Preparation and Electrochemical Properties of TiO2/BDD Composite Film Materials

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Abstract. Boron-doped diamond (BDD) has important applications in the catalytic degradation of wastewater. In this paper, the TiO2 was electro-phoretically deposited onto the silicon-based BDD film by an electrophoretic deposition method using a butyl titanate (TBOT) as the titanium source. The effect of the deposition time on the electrochemical properties of the TiO2/BDD composites was investigated. The phase and morphology were characterized by X-ray diffraction, laser Raman spectroscopy, and scanning electron microscopy. The electrical and electrochemical properties were characterized by Hall measurement system and electrochemical analyzer. The results showed that the performance of TiO2/BDD composites was significantly higher than that of single BDD electrode materials. The morphology of TiO2 films obtained by TiO2 deposition three times was better. The Hall mobility of most samples has improved, and the Hall mobility of sample 4 increased to 213 cm²/V·s, which is 3.5 times of the single BDD materials. The electrochemical potential window of sample 4 in alkaline, acidic and neutral electrolyte are 4.6 V, 4.3 V, 4.6 V.

1. Introduction
With the rapid development of industrialization, large amounts of the pollutants entered the surface water, due to the fact that the wastewater treatment facility did not match the scale of industrial production. Wastewater from petroleum, chemical, pesticide, printing and dyeing, papermaking and other industries is characterized by strong toxicity, poor biodegradability, complex pollution components and high content[1]. The traditional sewage treatment methods include physical, chemical and biological treatment methods, but the physical methods are complicated by the steps of adsorption, precipitation, filtration, oil separation, etc. The chemical methods are easy to produce secondary pollution due to the addition of chemical reagents, and the biological methods have long processing times and high environmental requirements [2].

As an environmentally friendly technology, electrocatalytic oxidation technology has a good industrial application prospect in industrial wastewater treatment. It has excellent characteristics such as high efficiency, thorough processing and simple process. Electrode materials are very important in
electrochemical oxidation technology. Boron-doped diamond (BDD) as an electrode material has a low background current, wide potential window and strong corrosion resistance, which has great application potential in the field of electrocatalytic oxidation [3]. The performance of a single material often does not meet the demand, and the cost in actual application is high, but its performance can be improved by compounding with other materials. As a P-type semiconductor material, the electrical properties of BDD can be improved by compounding with N-type semiconductor materials. Most photocatalysts such as TiO₂, ZnWO₄, γ-Bi₂MoO₆ and Bi₂WO₆ exhibit N-type semiconductor properties, causing the formation of P-N junctions, where electrons are depleted and the depletion region is known as the space charge region. In previous work, the semiconductor ZnO, TiO₂, ZnWO₄, γ-Bi₂MoO₆ and Bi₂WO₆ were deposited onto the semiconductor substrate, and the obtained film electrodes efficiently degraded organic contaminants via combined photocatalysis and electro-oxidation processes [4-7].

TiO₂ is a widely studied photocatalytic material with good photocatalytic properties in the ultraviolet region [8]. However, as a powder material, there is a problem that recovery is difficult and the recycling rate is low. Based on the characteristics of the two materials, the combination of TiO₂ and BDD can not only improve the electrocatalytic performance of BDD, but also fix TiO₂ on BDD, thereby improving the recycling rate. At the same time, the photocatalysis of TiO₂ is combined with the electrocatalysis of BDD, the synergistic effect of optoelectronics can improve the overall catalytic performance of the composites. Yuan et al. synthesized TiO₂ nanotube (TiNT) arrays on BDD by a liquid phase deposition method, the TiNT/BDD composite materials show significantly enhanced photocatalytic activities with good recyclable behavior, with respect to the cases of sole TiNTs [6]. Fernando et al. deposited nanoparticles TiO₂ (P25) on BDD by electrophoretic deposition, the use of nanostructured TiO₂ deposited onto BDD as anode in photoelectrocatalysis then exceeds the efficiency of anodic oxidation with the best anode known of BDD [9].

In this paper, TiO₂ was deposited on the surface of BDD by electrophoretic deposition method to prepare TiO₂/BDD composite film materials. The effects of deposition time on the morphology and properties of the films were investigated.

2. Experimental

2.1. Preparation of TiO₂/BDD

The TiO₂ sol was prepared by sol-gel method using butyl titanate (TBOT) as the titanium source, and the TiO₂ was electrophoretically deposited onto the silicon-based BDD film (purchased from Zhengzhou Research Institute for Abrasives & Grinding Co., Ltd.). The TiO₂/BDD composite film material was obtained by calcination in a muffle furnace. The specific steps are as follows:

![Figure 1. Schematic of synthesizing TiO₂/BDD Composite Films.](image-url)
(1) In the condition of 25°C, 15 mL TBOT and 33 mL anhydrous alcohol was mixed and stirred for 30 min to prepare the A solution; taken deionized water 4.5 mL, absolute ethanol 15 mL, mixed and stirred for 10 min, and adjust pH = 3 with glacial acetic acid to prepare the B solution. Then, the A solution was slowly dropped into the B solution under vigorous stirring. After the dropwise addition of the solution B, stirring was continued for 30 min, and then stand still 10 h for use.

