The Enhanced PC and PEC Oxidation of Formic Acid in Aqueous Solution Using a Cu-TiO_2/ITO Film

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Abstract

The photocatalytic (PC) and photoelectrocatalytic (PEC) activity of Cu-TiO_2/ITO films for degrading formic acid in aqueous solution was investigated in this study. Compared with a TiO_2/ITO film, the degradation efficiency of formic acid on the Cu-TiO_2 films increased markedly in both the PC and PEC oxidation processes. However, it was found that the photodeposited Cu metal on the Cu-TiO_2 films could electrochemically dissolute during the PEC reaction, while an electrical bias with the voltage higher than 1.48 V was applied. It is believed this is a common problem occurred for several metals deposition on the TiO_2 films, which results in a poor stability of the metal-deposited TiO_2 electrode in PEC processes. To improve the stability of the Cu-TiO_2 electrode, an alternative process between PC and PEC reactions was investigated. It was found that the dissolute Cu metal during the PEC process was re-deposited on the Cu-TiO_2 film again during the PC process. The experiments with repeated runs demonstrated that this alternative process could not only overcome the loss of Cu, but also enhance the PEC oxidation efficiency of the Cu-TiO_2 films.

Keywords: Cu deposition; Formic acid; Photocatalysis; Photoelectrochemistry; TiO_2;

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1. Introduction

In past decades, heterogeneous photocatalysis using titanium dioxide (TiO_2) has attracted increasing attention in the field of environmental research for photodegradation of undesirable organics in aqueous phases (Fujishima et al., 2000; Ceńti et al., 2002). However, the photocatalytic (PC) oxidation efficiency is greatly limited by the high extent of electron-hole recombination. Recently, a lot of investigations have been devoted to improving PC oxidation activity of TiO_2 catalysts by depositing various noble metals (Sasaki et al., 2001; Subramanian et al., 2001; Boccuzzi et al., 2002; Kamat, 2002). In these cases, a Schottky barrier between the metal and TiO_2 is formed, while the metal and TiO_2 Fermi levels becomes equilibrium. Under light irradiation, the conduction band electrons flow from TiO_2 to the deposited metal that can act as a sink for the photogenerated electrons. This migration of the generated electrons to metal particles can extend the lifetime of holes by suppressing the electron–hole recombination, which favors the PC oxidation of organic pollutants (Sasaki et al., 2001; Boccuzzi et al., 2002; Paola et al., 2002). On the other hand, if the accumulated negative charges are not consumed or not further transferred out of the metal particles, some photogenerated positive holes will be attracted by negatively-charged metal particles that may become recombination centers (Sclafani and Hermann, 1998). In fact, it has been reported that the PC oxidation activity of some metallized TiO_2 systems was comparable to (Chen et al., 1999), or even less than that of native TiO_2 (Mu et al., 1989; Al-Sayyed et al., 1991), although it is generally believed that the PC activity of TiO_2 can be improved by metallization. Furthermore, if the positively-charged holes, negatively-charged metal particles, and organic substances exist in a same reaction system, it is possible that the organic substances and the intermediates of their degradation could be either oxidized by the holes or reduced by the metal deposits. For example, Wang et al. (1998) have once observed the photoreduction of methylene blue in an Au/TiO_2 system. On the basis of the above considerations, it is important to further transfer the electrons trapped on the metal deposits out of the reaction system to ensure the organic substances oxidation in the

systems. Photoelectrocatalytic (PEC) oxidation has been proven to be more efficient than PC oxidation by driving the photogenerated electrons to a counter electrode via an external circuit (Kim and Anderson, 1994; Vinodgopal et al., 1994; Pelegrini et al., 1999; Li et al., 2000; Byrne et al., 2002). The external bias applied between the two electrodes not only spatially separates the capture of conduction band electrons from the oxidation process (Byrne et al., 2002) but also drives away the photogenerated electrons accumulated on the metal particles to another compartment of cell. Consequently, the electron-hole recombination is reduced and the oxidation sites are separated from the reduction sites as well. Recently a lot of research has been directed to the PEC degradation of organic substances with TiO_2 films (Kim and Anderson, 1994; Vinodgopal et al., 1994; Pelegrini et al., 1999; Li et al., 2000; Arabatzis et al., 2003), but not many with metal-loaded TiO_2 films. Hence, it is worth to make a comprehensive study about the PEC activity on metal-loaded TiO_2 films. The PEC effectiveness of an Ag-TiO_2 film was investigated in our previous study (He et al., 2002).

Moreover, the TiO_2-based PC oxidation techniques need to be eventually applied in water and wastewater treatment (Weiss et al., 2001). In practice, it will be more attractive to employ some low-cost metals instead of noble metals to modify TiO_2 films. In this experiment, Cu was selected as an expected metal to modify TiO_2 films. Although the PC oxidation performance in Cu-TiO_2 powder systems has been investigated by different researchers (Hirano et al., 1997; Litter, 1999; Beydoun et al., 2002; Paola et al., 2002), the PC and PEC oxidation performance in Cu-loaded TiO_2 film systems has not been reported yet. In this study, a TiO_2 film was deposited with Cu metal by a photoreduction process and the PC and PEC activity of the Cu-TiO_2 films was evaluated in the degradation of formic acid as a model chemical in aqueous solution, since formic acid has no light absorption in the range of 320-400 nm and has no spontaneous evaporation from aqueous solution (Kim and Anderson, 1994). Furthermore, formic acid not only exists in some actual industrial wastewaters such as the effluents from tanners, dye workshops, and printed fabrics mills (Claudel et al., 1984), but also is one of stable intermediates in the mineralization of many organic

pollutants (Chou et al., 1998; Davis and Green, 1999; Dinsdale et al., 2000) with resistance to further oxidation (Ogata et al., 1981).

