Environmental and Medical Applications of TiO₂ Photocatalysts and Boron-doped Diamond Electrodes

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ABSTRACT
This paper summarized the author’s recent studies about effective design of the systems for environmental and dental application of TiO₂ photocatalysts and boron-doped diamond (BDD) electrodes. The titanium mesh impregnated photocatalyst, TMiP™ has been fabricated as a novel photocatalytic filter. The high mechanical flexibility of TMiP allows us to design any geometry of modules by combination of UV-sources and the other technologies. In this paper, a practical air-cleaner using the TMiP-plasma synergistic reactor was fabricated and installed in a real-scale smoking room in the office. The amounts of the compounds in tobacco smoke were almost totally removed by the air-cleaner. On the other hands, the author also reported the possibilities of wastewater treatments by electrolysis with BDD electrodes. Based on these studies, a novel pinpoint ozone-water production unit for dental treatment using of BDD microelectrodes was developed. The unit showed almost the same sterilization ability as conventional 20 ppm of aqueous sodium hypochlorite treatment in in vitro assessment in the root-canal of bovine teeth. These results present several key solutions for practical applications of TiO₂ photocatalysis and BDD electrolysis.

Keywords : TiO₂ Photocatalysts, Boron-doped Diamond Electrodes, Environmental Purification, Dental Treatment

1. Introduction

TiO₂ photocatalysts can decompose organics, contaminants, and bacteria into the less harmful CO₂ and H₂O with its strong oxidation ability under UV light irradiation.1–4 Recently, application of photocatalysts for environmental purification has received growing attention. This trend can be observed in the market growth of industries related to photocatalysis (Fig. 1). Under these circumstance, and by comprehensive reviewing of the research, the author summarized several key requirements for an effective photocatalytic environmental purification as follows:5

i. Catalyst immobilization strategy for a cost-effective solid-liquid separation
ii. Integrated or coupling system for enhanced photo-mineralization or photo-disinfection kinetics
iii. Effective design of photocatalytic reactor system

Especially effective design of photocatalytic reactor system is the most important. Although the operation conditions (pH, temperature, and gas or water quality) also affect the efficiency, reactive surface area and mass transfer in the system are more important in many cases. Therefore, the reactor design for effective photocatalytic environmental purification can be classified into two main strategies: (1) enlargement of reactive surface area and (2) improvement of mass transfer.

On the other hands, electrolysis with boron-doped diamond (BDD) electrodes can also decompose organics. The wide potential window of BDD electrodes makes it possible to generate various highly active oxidants such as ozone which can oxidize aqueous contaminants and waterborne pathogens efficiently.6,7 Therefore, TiO₂ photocatalysts and BDD electrodes have a great advantage for environmental applications and disinfections.

Based on these backgrounds, this paper summarizes recent studies for effective design of the systems for environmental and dental application of TiO₂ photocatalysts and BDD electrodes.

2. Fabrication and Application of TiO₂-coated Ti-mesh as an Effective Photocatalytic Filter

In order to meet the above-mentioned requirements for an effective photocatalytic environmental purification, the titanium
A mesh impregnated photocatalyst, TMiP, has been fabricated (Fig. 2). We have found many advantages of TMiP and its usefulness for air or water purification. Because of the presence of a specific thickness of the TiO₂ layer (about several hundred nm) fabricated by anodizing, the TiO₂ nanoparticles were successfully sintered onto its surface without any binder. This advantage is similar to the usual photocatalytic filter by using ceramic foams, but TMiP does not break as easily as ceramic foams. Moreover, the high mechanical flexibility of Ti-mesh structure allows us to manipulate the TMiP. Therefore, any geometry of modules for environmental purification could be designed by combination of UV-sources and the other technologies such as plasma treatment.

Now various environmental purification units by using TMiP have been fabricated for application to various fields (Fig. 3). Among them, the author proposes a practical air-cleaner using photocatalysis-plasma synergistic reactor in the next section.

3. The Air-purification Ability of the Photocatalysis-plasma Synergistic Air-cleaner in the Smoking Room

Figure 4a shows a schematic illustration of a PACT-TMiP synergistic reactor. The reactor consists of two essential technologies: plasma assisted catalytic technology (PACT) reactor and the TMiP. Basic design and fabrication method of PACT reactor were

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described previously. A piece of corrugated TMiP was introduced in the gap of PACT reactor. The atmospheric dielectric barrier discharge between the electrodes of the reactor produces air plasma when AC voltages applied (10 kV, peak-to-peak, 25 kHz). Air was blown through the gap while maintaining a high level of surface contact with TMiP and plasma. Figure 4b shows a schematic illustration of a practical air-cleaner which consists of the PACT-TMiP reactor, a high efficiency particulate air (HEPA) filter, an ozone-cut filter, an activated carbon filter, and a fan. When the fan is turned on, air currents are generated inside the casing from the air inlet toward the air outlet passed through the filters and the PACT-TMiP reactor. Air flow rate was 1200 m$^3$/h.