(2) The sol prepared in the first step was used as the electrophoresis liquid, the BDD electrode as the cathode, the graphite as the anode, and the DC power source (MS1001D, Dongguan Maihao Electronic Technology Co., Ltd.) provides the 40 V DC voltage. With the total deposition time of 180 s unchanged, TiO₂ was deposited on four BDD electrodes for 1 time (180 s/time), 2 times (90 s/time), 3 times (60 s/time) and 4 times (45 s/time), respectively. The sample number named based on the times of TiO₂ depositions of samples. The sample 1, 2, 3, 4, 5 are original BDD, 1, 2, 3, 4 deposition times samples, respectively. After each deposition was completed, the samples were heat treated in a muffle furnace at 450 °C for 1 h, and finally TiO₂/BDD composite film electrode materials with different TiO₂ deposition times were obtained.

2.2. Characterization methods
The crystal phase composition of the phase was analyzed by X-ray diffractometer (PANalytical EMPYRAN, Malvern Panalytical Ltd.). Laser Raman spectrometer (LabRAM HR Evolution, HORIBA France SAS) was used to determine the structure information of the carbon material. SEM of the TiO₂ film electrophoretically deposited onto the BDD electrode was carried out using a field-emission scanning microscope (JSM-6700F, JEOL). The Hall measurement system (LakeShore 8400, Lake Shore Cryotronics, Inc.) was used to detect the electrical properties of the sample such as surface resistivity, carrier concentration and Hall mobility. The electrochemical properties of the samples were studied using an electrochemical analyzer (CHI604E, Shanghai Chen Hua Technology Co., Ltd.).

![Figure 2. (a, left) XRD and (b, right) Raman patterns of different deposition times TiO₂/BDD composite films (TiO₂ deposition times of samples 1, 2, 3, 4, 5 are 0, 1, 2, 3, 4, respectively.).](image)

3. Results and discussion

3.1. Phase analysis
XRD and Raman tests were performed on different samples, and the results are shown in Figure 2.

Figure 2(a) shows the XRD patterns of TiO₂/BDD composite films with different TiO₂ deposition times. The peaks at 25.28° of samples 2, 3, 4, and 5 correspond to the (101) crystal plane of anatase TiO₂. The peaks at 43.96° and 75.41° correspond to (111) and (220) crystal planes of diamond respectively; the peaks at 28.48°, 53.11°, 56.18° correspond to (111), (311), (301) crystal planes of the
silicon substrate, respectively. With the increase of the number of TiO\textsubscript{2} depositions, the peaks of TiO\textsubscript{2} is stronger and stronger, that are all peaks of anatase TiO\textsubscript{2} and belong to the tetragonal system.

It can be seen from figure 2(b) that there is a sharp peak near 1334.26 cm\textsuperscript{-1}, and the standard Raman peak of diamond is at 1332 cm\textsuperscript{-1}, indicating that the content of diamond phase is higher in the five samples. There are no obvious graphite peaks in the graph, indicating that the heat treatment did not result in significant diamond graphitization. Sample 5 has three peaks at 396.87 cm\textsuperscript{-1}, 517.06 cm\textsuperscript{-1}, 637.80 cm\textsuperscript{-1} corresponding to the Raman spectrum peak of anataseTiO\textsubscript{2}, which is consistent with the XRD test data [10].

![Figure 3. SEM images of different deposition times TiO\textsubscript{2}/BDD composite films(TiO\textsubscript{2} deposition times of (a), (b),(c), (d) are 0, 1, 2, 3, 4, respectively.).](image)

### 3.2. Microcosmic morphology analysis

Figure 3 (a) is SEM image of BDD electrode without deposition of TiO\textsubscript{2}, and Figure(b), (c), (d), (e) are SEM images of samples of TiO\textsubscript{2} deposited once, twice, three times, and four times on BDD, respectively. It can be seen that the deposition amount of TiO\textsubscript{2}is increased with the increase of deposition times. However, too much deposition of TiO\textsubscript{2} leads to more cracks, larger gaps and worse morphology in the film. Among all the samples, the surface morphology of the samples 3, 4 deposited with TiO\textsubscript{2} was the best, there are no obvious crack.