2. Experimental section

2.1. Preparation of TiO_2/ITO and Cu-TiO_2/ITO films

TiO_2 power (P25) was purchased from Degussa and the indium-tin oxide (ITO) conductive glass plates with a thickness of 1.3 mm were obtained from Shenzhen Nanya Technology Ltd. in China. TiO_2/ITO films were initially prepared according to the following procedure in the literature (Vinodgopal et al., 1993): 40 g of TiO_2 powder was added into 500 ml of deionzed water; The TiO_2 suspension was sonicated for 30 min to fully disperse the attached aggregates, and then vigorously agitated to form a suspension with fine TiO_2 particles; The TiO_2 particles in the suspension was coated on the ITO glass plate by dipping-casting. Then the TiO_2-coated ITO glass plate was dried for 15 min on a hot plate at 100 °C and then sintered in a muffle furnace at 400 °C for 2 h. The above coating, drying, and sintering were repeated three times until resulting TiO_2/ITO films were obtained. Then Cu-TiO_2/ITO films were prepared by a photoreduction process to deposit Cu on the TiO_2/ITO films. The photoreduction reaction was conducted in a PC reactor system as shown in Chamber A of Fig. 1, which consists of a 500-W high-pressure mercury lamp equipped with a double-walled quartz glass cooling tube and a rectangular quartz reactor (11.6 cm × 8.5 cm × 0.7 cm). The prepared TiO_2/ITO film (10.1 cm × 4.0 cm) was positioned inside the quarts reactor and immersed in solution containing 2 mM $CuSO_4$ and 10 mM formic acid with pH 4. The UV lamp had a maximum emission at 365 nm and the light intensity on the surface of TiO_2/ITO film was determined to be 2.1 mW cm^{-2} by a radiometer (UV-2000Z-MULTIBAND) from Hangzhou Instrument Ltd. Once the UV lamp was switched on, the photoreduction reaction was conducted and Cu was gradually deposited on the surface of the TiO_2/ITO film to result in the Cu-TiO_2/ITO films. The amount of Cu deposition was controlled by the illumination time.

2.2. Characterization of TiO_2/ITO and Cu-TiO_2/ITO films

The prepared TiO_2/ITO and Cu-TiO_2/ITO films were first examined by a spectrophotometer (UV-PC3101PC) from SHIMASZU in Japan with an integrating sphere (Specular Reflectance ATT.5DEG) to record the diffuse reflectance spectra (DRS), in which the baseline correction was done using a calibrated sample of barium sulfate. Both the TiO_2/ITO and Cu-TiO_2/ITO films were then examined by a scanning electron microscope (SEM, JSM-6330F). The films were further analyzed by X-ray diffraction (XRD) using a diffratometer (Rigaku, D/Max-IIIA) with radiation of Cu target ($K_\alpha 1$, λ = 1.54056 nm). Energy dispersive spectroscopy (EDS) was also obtained through a SEM (Hitachi, S-520) equipped with a link analyzer (Oxford, ISIS-300) to determine the amount of Cu deposition on the Cu-TiO_2/ITO films.

2.3. Experiments of PC and PEC oxidation

Formic acid chemical with analytical grade was supplied by Guangzhou Chem. Co. and used as a model chemical in this study. 10 mM formic acid solution was first prepared with an initial COD (Chemical oxygen demand) concentration of 157 mg l^{-1} and pH 2.73. About 35.0 ml of the 10 mM formic acid solution was used in both the PC and PEC reactions. The pH of the solution was adjusted by sodium hydroxide to 4 before the experiment and was not control during the reaction. The PC oxidation experiment was carried out in the PC reactor as shown in Fig. 1 (Chamber A), once the UV lamp was switched on and air bubbling was continuously provided. The PEC oxidation experiment was conducted with two chambers together as shown in Fig. 1. The two chambers (A and B) were connected via a salt bridge. To conduct PEC reaction, either a TiO_2/ITO or Cu-TiO_2/ITO plate was used as an anodic electrode, and a Pt electrode and saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. In the meantime, an electrical bias between the anodic and cathodic electrodes was applied by a potentiostat (Model CH 650).

2.4. Analytical method

COD was measured by the standard method (APHA, 1995). The degradation of

formic acid in aqueous solution during the PC and PEC oxidation was determined with COD variation. The Cu^{2+} concentration in aqueous solution was analyzed using ICP-AES (Perkin-Elmer Optima 3300DV).

3. Results and discussion

3.1. Characterization of TiO_2/ITO and Cu-TiO_2/ITO films

The quantity of TiO_2 loaded on the ITO plates was determined in the range of 0.94–1.00 mg cm^{-2} by weighing. To study morphology, the prepared TiO_2/ITO and Cu-TiO_2/ITO films were examined by SEM. From the SEM results, it was estimated that the TiO_2 film formed on the ITO plates had a thickness between 2–3 μm and the TiO_2 particle size of around 50 nm. Four SEM images of the TiO_2/ITO film and the Cu-TiO_2/ITO films generated at the photoreaction time of 5, 10, and 20 min are presented in Figs. 2a, 2b, 2c, and 2d, respectively. These SEM images showed the porous-structured surfaces similar to that reported by Vinodgopal and Kamat (1996). It can be seen that the Cu deposits formed in the early stage (5 min) were small in size and mainly filled in the gaps between TiO_2 particulates. As the photoreduction reaction was extended, the amount of Cu deposition increased significantly and the size of Cu deposits also enlarged. However, the Cu deposits were not uniformly spread over the whole surface of TiO_2 film. It seems that the Cu deposits generated in the later stage were more easily situated on the Cu deposits generated in the early stage. Furthermore, the image in Fig. 2c demonstrated that these bigger Cu crystals possessed a well-defined cubic morphology, different from the prismatic crystals reported by Ramanathan et al. (1997). However, the reason causing this morphology difference remains still unclear so far.

It was observed that there was a red layer on the surface of the Cu-TiO_2/ITO film, which was different from that of the TiO_2/ITO film. It was believed that the red layer resulted from the deposition of Cu from the photoreduction reaction. However, the photoreduction products of copper ion (Cu^{2+}) could be either copper metal (Cu^0) or/and Cu_2O (Cu^+). To further identify the composition of the prepared Cu-TiO_2/ITO films, a XRD examination was conducted and the analytical results are shown in Fig. 3. The

XRD results demonstrated that both anatase and rutile TiO_2 existed on the films, but anatase was dominated. It should be noted there are three peaks at 2θ angles of 43.280°, 50.420°, and 74.080°, corresponding to the *d*-values of 2.0887, 1.8084, and 1.2787, respectively, which represent metallic Cu (Cu^0) in accordance with the results by others (Wang et al., 2003; Zou et al., 2003). These results indicated that copper ion (Cu^{2+}) was reduced rather to copper metal (Cu^0) than to Cu_2O (Cu^+) during the photoreduciton reaction in this experiment.

An EDS analysis was carried out to determine the amount of the Cu deposition on the surface of TiO_2/ITO films. The results indicated that the amount of Cu on the three Cu-TiO_2/ITO films prepared at the photoreaction time of 5, 10, and 20 min were of 0.4%, 1.5%, and 2.0% (Wt. Cu/Wt. TiO_2), respectively. The EDS results also confirmed that more Cu was deposited when the time of photoreduction reaction was postponed. It was found that depositing rate of Cu on the TiO_2 surface was accelerated during the later stage of the photoreduction process. It is believed that the initially photodeposited Cu particles acted as crystallized nucleus and behaved like electron sinks to which photogenerated electrons could be spontaneously transferred so that the subsequent photodeposition of Cu occurred more readily on the surfaces of these primary Cu deposits than on that of TiO_2 particulates. It may be also a potential indication that the copper metal, like other noble metals, existing on the TiO_2 surface could improve the separation of photogenerated electron and hole efficiently.

