Design of BDD-TiO₂ Hybrid Electrode with P–N Function for Photoelectrocatalytic Degradation of Organic Contaminants

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Received November 4, 2007. Revised manuscript received
February 21, 2008. Accepted March 31, 2008.

P–N hybrid electrode of boron-doped diamond (BDD) and TiO₂ were designed and fabricated via selective deposition of TiO₂ onto BDD electrode. This hybrid electrode exhibit high photoelectrocatalytic activities toward degradation of acid orange II (AOII) and 2, 4-dichlorophenol (2, 4-DCP) due to the P–N effect and high electrocatalytic and photocatalytic activities of BDD electrode and TiO₂ particles. The structures of TiO₂ and BDD were confirmed by Raman spectra analysis. Atom force microscopy and scanning electron microscopy showed that the TiO₂ deposits consist of adherent nanomicro-sized particles, scattered on the BDD substrate. AOII and 2,4-DCP in a solution can be efficiently degraded at the hybrid electrode in the photoelectrocatalysis (PEC) process. Effect of applied bias potentials and solution pH values on AOII and 2,4-DCP degradation were investigated. In the electro-oxidation process, some intermediates such as phenols were detected and they accumulated with the reaction evolution based on the analysis of UV-vis and GC-MS variation. By contrast, phenols intermediates will be degraded with the reaction evolution in the photoelectrocatalysis process. And, organic aromatic and aliphatic carboxylic acids were detected. Furthermore, different degradation mechanism of AOII and 2,4-DCP in the electro-oxidation, photocatalysis, and photoelectrocatalysis is proposed.

Introduction

Combined electro-oxidation and photocatalysis using a semiconductor film electrode (PEC) has shown great potential for destruction of organic contaminants compared with individual electro-oxidation and photocatalysis (1–4). In previous work, the semiconductor of TiO₂, ZnWO₄, γ -Bi₂MoO₆, and Bi₂WO₆ are deposited onto indium-tin oxide (ITO) substrate and the obtained film electrode can efficiently degrade 4-chlorophenol and triazine-containing group azo dyes via combined photocatalysis and electro-oxidation process (5, 6). The ITO substrate is not satisfactory considered in the practical application of the film electrode due to its weak strength and low electrocatalytic activities.

Anodic oxidation with boron-doped diamond (BDD) anodes is a new advanced oxidation process with many advantages as compared to other known electrode materials due to its low and stable background current, wide working

potential window, and stable surface microstructure over a wide potential range (7). The outstanding electrochemical properties of BDD recommend this material as an excellent substrate for electrocatalytic oxide layer in anode oxidation of organic contaminants (8). Moreover, the BDD electrode exhibit p-type semiconductor properties. Most of photocatalysts such as TiO₂, ZnWO₄, γ -Bi₂MoO₆, and Bi₂WO₆ exhibit n-type semiconductor properties.

It is well-known that p–n junction cause a region at the junction where electrons are depleted. This depletion region is known as the space charge region. The space charges establish an electrostatic field inside the semiconductor that facilitates the transport of electrons from n-type semiconductor to p-type semiconductor. In a conventional photocatalytic system, the excited electrons and holes may migrate to the photocatalyst surface or otherwise recombine. If the conduction band electrons survive further recombination at the catalyst surface, the electrons and holes may undergo redox reactions with adsorbed species such as water, hydroxide ions, oxygen, and air pollutants (9). Unfortunately, under this condition, most of the excited electrons and holes are recombined before redox reactions take place, resulting in very poor quantum efficiency in the photocatalytic process. Recently, Profs. Crittenden, J. C. and Lee, J. S exhibited that the recombination of free electrons and holes in semiconductor photocatalytic process can be reduced using a p–n junction and its electrostatic potential (10, 11).

Herein, we describe a novel configuration of hybrid electrode designated as photoelectrocatalytic diodes (PECD). These contain nanoislands of n-type TiO₂ interfaced over a highly crystalline layered BDD electrode, yielding nanodimensional p–n junctions. This diode material shows greatly enhanced and stable photocatalytic activity for photocurrent generation and degradation of toxic organic pollutants; PECD exhibit strong electrocatalytic activities toward degradation of organic contaminants. Moreover, the organic pollutants can be efficiently degraded via the combined photocatalysis and electro-oxidation process. Azo dye of acid Orange II (AO II) and 2, 4-dichlorophenol (2, 4-DCP) were selected in the present study (molecular structure shown below). AO II and 2, 4-DCP are common and representative species of the organic contaminants in waters. And, the degradation of this dye and 2,4-DCP has been studied in detailed (12–17). Thus, it is convenient to study the degradation process of AO II and 2,4-DCP.