A schematic illustration of the proposed test method for the practical air-cleaner is shown in Fig. 4c. The real-scale smoking room with the practical air-cleaner was fabricated in the non-smoking office room. Air currents are generated inside the office room from the air inlets toward the air outlets passed through the smoking room. In this condition, cigarettes were simultaneously burned in sets of eight. Each set of cigarettes were sequentially burned in the smoking room. After 30 minutes from the burning of a first set of eight cigarettes, the amounts of gaseous compounds, total volatile organic compounds (TVOC), and total suspended particulates (TSP) were measured at near the air inlet (point 1), center of the smoking room (point 2), air outlet of the air-cleaner (point 3), and center of the non-smoking room (point 4). An important point is that contaminated air would be treated by the air-cleaner just once, i.e. this is a “one-pass system”.

Figure 5 shows the amounts of the compounds in tobacco smoke at near the air inlet (point 1 in Fig. 4c), center of the smoking room (point 2 in Fig. 4c), air outlet of the air-cleaner (point 3 in Fig. 4c), and center of the non-smoking room (point 4 in Fig. 4c). It seems that the amounts of all compounds increased by simultaneously burning of the cigarettes in the smoking room (point 2 in Fig. 4c). Especially the amount of nicotine dramatically increased. Interestingly, the amounts of the compounds were significantly decreased at air outlet of the air-cleaner (point 3 in Fig. 4c). Finally, the amounts of these compounds were kept at low-level in non-smoking room (point 4 in Fig. 4c). This result indicates that the air-cleaner could decompose and/or remove the compounds efficiently.

Figure 4. (Color online) Schematic illustrations of a plasma-TMiP synergistic reactor (a), a practical air-purifier (b), and the test method in the real-scale smoking room for evaluation of air-purification ability of the air-purifier (c). Reprinted from Chemical Engineering Journal, 209, T. Ochiai, Y. Hayashi, M. Ito, K. Nakata, T. Murakami, Y. Morito and A. Fujishima, An effective method for a separation of smoking area by using novel photocatalysis-plasma synergistic air-cleaner, 313–317, Copyright (2012), with permission from Elsevier.

Figure 5. (Color online) The amounts of the compounds in tobacco smoke at each measuring points shown in Fig. 4c. Black: near the air inlet (Fig. 4c, point 1); blue: center of the smoking room (Fig. 4c, point 2); red: air outlet of the air cleaner (Fig. 4c, point 3); green: center of the non-smoking room (Fig. 4c, point 4). Reprinted from Chemical Engineering Journal, 209, T. Ochiai, Y. Hayashi, M. Ito, K. Nakata, T. Murakami, Y. Morito and A. Fujishima, An effective method for a separation of smoking area by using novel photocatalysis-plasma synergistic air-cleaner, 313–317, Copyright (2012), with permission from Elsevier.
Besov et al. reported a similar effective acetone destruction by the barrier discharge reactor in combination with photocatalyst carrying support. They concluded that the synergistic effect could be attributed to the following effects: (1) Oxidation or photo-oxidation of the intermediate products over photocatalyst with ozone participation; (2) Increasing of adsorption of intermediate products in barrier discharge over the photocatalyst surface. Taken together, present system which realize a better contact among the TMiP surface, the gas phase, and reactive species generated by air-plasma is effective to have the benefit of plasma enhanced photocatalysis. At the same time, HEPA and activated carbon filters remove the compounds. In addition, ozone-cut filter using a MnO2-based catalyst could not only decompose excess ozone generated by air-plasma but also produce additional reactive species without injecting more energy. Jarrige and Vervisch tested a pulsed corona discharges reactor combined with fixed-bed catalytic post-treatment using a MnO2-based catalyst. They concluded that ozone-promoted cleaning of the catalyst seems to be a promising for air-purification. Therefore, the arrangement of the filters and the reactor in the present air-cleaner is one of the most effective designs for the “one-pass” system for the separation of smoking area.

4. Application of BDD Electrode for Wastewater Treatment

The author also reported the possibilities of wastewater treatments by electrolysis with designed flow cell reactor using a BDD electrode (Fig. 6). A BDD-deposited Nb plate was used as the anode, and a Pt-deposited Ti plate was used as the cathode in the reactor. Both electrodes had a geometric area of 77.4 cm², and the electrode gap was 10 mm. The wastewater samples were circulated through the reactor by a pump and electrolyzed under galvanostatic electrode gap was 10 mm. The wastewater samples were circulated sequential wastewater treatment system using the reactors and the electrode (Fig. 6).21

Figure 6. (Color online) Schematic image of the flow cell reactor using BDD electrode and its applications for wastewater treatments. Reprinted from Water Research, 44, T. Ochiai, T. Murakami, A. Fujishima, Y. Y. Yao, D. A. Tryk, Y. Kubota, Development of solar-driven electrochemical and photocatalytic water treatment system using a boron-doped diamond electrode and TiO2 photocatalyst, 904–910, Copyright (2010), with permission from Elsevier.