3.2. PC oxidation

The PC oxidation activity of the TiO_2/ITO and Cu-TiO_2/ITO films was evaluated in the degradation of formic acid in aqueous solution in term of COD removal. A set of PC oxidation tests was carried out in formic acid solution with the initial COD concentration of 157 mg l^{-1} using different Cu-TiO_2/ITO films. All tests lasted for 60 min and the results are shown as the curve B in Fig. 4a. It can be seen that the COD removal efficiency was significantly affected by the amount of Cu deposition. The COD removal increased with the increase of Cu deposition initially and then achieved a

maximum value gradually. Once the amount of Cu deposition was further increased, the COD removal began to decrease. The experiment demonstrated that the Cu-TiO_2/ITO film with 1.5% Cu achieved the best performance in terms of COD removal (53%), which was significantly higher than that of TiO_2/ITO film (39%). These results indicated that the 1.5% Cu deposited on the TiO_2 film was an optimum dosage on the Cu-TiO_2/ITO film. Consequently, the Cu-TiO_2/ITO film with 1.5% Cu was applied in the following experiments.

To better understand the dependence of COD removal efficiency on the amount of Cu deposition, the open circuit photovoltage (V_{oc}) of the Cu-TiO_2/ITO films with different Cu amounts was determined using the potentiostat under UV illumination. The results of V_{oc} vs. the amount of Cu deposition are presented in Fig. 4b. It can be clearly seen that the V_{oc} decreased with the increase of the amount of Cu deposition first and then increased once the amount of Cu deposition exceeded 1.5%. In this experiment, a minimum V_{oc} of - 0.53 V was obtained with about 1.5% Cu on the TiO_2/ITO film. Generally speaking, the magnitude of V_{oc} represents the energy difference between the Fermi level of semiconductor film and the reduction potential of the redox couple in the solution. Any accumulation of electrons in the TiO_2 film would shift the Fermi level to more negative potential, leading to a more negative V_{oc}. The observed shift of V_{oc} to negative direction in this study denoted that these deposited Cu could increase the accumulation of photogenerated electrons. In this case, the deposited Cu acted as an electron sink, which was beneficial to PC oxidation of organics. The positive shift of V_{oc} is consistent with the fact that the effect of blocking light of the excessive Cu deposition decreased the effective area of illumination on the TiO_2 film and the number of the subsequent photogenerated electrons correspondingly, that was detrimental to PC oxidation. The most negative value of V_{oc} represented a balance result of the above two effects. Based on the above experimental results, the Cu-TiO_2/ITO film with 1.5% Cu achieved the most negative value of V_{oc}, which was well-matched with the optimum amount found in the PC oxidation reaction. These results may imply that the optimum amount of Cu deposition on the TiO_2 film depends

on a balance between the photocatalytic activity promotion effect and light blocking effect in the photocatalytic reaction.

In addition, the TiO_2/ITO and Cu-TiO_2/ITO films were analyzed by DRS and the analytical results are shown in Fig. 5. In which, the curves A, B, and C represent the DRS of the Cu-TiO_2/ITO films formed in the early stage of photoreduction process at 0, 2, and 5 min, respectively. It can be seen that a main peak at 406.5 nm dropped dramatically within the first 5 min. The curves D, E, F, and G represent the DRS of the Cu-TiO_2/ITO films formed in the later stage of photoreduction process at 10, 20, 30, and 40 min, respectively. It was found that the DRS increased gradually particularly in the longer region of > 600 nm. It should be indicated that the curve D representing the photoreduction time of 10 min behaved as a turning point. It is very interesting that this critical photoreduction time of 10 min was just corresponded to the production of Cu-TiO_2/ITO film with 1.5% Cu.

However, it is uncertain at this moment whether there is a similar corresponding relation between the optimal amount of metal deposition and the turning point of the reflectance spectra for other metal-TiO_2 films as well, in other words, whether the turning point can be considered as a criterion of the optimal amount of metal deposition. A further investigation regarding this phenomenon is recommended.

3.3. PEC oxidation

Compared with the PC oxidation, the PEC experiment was also conducted in the two-chamber photoreactor system as shown in Fig. 1. In which, the Cu-TiO_2/ITO films with different amount of Cu deposition were applied as an anodic electrode and a Pt plate was used as a catholic electrode. In the meantime, an electrical bias of 0.8 V vs. SCE was applied to anodic electrode. The COD removal in formic acid solution was investigated and the experimental results are shown as the curve A in Fig. 4a. It can be seen that the COD removal efficiency of the PEC process was significantly higher than that of the PC process. It was found that the Cu-TiO_2/ITO film with 1.5% Cu achieved the best COD removal efficiency of 67% in the PEC process, while was only 53% in the PC process. It was also confirmed that all the Cu-TiO_2/ITO films performed better

than the TiO_2/ITO film in this PEC reaction system, which implies that the deposited Cu can not only trap the photogenerated electrons but also assist the external electric field to migrate these electrons from the Cu-TiO_2/ITO film to the counter electrode in another chamber of the reactor.

To study the effects of applied bias on the photocatalytic performance in the PEC reaction system, both the TiO_2/ITO and Cu-TiO_2/ITO films with 1.5% Cu were used to conduct formic acid degradation by applying different anodic bias in the range of 0-9.1 V. Both sets of experimental results are presented in Fig. 6. The experiment confirmed that the COD removal efficiency in the PEC oxidation process was generally better than that in the PC oxidation process in the whole range of 0-9.1 V. But the curves A and B demonstrated the different behaviors affected by anodic bias. The COD removal with the TiO_2/ITO electrode increased rapidly at the lower range of anodic bias between 0-0.8 V and further increased slowly once the anodic bias was higher than 2 V vs. SCE. The dependence of COD removal efficiency on the applied anodic bias in this study was found to be similar to that reported by Candal et al. (2000). However, although the COD removal with the Cu-TiO_2/ITO electrode also increased quickly at the lower range of anodic bias, it decreased rapidly while the anodic bias exceeded 0.8 V vs. SCE. This result indicated that there was an optimum bias using the Cu-TiO_2/ITO electrode in the formic acid degradation with a very sensitive effect. The anodic bias of 0.8 V vs. SCE was found to be the optimum voltage in this experimental condition, which achieved a maximum COD removal of 67%.

The enhancement of COD removal efficiency in the experiments can be ascribed to that the externally applied anodic bias drives away the photogenerated electrons accumulated on Cu deposits via the external circuit, thus reducing the recombination of photogenerated electrons and holes and promoting the oxidation of formic acid. The decrease in COD removal efficiency at the higher range of anodic bias was probably due to the electrochemical oxidation of Cu, leading to Cu dissolution from the Cu-TiO_2/ITO surface, since the voltage of the applied anodic bias was higher than the reduction potential of Cu ($E^0_{Cu^{2+}/Cu} = 0.345$ V) (Latimer, 1952).