Experimental Section

Fabrication and Characterization of Hybrid Electrode.

Highly BDD electrode used in this work were purchased by CSEM (Switzerland) and synthesized on single crystal p-type Si (100) wafers, with resistivity of 0.1 Ω cm, by the hot filament chemical vapor deposition technique. Porous TiO₂ films with a thickness of ca. 100 nm were selectively deposited onto the BDD surface from a sol–gel via a dip-coating method as described previously (18). The obtained material was named as hybrid electrode. Raman spectra of PECD were conducted on a Renishaw RM1000 spectrometer, the wavelength of the laser light is 514 nm. UV–visible absorption spectra of the samples were recorded on a UV–vis spectrophotometer (Hitachi UV-3100) with an integrating sphere attachment. The surface morphology of PECD was characterized by a JSM 6301 electron-scanning microscope (SEM) and an atomic force microscope (AFM) (Multimode Nanoscope III, Digital Instrument Inc., U.S.). A gold-coated Si₃N₄ tip was used in the contact mode.

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FIGURE 1. Raman spectra of BDD and BDD-TiO₂ hybrid electrode.

Degradation Experiment. Degradation experiments were performed in a cylindrical quartz reactor. The reactor, which contained a 60 mL sample solution allowing 4.5 cm of the supported film electrode to be immersed into the solution, was placed 3 cm in front of a 150 W Xe lamp purchased from the German Osram. The intensity of light, as measured by a irradiance meter (Instruments of Beijing Normal University) was c.a. Twenty-five mW/cm² at 4 cm into the reactor, the position where PECVD was placed. The PEC reaction employed a basic electrochemical system (Princeton Applied Research) connected with a counter-electrode (Pt wire, 70 mm in length with a 0.4-mm diameter), a working electrode (hybrid electrode, active area of 11 cm²), and a reference electrode (a saturated calomel electrode (SCE)). 0.12 mg/L Na₂SO₄ solution was used as electrolyte solution. Initial concentration of dye solution and 2,4-DCP solution was 20 mg/L, and their concentration variation was examined by a U-3010 spectrophotometer and Hitachi HPLC on an ODS-3.5 μ m column with an eluent of methanol/water (70/30% V/V, 1.0 mL/min) (Hitachi, Japan). All experiments were carried out at least in duplicate. The reported values are within the experimental error of $\pm 2.5\%$. Electrochemical impedance spectra (EIS) were recorded in the potentiostatic mode. The amplitude of the sinusoidal wave was 30 mV, and the frequency range of the sinusoidal was 100 kHz to 0.01 Hz. For GC-MS analysis, the residue was trimethylsilylated with 0.2 mL of anhydrous pyridine, 0.1 mL of hexamethyldisilazane, and 0.05 mL of chlorotrimethylsilane at room temperature. GC-MS analysis was carried out on an Agilent 6890GC/5973MSD with a DB-5 MS capillary column.

Results and Discussion

Structure Characterization of Hybrid Electrode. Figure 1 shows the Raman spectrum of PECVD as well as BDD electrode. There is a sharp peak around 1334 cm⁻¹, slightly away from

the characteristic signature of the diamond structure, 1332 cm⁻¹, revealing the presence of diamond for the BDD and hybrid electrode (8). It was reported that peaks at 142, 404, 516, and 635 cm⁻¹ are characteristic of anatase (19). The increase of Raman shift from 142 to 145 cm⁻¹ indicates that the diameter of TiO₂ in PECVD is in the range of 4–8 nm according to the expressions provided by Kelly et al. (19). As shown in Supporting Information Figure S1, the diamond crystals are highly faceted and have an average size of about 2 μ m. A well-decorated TiO₂ film and uniform distribution of the deposited particles on BDD were observed in comparison to bare BDD. The film is perfect without any noticeable cracks, which ensures the high stability of PECVD as seen subsequently. A 10 $\times$ 10 μ m AFM image of the surface of the unmodified BDD film (on silicon substrate) is shown in Figure 2(a). The figure reveals that the BDD film is composed of many twinned randomly oriented crystallites with clearly defined grain boundaries. In comparison, Figure 2(b) shows an AFM image of the same TiO₂ modified BDD electrode. Clearly, the characteristic surface morphology of the electrode has changed. Some agglomerations of metallic oxides can be observed indicating sites of heterogeneous deposition.