| Samples | Hall mobility (cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1}) | Sheet carrier concentration(cm\textsuperscript{2}) | Sheet Hall coefficient(Ω/□) |
|---------|--------------------------------|-----------------|--------------------------|
| 1       | 60                             | 3.55×10\textsuperscript{10} | 2.93                     |
| 2       | 74.1                           | 2.85×10\textsuperscript{10} | 2.96                     |
| 3       | 55.3                           | 4.18×10\textsuperscript{10} | 2.70                     |
| 4       | 213                            | 3.05×10\textsuperscript{15} | 9.62                     |
| 5       | 92.9                           | 3.48×10\textsuperscript{16} | 1.93                     |
3.3. Electrical and electrochemical performance

Table 1 presents the electrical properties of the BDD and TiO\textsubscript{2}/BDD composite. It can be seen that the electrical properties of electrode materials deposited with TiO\textsubscript{2} have changed significantly. The Hall mobility of most samples has been improved, and the Hall mobility of sample 4 increased to 213 cm\textsuperscript{2}/V·s, which is 3.5 times of the single BDD materials. This is advantageous for the electrochemical oxidation reactions.

![Figure 4](image)

**Figure 4.** Cyclic voltammetry curves of TiO\textsubscript{2}/BDD electrode under different electrolyte conditions (a: 0.1 mol/L NaOH; b: 0.1 mol/L H\textsubscript{2}SO\textsubscript{4}; c: 0.1 mol/L Na\textsubscript{2}SO\textsubscript{4}).

The cyclic voltammetry curves of samples in 0.1 mol/L H\textsubscript{2}SO\textsubscript{4}, 0.1 mol/L NaOH, and 0.1 mol/L Na\textsubscript{2}SO\textsubscript{4} electrolyte are shown in Figure 4, the scan rate is 200 mV/s. It can be seen that the electrochemical potential windows of the original BDD electrode in alkaline, acidic and neutral conditions are 3.7 V, 3.5 V and 4.3 V, respectively. When the original BDD electrode is under neutral conditions, the electrochemical potential window is the largest. However, the electrochemical potential window of the BDD electrode on which TiO\textsubscript{2} was deposited are wider than the electrochemical potential window of the original BDD electrode in an acidic, alkaline and neutral environment. The electrochemical potential window of sample 4 in alkaline, acidic and neutral electrolyte are 4.6 V, 4.3 V, 4.6 V. Comparing the electrochemical potential windows in three environments, it can be seen that the electrochemical potential windows of most samples in the alkaline environment are wider. This is because the solution contains a large amount of OH\textsuperscript{-}, •OH is preferentially generated near the electrode, and the oxygen evolution reaction requires a larger potential to occur.

Figure 5 (a) shows the cyclic voltammetry curves of samples with different deposition times in a mixture of 5 mmol/L K\textsubscript{3}Fe(CN)\textsubscript{6} and 1 mol/L KCl. The cyclic voltammetry scan rate is 50 mV/s. The
TiO₂ modified electrode has better redox ability than the unmodified BDD electrode. Among them, sample 4 has the best performance and has a strong redox peak, which is more advantageous in electrocatalytic organic matter. Sample 3 has the good surface morphology, and its redox capacity is second only to sample 4. Sample 5 has the largest amount of TiO₂ deposition, but the surface morphology is poor, and its redox ability is relatively poor.

Figure 5. Cyclic voltammetry curves of TiO₂/BDD electrode under 5 mmol/L K₃Fe(CN)₆, 1 mol/L KCl electrolyte (a: single cyclic voltammogram curves of samples; b: multiple cyclic voltammogram curves of sample 1; c: multiple cyclic voltammogram curves of sample 4).

The cyclic voltammetry curves of Figure 5 (b) and (c) shows that the redox capacity of the TiO₂ modified electrode increases with the number of cycles, but the performance of the unmodified electrode hardly changes with the number of cycles, which may be related to the formation of PN junctions with the combination of BDD/TiO₂ materials. This indicates that TiO₂ is strongly adsorbed on the BDD surface, and there is no significant performance degradation in multiple cycles.

4. Conclusions
The TiO₂ sol was prepared by sol-gel method and then electrophoretically deposited on BDD film. The prepared TiO₂/BDD composite electrode materials can significantly improve the electrochemical performance of single BDD materials, and TiO₂ can be firmly adhered to BDD. The deposition times of TiO₂ in the same period of time can significantly affect the surface morphology, electrical and electrochemical properties of the composite electrode materials. When TiO₂ is deposited three times at 40 V DC voltage (each deposition for 60 s), the composite electrode materials obtained has optimal surface topography, electrical and electrochemical properties. Its Hall mobility reached 213cm²/V·s,
an increase of 3.5 times, and the area of redox peaks in the cyclic voltammetry curve is the largest, indicating that its redox property is the best.

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