The above phenomenon was only found on the basis of single-run experiment using

the Cu-TiO_2/ITO film. From an engineering point of view, stability of the Cu-TiO_2/ITO electrode used in water and wastewater treatment must be counted as one of critical factors. Therefore, three sets of tests using the Cu-TiO_2/ITO electrode were carried out to degrade formic acid in aqueous solution by applying different anodic bias of 0 V as PC oxidation, 0.8 and 4.2 V as PEC oxidation. Each test lasted for 60 min. Under each experimental condition, the same Cu-TiO_2/ITO electrode was repeatedly used for 5 times and the COD removal efficiency was determined respectively as shown in Fig. 7. The curve D in Fig. 7 representing the PC oxidation process (no bias applied) demonstrated the COD removal efficiency was well maintained after 5 times runs. However, it was found the COD removal efficiency in the PEC oxidation process by applying the bias of 0.8 and 4.2 V (Curves B and C) decreased gradually, once the number of runs increased. It can be seen that more deduction of COD removal efficiency with a higher anodic bias of 4.2 than that of 0.8 V. Consequently, the EDS examination was conducted again to determine the Cu content on the Cu-TiO_2/ITO film. It was found Cu content decreased from 1.5% to 0.4% after 5 batch runs with application of 4.2 V anodic bias. In the resulting solution of the fifth run, the concentration of Cu^{2+} residual was found to be 1.92 mg l^{-1}. The surface morphology of the used Cu-TiO_2/ITO film was also examined by SEM and the images before and after the PEC reaction are shown in Fig. 8. It can be compared that the Cu crystals in Fig. 8b became much smaller than those in Fig. 8a with a significant change in shape. These results confirmed the existence of Cu dissolution from the Cu-TiO_2/ITO film in the PEC process, while an anodic bias applied was higher than 0.8 V.

3.4. Alternation between PC and PEC oxidation

To overcome the electrochemical dissolution of Cu from the Cu-TiO_2/ITO film, an alternative process between the PC and PEC oxidation was investigated. This approach is based on the fact that Cu^{2+} ions are easily photo-reduced in absence of anodic bias. Thereby, if an electrical bias between two electrodes in the reactor system was switched on to conduct a PEC process and alternatively switched off to conduct a PE process, it would be possible that the electrochemically dissolved Cu^{2+} ions in the PEC process are

photo-reduced and re-deposited on the Cu-TiO_2/ITO film again in the PC process. Therefore, five experiments were conducted by combining PC and PEC oxidation with different cycles of: (A) 60-min PEC only; (B) 5-min PC + 5-min PEC; (C) 2.5-min PC + 2.5-min PEC; (D) 4-min PEC + 1-min PC; and (E) 1-min PEC + 4-min PC. In the experiments, an electrical bias of 4.2 V was applied to the anodic electrode and each run lasted for 60 min. The experimental results in terms of COD removals are shown in Fig. 9. It was found that the COD removal efficiency in all alternative processes was higher than that (Column A) in the PEC process only. However, the extent of enhancement varied with different alternative cycles. From the experimental results, it seems that a higher COD removal efficiency could be achieved by using two intervals close to each other. For example, the alternative process of 2.5-min PEC and 2.5-min PC achieved the COD removal by 70% (Column C) after 60 min. This alternative process was repeated for 5 times and it was also observed that the COD removal efficiency remained constantly as the curve A in Fig. 7. The Cu-TiO_2/ITO film after 5 times use in the alternative process was finally analyzed by EDS again. The analytical results demonstrated that amount of 1.45% Cu was found on the TiO_2/ITO film, which was very close to its initial amount of 1.5% and much higher than 0.4% Cu determined in the previous PEC process. In the resulting solution of the fifth run, no Cu^{2+} ion was detected with the ICP-AES analysis (detection limit = 0.006 mg l^{-1}). These findings demonstrated that the Cu deposits on the surface of Cu-TiO_2/ITO film did experience the dissolution and deposition repeatedly in the alternative process.

4. Conclusion

This study has confirmed that the photocatalytic activity of a TiO_2 film in the PC and PEC oxidation processes can be improved by photodepositing Cu metal on its surface through a photoreduction process. However, the electrochemical dissolution of the deposited metals on TiO_2 film would be a technical problem in PEC oxidation processes, if they have a target to be applied in practice for water and wastewater treatment. A new process developed in this study to alternate PC and PEC processes intermittently may provide a positive approach to well maintain the metal deposits on

the TiO_2 films.

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Literature cited

Al-Sayyed, G., D'Oliveira, J.C., Pichat, P., 1991. Semiconductor-sensitized photodegradation of 4-chlorophenol in water. J. Photochem. Photobiol. A: Chem. 58, 99-114.

APHA 1995. Standard methods for the examination of water and wastewater, 20th. ed., American Public Health Association, Washington D. C.

Arabatzis, I.M., Stergiopoulos, T., Bernard, M.C., Labou, D., Neophytides, S.G., Falaras P., 2003. Silver-modified titanium dioxide thin films for efficient photodegradation of methyl orange. Appl. Catal. B 42, 187-201.

Beydoun, D., Tse, H., Amal, R., Low, G., McEvoy, S., 2002. Effect of copper (II) on the photocatalytic degradation of sucrose. J. Mol. Catal. A: Chem. 177, 265-272.

Boccuzzi, F., Chiorino, A., Manzoli, M., Andreeva, D., Tabakova, T., Ilieva, L., Iadakiev, V., 2002. Gold, silver and copper catalysts supported on TiO_2 for pure hydrogen production. Catal. Today 75, 169-175.

Byrne, J.A., Davidson, A., Dunlop, P.S.M., Eggins, B.R., 2002. Water treatment using nano-crystalline TiO_2 electrodes. J. Photochem. Photobiol. A: Chem. 148, 365-374.

Candal, R.J., Zeltner, W.A., Anderson, M.A., 2000. Effects of pH and applied potential on photocurrent and oxidation rate of saline solutions of formic acid in a photoelectrocatalytic reactor. Environ. Sci. Technol. 34, 3443-3451.

Ceńti, G., Ciambelli, P., Perathoner, S., Russo, P., 2002. Environmental catalysis: trends and outlook. Catal. Today 75, 3-15.

Chen, J., Ollis, D.F., Rulkens, W.H., Bruniing, H., 1999. Photocatalyzed oxidation of alcohols and organochlorides in the presence of native TiO_2 and metallized TiO_2 suspensions. Part (I): photocatalytic activity and pH influence. Wat. Res. 33, 661-668.

Chou, S., Huang, Y.H., Lee, S.N., Huang, G.H., Huang, C., 1998. Treatment of high strength hexamine-containing wastewater by electro-Fenton method. Wat. Res. 33, 751-759.