Photoelectrochemical Properties of the Hybrid Electrode. The photoelectrochemical properties of PECVDs were examined in 0.1 M Na₂SO₄ electrolyte. Figure 3 shows the current response with and without Xe lamp irradiation of this hybrid electrode. It should be noted that both cathodic and anodic photocurrents were observed. The cathodic photocurrent could be due to the BDD substrate, which is a p-type semiconductor (20). No obvious photoanodic current was observed for bare BDD electrode under the same experimental conditions. Therefore, the anodic photocurrent obtained for PECVD is ascribed to the presence of TiO₂ on BDD surface. The high current generation of this hybrid electrode is probably due to the large surface area of the electrodeposited particles on the rough BDD surface. This may result in a significant increase of the active area compared to the geometric one. Figure 4 shows the EIS response of PECVD under dark and photoirradiation conditions. It is clear that the size of the arc radius on the EIS Nyquist plot is largely reduced due to the photoirradiation. Under photoirradiation, the photogenerated electrons and holes will produced from excited TiO₂. The electrons will flow into BDD electrode and outside circuit. Thus, the interface resistance will reduce and the size of the arc radius

FIGURE 2. AFM images of (A) BDD electrode and (B) BDD-TiO₂ hybrid electrode (scale size 10.0 μ m; data scale 350 nm).

FIGURE 3. Current variation of BDD and TiO_2 -BDD hybrid electrode under dark and UV light irradiation. (Scan rate = 10 mVs^{-1} , pH 6.0, $1.2 \text{ mg/L Na}_2\text{SO}_4$).

FIGURE 4. Effect of irradiation on EIS variation of BDD- TiO_2 and TiO_2 -ITO ($0.1 \text{ M Na}_2\text{SO}_4$).

FIGURE 5. Degradation of AO II under a, direct photolysis; b, photocatalysis; c, electro-oxidation (1 V); d, PEC process (1 V); e, PEC process (2 V) (20 ppm , 60 mL reaction solution, $1.2 \text{ mg/L Na}_2\text{SO}_4$, 20 W UV light).

on the EIS Nyquist plot reduces. Meantime, the arc radius on the EIS Nyquist plot reflects the rate of electrode reaction, which exhibited that the photoirradiation can increase the degradation rate of target compounds (21). Furthermore, as shown in Figure 4, the arc radius of BDD- TiO_2 hybrid electrode is smaller than that of TiO_2 -ITO electrode, which were prepared from sol-gel-solution via dip-coating method and calcined at 500°C according to the method (18) under dark and photoirradiation conditions. The smaller arc radius mean that the redox reaction occurring at the BDD- TiO_2 electrode proceed faster than that at the TiO_2 -ITO electrode.

Degradation of Target Contaminants. As shown in Figure 5, AOII can be photocatalytically degraded at PECd. Under UV light irradiation of PECd, the photogenerated electron and hole were produced from TiO_2 particles. And, hydroxyl radicals ($\bullet\text{OH}$) are produced. These active radicals are responsible for AO II degradation. It can also be seen from Figure 5 that AOII can be efficiently degraded via the electro-oxidation process at PECd at the bias potential of 2.5 V . By contrast, the loss of AOII at hybrid electrode is lower than that at pure electrode under same condition, which may due to the less reaction area due to the TiO_2 deposition. Clearly, the degradation rate of AOII was the largest under PEC process with the same bias potential.

To try to obtain more information about the mechanisms of the oxidation process, several voltammetric measurements

FIGURE 6. Degradation of 2,4-DCP under various conditions (20 ppm , 60 mL reaction solution, $1.2 \text{ mg/L Na}_2\text{SO}_4$, Xe lamp irradiation, applied bias potential 2.5 V).

