocatalytic electrode.

### Acknowledgement

This work was supported by National Science Council of Taiwan (Grant No. NSC 93-2211-E-324-008). Contents of this paper did not necessarily reflect the views of the funding agency.

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