Claudel, B., Nueilati, M., Andrieu, J., 1984. Oxidation of formic-acid in aqueous-solution by palladium catalysts. Appl. Catal. 11, 217-225.

Davis, A.P., Green, D.L., 1999. Photocatalytic oxidation of cadmium-EDTA with titanium dioxide. Environ. Sci. Technol. 33, 609-617.

Dinsdale, R.M., Hwkes, F.R., Hawkes, D.L., 2000. Anaerobic digestion of short chain organic acids in an expanded granular sludge bed reactor. Wat. Res. 34, 2433-2438.

Fujishima, A., Rao, T.N., Tryk, A., 2000. Titanium dioxide photocatalysis. J. Photochem. Photobiolo. C: Photochem. Rev. 1, 1-21.

He, C., Xiong, Y., Zhu, X.H., 2002. A novel method for improving photocatalytic activity of TiO_2 film: the combination of Ag deposition with application of external electric field. Thin Solid Films 422, 235-238.

Hirano, K., Asyama, H., Hoshino, A., Wakatsuki, H., 1997. Metal powder addition effect on the photocatalytic reactions and the photo-generated electric charge collected at an inert electrode in aqueous TiO_2 suspensions. J. Photochem. Photobiol. A: Chem. 110, 307-311.

Kamat, P.V., 2002. Photophysical, photochemical and photocatalytic aspects of metal nanoparticles. J. Phys. Chem. B 106, 7729-7744.

Kim, D.H., Anderson, M.A., 1994. Photoelectrocatalytic degradation of formic-acid using a porous TiO_2 Thin-film electrode. Environ. Sci. Technol. 28, 479-483.

Latimer, W.M. (2nd ed.), 1952. Oxidation potentials. Prentice-Hall, New York.

Li, X.Z., Liu, H.L., Yue, P.T., Sun, Y.P., 2000. Photoelectrocatalytic oxidation of rose bengal in aqueous solution using a Ti/TiO_2 mesh electrode. Environ. Sci. Technol. 34, 4401-4406.

Litter, M.I., 1999. Heterogeneous photocatalysis: transition metal ions in photocatalytic systems. Appl. Catal. B 23, 89-114.

Mu, W., Herrmann, J.M., Pichat, P., 1989. Room-temperature photocatalytic oxidation of liquid cyclohexane into cyclohexanone over neat and modified TiO_2. Catal. Lett. 3, 73-84.

Ogata, Y., Tomizawa, K., Takagi, K., 1981. Photo-oxidation of formic, acetic, and propionic acids with aqueous hydrogen-peroxide. Can. J. Chem. 59, 14-18.

Paola, A.D., Garcia-Lopez, E., Ikeda, S., Marci, G., Ohtani, B., Palmisano, L., 2002. Photocatalytic degradation of organic compounds in aqueous systems by transition metal doped polycrystalline TiO_2. Catal. Today 75, 87-93.

Pelegrini, R., Perqlta-Zamora, P., Andrade, A.R., Reyes, J., Duran, N., 1999. Electrochemically assisted photocatalytic degradation of reactive dyes. Appl. Catal. B 22, 83-90.

Ramanathan, K., Avnir, D., Modestov, A., Lev, O., 1997. Sol-gel derived ormosil-exfoliated graphite-TiO_2 composite floating catalyst: photodeposition of copper. Chem. Mater. 9, 2533- 2540.

Sasaki, T., Koshizaki, N., Yoon, J.W., Beck, K.M., 2001. Preparation of Pt/TiO_2 nanocomposite thin films by pulsed laser deposition and their photoelectrochemical behaviours. J. Photochem. Photobiolo. A: Chem. 145, 11-16.

Sclafani, A., Hermann, J.M., 1998. Influence of metallic silver and of platinum-silver bimetallic deposits on the photocatalytic activity of titania (anatase and rutile) in organic and aqueous media. J. Photochem. Photobiolo. A: Chem. 113, 181-188.

Subramanian, V., Wolf, E., Kamat, P.V., 2001. Semiconductor-metal composite nanostructures: to what extent do metal nanoparticles improve the photocatalytic activity of TiO_2 films? J. Phys. Chem. B 105, 11439-11446.

Vinodgopal, K., Stafford, U., Gray, K.A., Kamat, P.V., 1994. Electrochemically assisted photocatalysis. 2. The role of oxygen and reaction intermediates in the degradation of 4-chlorophenol on immobilized TiO_2 particulate films. J. Phys. Chem. 98, 6797 – 6803.

Vinodgopal, K., Hotchandani, S., Kamat, P.V., 1993. Electrochemically assisted

photocatalysis: titania particulate film electrodes for photocatalytic degradation of 4-chlorophenol. J. Phys. Chem. 97, 9040- 9044.

Vinodgopal, K., Kamat, P.V., 1996. Combine electrochemistry with photocatalysis. CHEMTECH 26, 18-22.

Wang, C.Y., Liu, C.Y., Zheng, X., Chen, J., Shen, T., 1998. The surface chemistry of hybrid nanometer-sized particles I. Photochemical deposition of gold on ultrafine TiO_2 particles. Colloids Surf. A: Physicochem. Eng. Aspects 131, 271-280.

Wang, Z., Wang, W., Lu, G., 2003. Studies on the active species and on dispersion of Cu in Cu/SiO_2 and $Cu/Zn/SiO_2$ for hydrogen production via methanol partial oxidation. Int. J. Hydrogen Energy., 28, 151-158.

Weiss, H., Fernadez, A., Kisch, H., 2001. Electronic semiconductor-support interaction - a novel effect in semiconductor photocatalysis. Angew. Chem. Int. Ed. 40, 3825.

Zou, W.Y., Cai, Q., Cui, F.Z., Li, H.D., 2003. Electrochemical synthesis and characterization of mesoporous Cu/Cu_2O films. Mater. Lett. 57, 1934-1940.