FIGURE 7. HPLC distribution of intermediates produced in the photocatalytic and electrochemical degradation.

FIGURE 8. Photoelectrocatalytic degradation of AO II at hybrid electrode with various applied bias potentials (20 ppm , 60 mL reaction solution, $1.2 \text{ mg/L Na}_2\text{SO}_4$, 20 W UV light).

were carried out. As shown in Supporting Information Figure S2, at the potential of ca. 1.0 V , the current densities increase with the concentration of AO II up to 30 mg/L . But it decreases when the concentration of AO II was 50 mg/L , which may be due to the heavy block at high AO II concentration. The enhanced current is generated from the direct electro-oxidation of AO II. When the potential exceeds 1.3 V , the anode currents increased largely with the potential, which may result from electro-oxidation of AO II plus the evolution of oxygen. With the evolution of oxygen, the active species such as hydroxyl radicals, H_2O_2 , or O_3 can be formed (22), which lead to the indirect oxidation of AO II.

For better understanding of the catalytic activities of PECd, the degradation of 2,4-DCP was also carried out under the otherwise identical conditions (17). 2,4-DCP represents a typical class of the organic pollutants found in aqueous systems. As shown in Figure 6, 2,4-DCP can be efficiently degraded in the PEC process with the applied bias potential of 2.5 V , which confirms the high photoelectrocatalytic activities of PECd. Moreover, it is clearly observed in Figure 7 that some intermediates were produced and accumulated in the electrochemical oxidation process. In contrast, some intermediates were produced in the PEC process at the early

FIGURE 9. Temporal absorbance variation of UV–vis of AOII in different processes (20 mg/L AOII; 1.2 mg/L Na_2SO_4 aqueous solution).

SCHEME 1. Molecular Structure of Acid Orange II and 2,4-Dichlorophenol

reaction state, which degraded gradually with the reaction evolution. These intermediates will be furthermore identified.

Effect of Applied Bias Potential. As shown in Figure 8, with the increase of external potential, degradation rate of AO II increases gradually. The application of potentials greater than the flat band potential of hybrid electrode across a photoelectrode increases the concentration of photogenerated holes or hydroxyl radicals on the surface by decreasing the rate of recombination of photogenerated holes and electrons. As a result, as the potential increases, the rate of AO II degradation increases, until most of the photogenerated electrons are removed either by the electric field or by reaction with dissolved oxygen. Further increase of the applied potential beyond the redox potential of AO II improves the degradation rate of AO II. In this case, the degradation of AO II was carried out by the combined electro-oxidation and photocatalysis simultaneously.

With respect to BDD electro-oxidation, in the potential region of water stability ($E < 2.0$ V vs SCE) they can occur direct electron transfer reactions on BDD surface that readily results in electrode fouling due to the formation of a polymeric film on its surface. In the potential region of water decomposition ($E > 2.0$ V vs SCE) complex oxidation reactions can take place on BDD electrodes by active intermediates,

probably electrogenerated hydroxyl radicals, that can avoid the electrode fouling. During bulk electrolyses at low current density, AO II is oxidized to aromatic compounds (benzoquinone, hydroquinone, and catechol) due to a low local concentration on the anode surface of electrogenerated hydroxyl radicals. During bulk electrolyses at high current density, AO II is readily combusted to CO_2 on the anode surface of large amount of electrogenerated hydroxyl radicals (23).

The reactions of PEC oxidation of pollutants occur heterogeneously. Pollutants must be transported to the electrode surface first, and then be oxidized there. The pollutant degradation may be subjected to current control or mass transfer control. Initially, the AO II concentration was relatively high, and accordingly the AO II reduction rate was subjected to the current control (24). As the AO II concentration was lowered to a certain level, the AO II reduction rate was subjected to the mass transfer control. In that case, part of current supplied was used to oxidize pollutants, part of current supplied was used to assist AO II photocatalysis, and the rest current was wasted for generation of oxygen.

Effect of pH on AOII Degradation. In order to know if this hybrid electrode can work well in oxidizing AO II in a wide pH range, the concentration variation with the charge loading at three different initial pH values was investigated. It is observed from Supporting Information Figure S3 that alkaline media was favorable for AO II degradation. Nevertheless, the pH effect is not significant. Even at a pH value of 2.2, AO II was efficiently degraded within 3 h. This is very important because industrial wastewater may have different pH values. The wide effective pH range implies that pH adjustment before treatment is not necessary in most cases.