5. Pinpoint Ozone-water Production Unit by Using of BDD Microelectrodes for Dental Treatment

As mentioned above, the application of BDD electrodes is promising for electrolyzing water to produce ozone because of their superior chemical and dimensional stability, as well as their large overpotential for the oxygen evolution reaction. Thus, electrolysis with BDD electrodes can disinfect waterborne pathogens efficiently. On the other hand, ozone has received growing attention as a useful tool for dental treatment because of its disruptive effect on cariogenic bacteria, resulting in elimination of acidogenic bacteria. However, while laboratory studies suggest a promising potential of ozone in dentistry, this has not been fully realised in clinical studies to date. Based on these backgrounds, we developed novel pinpoint ozone-water production unit for dental treatment by using of BDD microelectrodes. Figure 8 shows a...
The values of the previously reported data. A strip of an aluminum foil with an ion-exchange membrane was estimated as almost 1% by comparison of previously reported data. A strip of an aluminum foil with an ion-exchange membrane (Nafion®) was spirally wound around the BDD microelectrode which was used as an anode. When DC voltage was applied between the anode and the cathode in the water, electrolysis proceeds as follows:

anode (BDD): \( 3\text{H}_2\text{O} \rightarrow \text{O}_3 + 6\text{H}^+ + 6\text{e}^- \)

cathode (Al): \( 6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{H}_2 \)

The ozone concentration produced by the unit reached 6.4 mg/L after 5 min of electrolysis in 0.3 mL of distilled water under potentiostatic conditions with 7.5 V of the terminal voltage of the unit. On the other hand, disinfection test was performed at the same condition as above-mentioned electrolysis in 0.3 mL of bacterial suspensions. Escherichia coli (E. coli) and Enterococcus faecalis (E. faecalis) were used as the test bacteria to assess the disinfection efficiency of the unit. Bacterial densities of E. coli and E. faecalis at a function of electrolysis time were fitted with a pseudo-first-order kinetics given by the following equation: \( C = C_0 \cdot \exp(-k_1 t) \). Where \( C_0 \) is the initial bacterial density and \( k_1 \) is the observed rate constant. The values of the \( k_1 \) were calculated by exponential fitting of the plot to 1.4 and 5.0 min\(^{-1} \) for E. coli and E. faecalis, respectively. These results suggest that the unit is useful for disinfection in practical uses.

In order to assess the usage of the unit for dental treatment in biological circumstances, in vitro disinfection test was carried out as follows. Biofilms of Porphyromonas gingivalis (P. gingivalis) were formed in root canal of bovine teeth. 0.05–0.1 mL of phosphate buffer saline (PBS) was poured into the root-canal. The unit was inserted into the root-canal. After pre-determined time of electrolysis under potentiostatic conditions with 7.5 V of the terminal voltage of the unit, bacterial cell viability was checked by conventional alamarBlue™ assay. For comparison, usual 20 ppm of NaClO treatment was also performed. Survival rates of P. gingivalis at a function of treatment time were shown in Fig. 9. The unit showed almost the same disinfection ability as 20 ppm of aqueous NaOCl treatment in this in vitro assessment in the root-canal of bovine teeth. In conclusion, the superiority of BDD microelectrodes over simple pinpoint ozone-water production unit, in terms of the larger activities for ozone production and disinfection, was demonstrated. This research would be attractive to develop a practical unit for dental treatment. However, further investigations (cultivation, improvement of fabrication method, clinical study) are required to bring it to practical stage.

6. Conclusions

This paper surveyed here hopefully underlines the fact that the closely-related TiO\(_2\) photocatalysis and BDD electrolysis are extremely versatile and can be used in numerous ways to both environmental purification functions and disinfection for dental treatment. Although numerous research and development have proposed, further technological breakthroughs are required for practical applications of TiO\(_2\) photocatalysis and BDD electrolysis. This paper presented several key solutions to meet these requirements. For examples, a novel photocatalytic filter based on titanium mesh sheet and its environmental applications, a practical air-purifier by using of photocatalysis-plasma synergistic reactor, and a pinpoint ozone-water production unit by using of BDD microelectrodes for dental treatment. In summary, we can expect that the continuous improvements of the material property and the reactor design would create a large number of effective systems. Finally, we feel that, TiO\(_2\) photocatalysis and BDD electrolysis can realize a healthy and comfortable living environment.

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