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Fig. 1

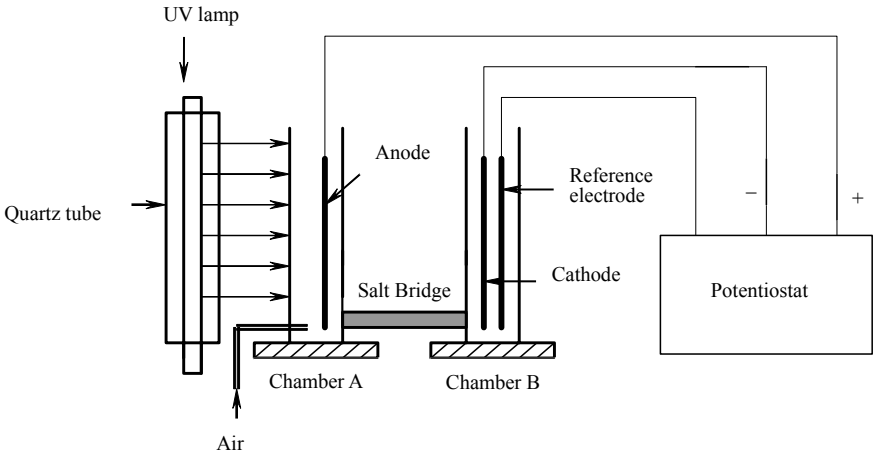
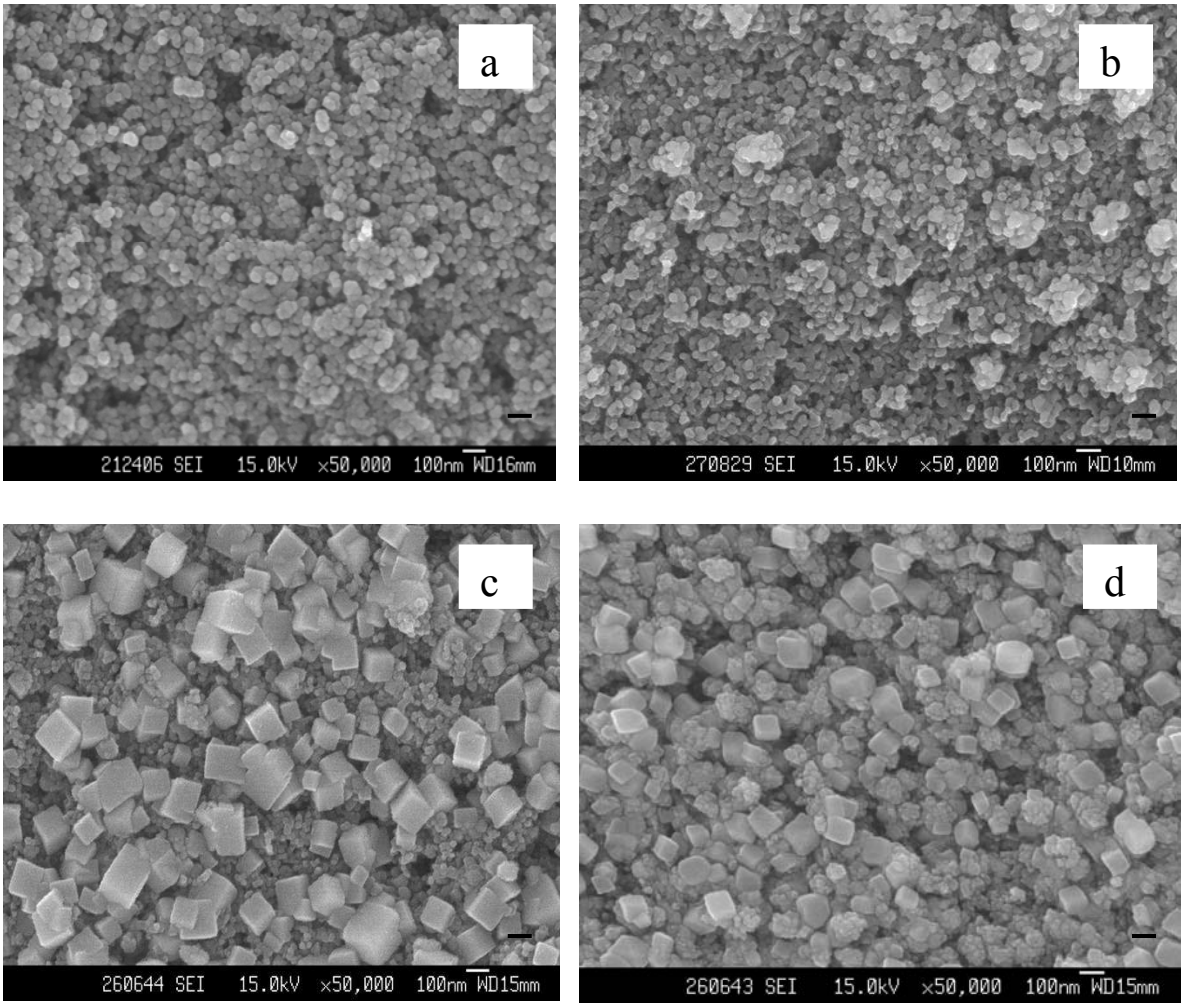

UV lamp
Quartz tube
Anode
Reference electrode
−
+
Salt Bridge
Cathode
Potentiostat
Chamber A
Chamber B
Air

Fig. 2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212406 SEI 15.0kV ×50,000 100nm WD16mm
b
270829 SEI 15.0kV ×50,000 100nm WD10mm
c
260644 SEI 15.0kV ×50,000 100nm WD15mm
d
260643 SEI 15.0kV ×50,000 100nm WD15mm

Fig. 3

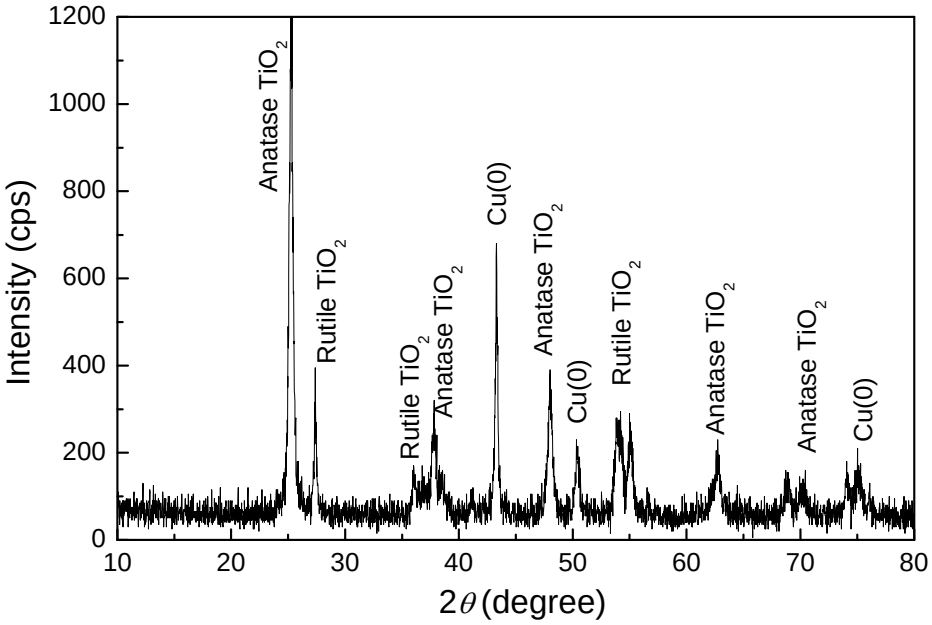

Intensity (cps)
2θ (degree)
Anatase TiO2
Rutile TiO2
Rutile TiO2
Anatase TiO2
Cu(0)
Anatase TiO2
Cu(0)
Rutile TiO2
Anatase TiO2
Anatase TiO2
Cu(0)