AO II has a sulfonic group in its molecular structure, which is negatively charged, the alkaline solution favors adsorption of AOII onto the electrode surface, leading to the improvement of the degradation efficiency to some extent. In alkaline solution, where TiO_2 is negatively charged, less adsorption of AO II onto TiO_2 surface takes place, which will decrease the photocatalytic degradation rate of AO II. However, high degradation efficiency was still obtained, which may be partly attributed to more hydroxyl radicals produced under alkaline conditions due to more hydroxide ions available on TiO_2 surface.

Degradation Intermediates of AOII. The characteristic absorbance bands of UV-vis spectrum of AOII are at 228 nm, 250 nm, and 310 nm in the UV, and at 487 nm in the visible region. The low-energy absorption band at 487 nm is assigned to the $n-\pi^*$ transition of the ($-N=N-$) group; the band at 310 nm corresponds to the $\pi-\pi^*$ transitions of the aromatic rings together with that of the ($-N=N-$) group of the azo dye (25). As shown in Figure 9, the peak at 487 nm of AOII decreased quickly with reaction time in the photocatalysis, electro-oxidation, and PEC process. These results indicated that the doubly bonded nitrogen in the dye was destroyed efficiently. Furthermore, it is clearly observed that the peak at 255 nm appear and increase with the extension of reaction time in the electro-oxidation process. The absorption maximum at 254 nm mainly corresponds to phenol in the AO II structure (26). This phenomenon did not appear in the photocatalysis and PEC process.

Degradation intermediates of AOII in the photocatalysis, electro-oxidation, and PEC process were analyzed by a GC-MS, respectively. As listed in Supporting Information Table 1 and Figure S4, in the PEC process, many organic acids, such as formic acid, acetic acid, oxalic acid, and succinic acid were detected. Moreover, 1,2-diphenol appeared at 2 h were not detected at 4 h; they were degraded as the PEC reaction preceded. In the electro-oxidation process, more intermediates were detected and some phenol or benzene compounds were also detected, which did not disappear within the reaction time. The benzene molecules may be released from the breaking of the C-N single bond between azo group and benzene ring (27).

Meantime, in the electrochemical degradation of AOII, it was observed that the solutions became a little bit turbid after electrochemical oxidation. Mass spectrometry analysis demonstrated that the turbid substances were polymeric intermediate products. It should be noted that formation of polymeric products in anodic oxidation process is not a new finding, but a common phenomenon (28, 29). AO II has a hydroxyl group like phenol as shown in Scheme 1, which will result in the generation of polymeric products in oxidizing AO II in the electro-oxidation process (30). However, the turbid solution was not observed in the photocatalytic and PEC process. In the photocatalytic process, the rupture at the $N=N$ bond will lead to the formation of benzene and naphthalene ring followed by a myriad of intermediates such as phenol, oxalate, malonate, etc (31). In PEC process, AOII was efficiently degraded and no turbid solutions appear and small molecular acids are produced as shown in Supporting Information Table 1, which indicated that the AOII can be efficiently degraded in the PEC process.

Additionally, PEC degradation of AO II was repeatedly performed for five times at the bias potential of 2.5 V for 4 h; the results indicated that the degradation efficiencies were rather stable with a relative standard deviation of 2.8%, which further confirms the stability of PECD. These results indicated that the use of BDD as a substrate allows the deposition of isolated TiO_2 particles or discontinuous films, thus maximizing the utilization of the catalyst by avoiding the need for thick films. Electrodes obtained by the deposition of an appropriate amount of TiO_2 on the BDD surface exhibited excellent photoelectrocatalytic performances for organic contaminants degradation. Deposition of other semiconductor photocatalysts such as ZnWO_4 and $\gamma\text{-Bi}_2\text{MoO}_6$ on BDD electrode is performing.

Acknowledgments

This work was supported by National Natural Science Foundation of P.R. China (50778172 and 50621804). We gratefully acknowledge the anonymous reviewers whose comments helped to improve the manuscript.