Fig. 4

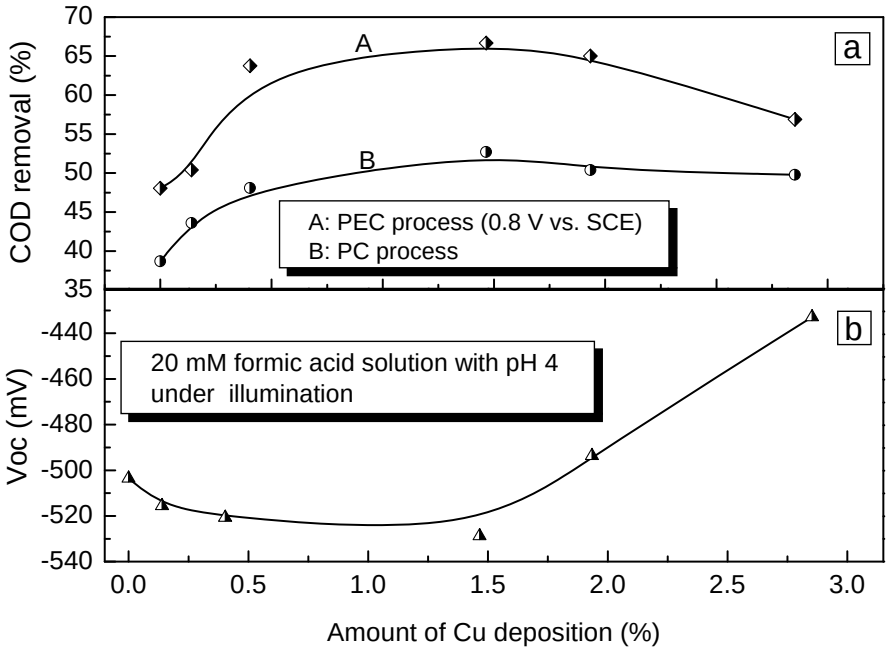

COD removal (%)
70
65
60
55
50
45
40
35
A
B
a
A: PEC process (0.8 V vs. SCE)
B: PC process
Voc (mV)
-440
-460
-480
-500
-520
-540
b
20 mM formic acid solution with pH 4
under illumination
0.0
0.5
1.0
1.5
2.0
2.5
3.0
Amount of Cu deposition (%)

Fig. 5

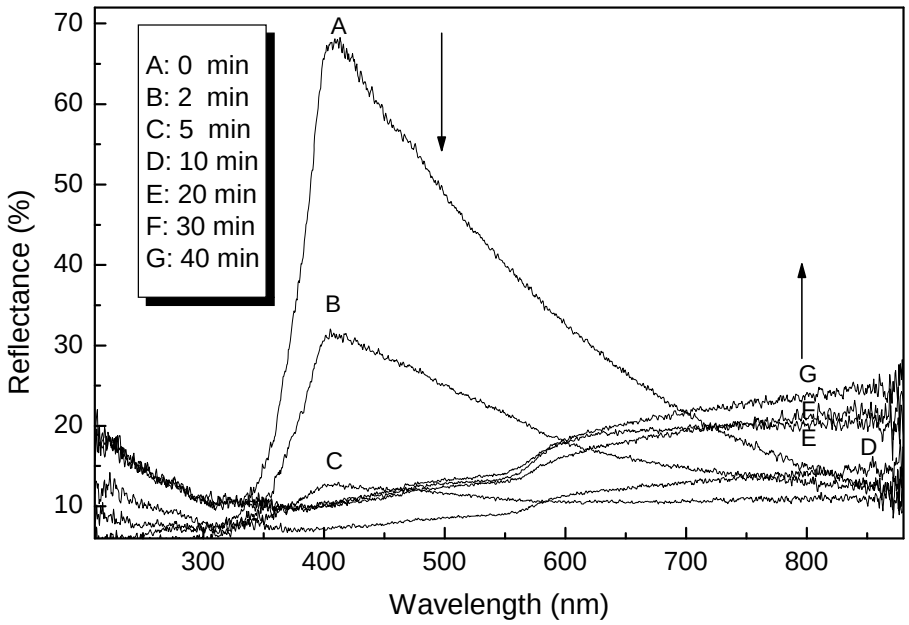

A: 0 min
B: 2 min
C: 5 min
D: 10 min
E: 20 min
F: 30 min
G: 40 min
A
B
C
D
E
F
G
Reflectance (%)
Wavelength (nm)
70
60
50
40
30
20
10
300
400
500
600
700
800

Fig. 6

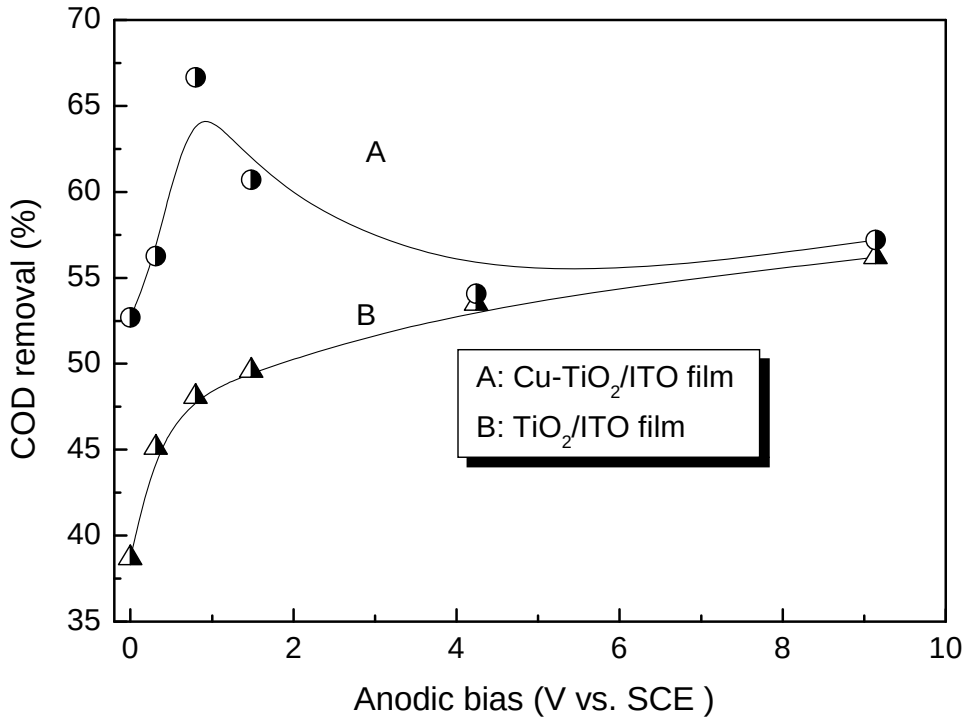

COD removal (%)
Anodic bias (V vs. SCE)
A
B
A: Cu-TiO2/ITO film
B: TiO2/ITO film
70
65
60
55
50
45
40
35
0
2
4
6
8
10