Supporting Information Available

Additional details are found in four figures and one table. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- (1) Pelegrini, R. T.; Freire, R. S.; Duran, N.; Bertazzoli, R. Photo-assisted electrochemical degradation of organic pollutants on a dsa type oxide electrode: process test for a phenol synthetic solution and its application for the E1 Bleach Kraft mill effluent. *Environ. Sci. Technol.* **2001**, 35 (13), 2849–2853.
- (2) An, T.; Xiong, Y.; Li, G.; Zha, C.; Zhu, X. Synergetic effect in degradation of formic acid using a new photoelectrochemical reactor. *J. Photochem. Photobiol. A* **2002**, 152 (1–3), 155–165.
- (3) Quan, X.; Chen, S.; Su, J.; Chen, J.; Chen, G. Synergetic degradation of 2,4-D by integrated photo- and electrochemical catalysis on a Pt doped TiO_2/Ti electrode. *Sep. Purif. Technol.* **2004**, 34 (1–3), 73–79.
- (4) Pinhedo, L.; Pelegrini, R.; Bertazzoli, R.; Motheo, A. J. Photo-electrochemical degradation of humic acid on a $(\text{TiO}_2)_{0.7}(\text{RuO}_2)_{0.3}$ dimensionally stable anode. *Appl. Catal., B* **2005**, 57 (2), 75–81.
- (5) Zhao, X.; Xu, T.; Yao, W.; Zhang, C.; Zhu, Y. Photoelectrocatalytic degradation of 4-chlorophenol at Bi_2WO_6 nanoflake film electrode under visible light irradiation. *Appl. Catal., B* **2007**, 72 (1–2), 92–97.
- (6) Zhao, X.; Zhu, Y. Synergetic degradation of rhodamine B at a porous ZnWO_4 film electrode by combined electro-oxidation and photocatalysis. *Environ. Sci. Technol.* **2006**, 40 (10), 3367–3372.
- (7) Wang, J.; Farrell, J. Electrochemical inactivation of triclosan with boron doped diamond film electrodes. *Environ. Sci. Technol.* **2004**, 38 (19), 5232–5237.
- (8) Chen, X.; Chen, G.; Gao, F.; Yue, P. L. High-performance Ti/BDD electrodes for pollutant oxidation. *Environ. Sci. Technol.* **2003**, 37 (21), 5021–5026.
- (9) Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. Environmental applications of semiconductor photocatalysis. *Chem. Rev.* **1995**, 95 (1), 69–96.
- (10) Chen, Y.; Crittenden, J. C.; Hackney, S.; Sutter, L.; Hand, D. W. Preparation of a novel TiO_2 -based p-n junction nanotube photocatalyst. *Environ. Sci. Technol.* **2005**, 39 (5), 1201–1208.
- (11) Hyun, G.; Kim, D.; Pramod, H.; Borse, Dr.; WonyongChoi, Prof.; Jae S. Lee. Photocatalytic nanodiodes for visible-light photocatalysis. *Angew. Chem. Int. Ed.* **2005**, 44, 4585–4589.
- (12) Chen, X.; Chen, G. Anodic oxidation of Orange II on Ti/BDD electrode: Variable effects. *Sep. Purif. Technol.* **2006**, 48 (1), 45–49.
- (13) Li, G.; Qu, J.; Zhang, X.; Liu, H.; Liu, H. Electrochemically assisted photocatalytic degradation of Orange II: Influence of initial pH values. *J. Mol. Catal. A: Chem* **2006**, 259 (1–2), 238–244.
- (14) Feng, J.; Hu, X.; Yue, P. L.; Zhu, H. Y.; Lu, G. Q. Degradation of azo-dye Orange II by a photoassisted Fenton reaction using a novel composite of iron oxide and silicate nanoparticles as a catalyst. *Ind. Eng. Chem. Res.* **2003**, 42 (10), 2058–2066.
- (15) Lucarelli, L.; Nadtochenko, V.; Kiwi, J. Environmental photochemistry: quantitative adsorption and FTIR studies during the TiO_2 -photocatalyzed degradation of Orange II. *Langmuir* **2000**, 16 (3), 1102–1108.
- (16) Pera-Titus, M.; Garcia-Molina, V.; Banos, M. A.; Gimenez, J.; Esplugas, S. Degradation of chlorophenols by means of advanced oxidation processes: a general review. *Appl. Catal., B* **2004**, 47 (4), 219–256.
- (17) Ji, H.; Song, W.; Chen, C.; Yuan, H.; Ma, W.; Zhao, J. Anchored oxygen-donor coordination to iron for photodegradation of organic pollutants. *Environ. Sci. Technol.* **2007**, 41 (14), 5103–5107.
- (18) Shang, J.; Li, W.; Zhu, Y. Structure and photocatalytic characteristics of TiO_2 film photocatalyst coated on stainless steel webnet. *J. Mol. Catal. A: Chem.* **2003**, 202 (1–2), 187–195.
- (19) Kelly, S.; Pollak, F. H.; Tomkiewicz, M. Raman spectroscopy as a morphological probe for TiO_2 aerogels. *J. Phys. Chem. B* **1997**, 101 (14), 2730–2734.
- (20) Pleskov, Y. V.; Krotova, M. D.; Elkin, V. V.; Ralchenko, V. G.; Khomich, A. V.; Khmel'nitskiy, R. A. The vacuum-annealed undoped polycrystalline CVD diamond electrodes: the impedance-spectroscopy and photoelectrochemical studies. *Electrochim. Acta* **2005**, 50 (5), 1149–1156.
- (21) Liu, H.; Cheng, S.; Wu, M.; Wu, H.; Zhang, J.; Li, W.; Cao, C. Photoelectrocatalytic degradation of sulfosalicylic acid and

- its electrochemical impedance spectroscopy investigation. *J. Phys. Chem. A* **2000**, 104 (30), 7016–7020.
- (22) Jeong, J.; Kim, J. Y.; Yoon, J. The role of reactive oxygen species in the electrochemical inactivation of microorganisms. *Environ. Sci. Technol.* **2006**, 40 (19), 6117–6122.
- (23) Iniesta, J.; Michaud, P. A.; Panizza, M.; Cerisola, G.; Aldaz, A.; Comninellis, C. Electrochemical oxidation of phenol at boron-doped diamond electrode. *Electrochim. Acta* **2001**, 46 (23), 3573–3578.
- (24) Panizza, M.; Michaud, P. A.; Cerisola, G.; Comninellis, C. Anodic oxidation of 2-naphthol at boron-doped diamond electrodes. *J. Electroanal. Chem.* **2001**, 507 (1–2), 206–214.
- (25) Ramirez, J. H.; Costa, C. A.; Madeira, L. M. Experimental design to optimize the degradation of the synthetic dye Orange II using Fenton's reagent. *Catal. Today*. **2005**, 107–108, 68–76.
- (26) Song, S.; Xu, L.; He, Z.; Chen, J.; Xiao, X.; Yan, B. Mechanism of the Photocatalytic degradation of C.I. reactive black 5 at pH 12.0 using SrTiO₃/CeO₂ as the catalyst. *Environ. Sci. Technol.* **2007**.
- (27) Spadaro, J. T.; Isabelle, L.; Renganathan, V. Hydroxyl radical mediated degradation of azo dyes: evidence for benzene generation. *Environ. Sci. Technol.* **1994**, 28 (7), 1389–1393.
- (28) Muna, G. W.; Tasheva, N.; Swain, G. M. Electro-oxidation and amperometric detection of chlorinated phenols at boron-doped diamond electrodes: a comparison of microcrystalline and nanocrystalline thin films. *Environ. Sci. Technol.* **2004**, 38 (13), 3674–3682.
- (29) Bensalah, N.; Gadri, A.; Canizares, P.; Saez, C.; Lobato, J.; Rodrigo, M. A. Electrochemical oxidation of hydroquinone, resorcinol, and catechol on boron-doped diamond anodes. *Environ. Sci. Technol.* **2005**, 39 (18), 7234–7239.
- (30) Chen, X.; Chen, G.; Yue, P. L. Anodic oxidation of dyes at novel Ti/B-diamond electrodes. *Chem. Eng. Sci.* **2003**, 58 (3–6), 995–1001.
- (31) Bhattacharyya, A.; Kawi, S.; Ray, M. B. Photocatalytic degradation of Orange II by TiO₂ catalysts supported on adsorbents. *Catal. Today* **2004**, 98 (3), 431–439.

ES702769P