Fig. 7

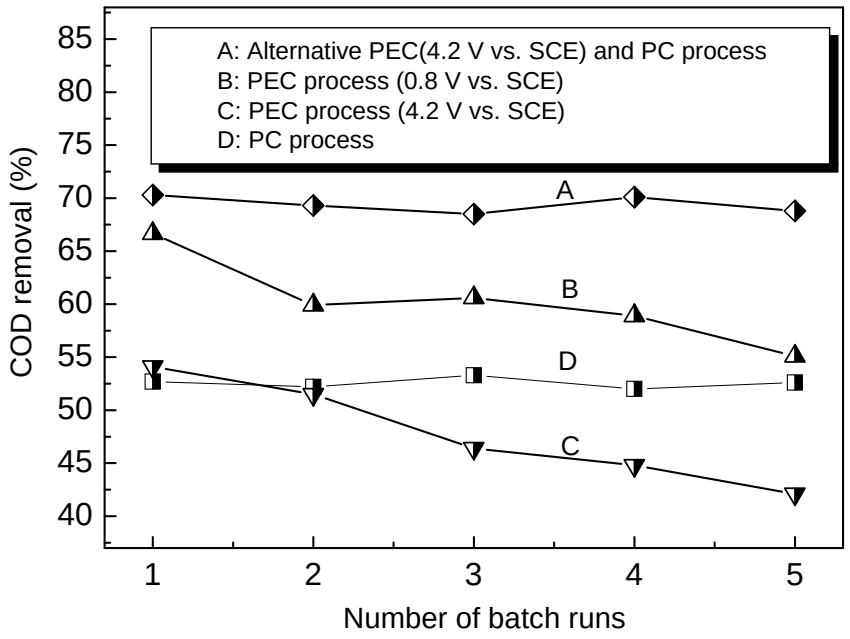
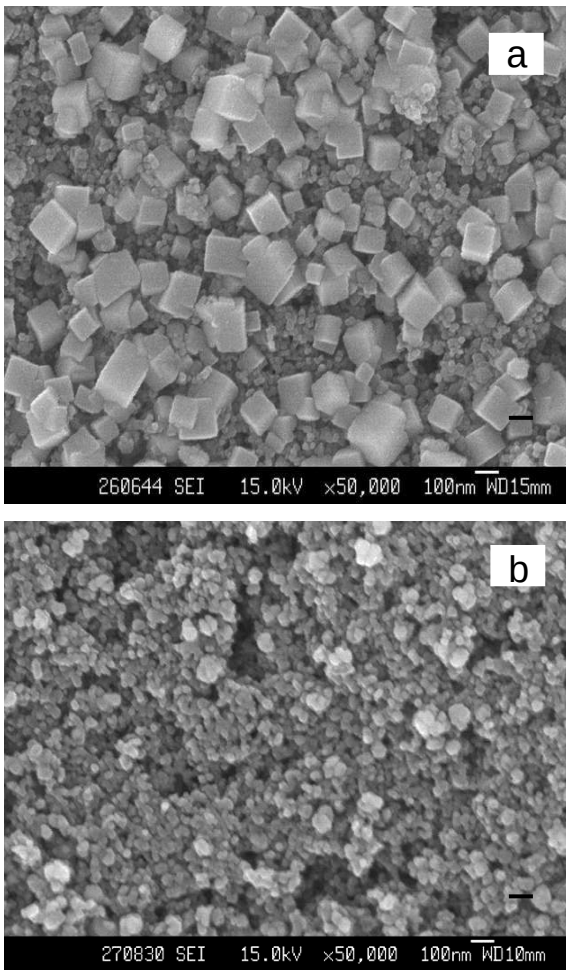

A: Alternative PEC(4.2 V vs. SCE) and PC process
B: PEC process (0.8 V vs. SCE)
C: PEC process (4.2 V vs. SCE)
D: PC process
A
B
C
D
COD removal (%)
Number of batch runs
85
80
75
70
65
60
55
50
45
40
1
2
3
4
5

Fig.8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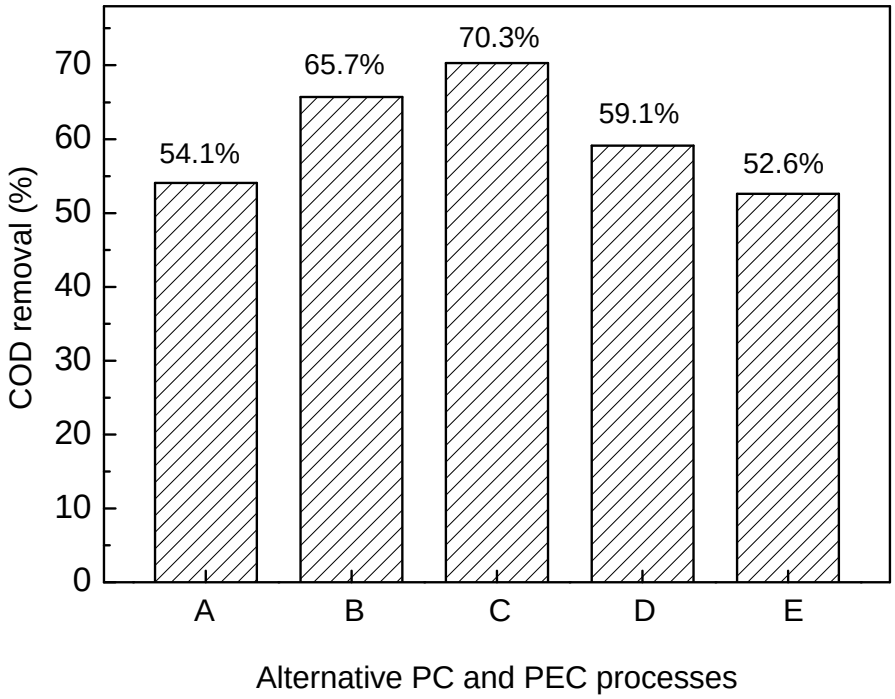
260644 SEI 15.0kV x50,000 100nm WD15mm
b
270830 SEI 15.0kV x50,000 100nm WD10mm

Fig. 9


COD removal (%)
0
10
20
30
40
50
60
70
54.1%
65.7%
70.3%
59.1%
52.6%
A
B
C
D
E
Alternative PC and PEC processes