Correlation of the role of boron concentration on the microstructure and electrochemical properties of diamond electrodes

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ABSTRACT

In this article, a series of highly boron-doped diamond ([B] > 10^{21} \text{ cm}^{-3}) electrodes with small gradient variations in boron concentration were prepared by hot filament chemical vapor deposition (HF-CVD). Reactive blue 19 (RB-19) dye solution was used as a prototype wastewater. Interestingly, we found that the electrochemical properties (electrochemically active surface area and oxygen evolution potential) and the electrochemical degradation performance did not deteriorate linearly with increasing boron concentration. Specifically, the electrochemically active surface area of the electrode at [B]/[C] = 50,000 ppm was the highest of 9.366 cm², the chromaticity removal rate of RB-19 dye wastewater reached 100% after 90 min, and the TOC removal rate reached 74.48% after 180 min with the lowest energy consumption.

1. Introduction

Boron-doped diamond (BDD) is a star material in the field of sewage treatment. The carbon atoms of BDD form tetrahedral structure by sp³ orbital hybridization, and its covalent C-C bond has a very large bond energy, giving it high stability and high corrosion resistance [1]. In addition, diamond has high surface chemical inertia and low adsorption to oxygen molecules, which makes it a very high oxygen evolution potential (OEP), almost up to 3.0 V vs standard hydrogen electrode (SHE) [2]. Recently, numerous articles have reviewed the application of diamond in the degradation of pollutants from wastewater [1,3–5].

Pure diamond is a typical insulating material and is not a good alternative for electrochemical oxidation area, doping is an effective method to improve electrical conductivity [6]. The extremely short C-C covalent bond of diamond (1.55 Å) gives it many desirable properties, but also limits the incorporation of most dopants and their concentration [7]. The atomic radius of boron (84 pm) is close to that of carbon (77 pm, sp³); thus, boron atoms can replace C atoms and mix into the crystal lattice of diamond well. Moreover, boron could act as an p-type doping element in diamond lattice, which can increase the number of charge carriers in diamond materials and raise the dynamic rate of electron transfer on the surface of materials, thus improving the corresponding electrochemical performance [8]. The optimization degree of performance depends on the concentration of boron atoms. Ekimov et al. found that low boron concentration (n = 10^{17}–10^{19} \text{ cm}^{-3}) endowed diamond with semiconductor conductivity and activation energy of ~ 0.35 eV. As the concentration increased to 10^{20} \text{ cm}^{-3}, the activation energy gradually decreased; when n = 10^{20} \text{ cm}^{-3}, the conductivity acquired metal-like properties near room temperature [7].

In the case of water treatment based on diamond electrode, however, the effect of boron doping is not simply a case of more is better. Firstly, when boron is doped to diamond structure, boron atoms are preferentially added to the grain rather than at the grain boundaries [9], resulting in tensile stresses due to the expansion of the diamond lattice as the radius of boron atoms is greater than that of carbon atoms. In addition, it has been shown that highly B-doped electrodes have more impurity phases such as sp² bond carbon [10] and boron aggregates [11] compared to low B-doped BDD electrodes. The presence of tensile stress and impurity phases can lead to deterioration of the rigid diamond lattice [12,13], reducing stability of BDD electrodes during wastewater degradation [14,15]. Secondly, the electrochemical processes, specifically hydrogen and oxygen evolution reactions, which limit the working potential window are also dependent on boron doping level, as they are associated with adsorption of water molecules/protons.
or intermediates of limiting reactions (e.g. atomic hydrogen). Highly boron doped diamond films exhibit narrower working potential windows in both positive and negative potential regions in comparison with lowly doped diamond [13]. The decrease in OEP causes an increase in side reactions (e.g. oxygen evolution reactions) in the electrocatalytic process, which greatly affects the electrode degradation efficiency. Bogdanowicz et al. [16] investigated the effect of [B]/[C] ratio on the Si/BDD crystal structure, layer conductivity and sp³/sp² ratio, as well as the extent of degradation and mineralization of selected aromatic contaminants. The results showed that the content of the sp² phase increased with increasing [B]/[C] and that the degree of boron doping influenced the number of small grains on the surface of the diamond electrode, the density of active sites and the oxidation rate of reactive dyes. Thus, highly doped boron electrodes show faster dye removal efficiency and more efficient chlorine oxidant generation in the NaCl electrolyte. Feng et al. [12] prepared BDD electrodes with different boron doping concentrations ranging from 4/199/1 to 4/185/15 using CH₄/H₂/B(OCH₃)₃ gas as raw material, and they found that the boron doping level and the thermal stress were the main factors affecting the electrocatalytic performance of the electrode. Low boron doping levels (4/199/1) reduced the electrical conductivity and electrocatalytic activity of the films. When the ratio exceeded 4/195/5 and the carrier concentration reached around 10²⁰ cm⁻³, the thermal stress in the films led to the expansion of the diamond lattice, which affected the electrocatalytic properties of the electrode.

However, it is worth noting that researchers tend to take a large span of boron concentration to compare the effect of boron concentration, and the experimentally selected boron concentrations tend to vary widely in gradient, especially in the high boron doping range (10²⁰ ~ 10²³ cm⁻³), lacking a more systematic study. This may result in some valuable phenomena being masked. Watanabe et al. [17] prepared BDD electrodes with different B/C ratios (i.e. 0.5%, 1%, and 5%) and found that because of the B-doping limit, the boron concentration of 5% B/C was only slightly higher than that of 1% B/C, so it could maintain a high electrode stability, but at the same time 5% electrodes had more sp² phases and therefore had better electrochemical performance compared to 1% B/C.

In this work, a series of Si/BDD electrodes with different boron doping concentrations (1.21 × 10¹⁲ cm⁻³ ~ 9.11 × 10¹¹ cm⁻³) were designed in a targeted range of high boron concentrations. The microstructure and electrochemical properties were characterized, and the active blue 19 simulated wastewater degradation experiments was carried out. The results revealed that the OEP, electrochemical active surface area (EASA) and degradation capacity of diamond at high boron doping concentrations did not vary linearly with increasing boron concentration, but showed a trend of decreasing, then increasing and then decreasing, and the highest degradation efficiency was achieved at [B]/[C] = 50,000 ppm.

2. Preparation and characterization of materials

2.1. Preparation of Si/BDD electrodes

Seven BDD electrodes with different B-source (H₂:B₂H₆ = 95:5) fluxes (0.1, 0.3, 0.6, 0.9, 1.2, 1.5, 1.8 sccm) were deposited by (HFCVD) with multiple straight filaments in parallel structure. Their dimensions were all 20 mm × 25 mm and the deposited BDD electrodes were numbered as BDD₀.₁, BDD₀.₃, BDD₀.₆, BDD₀.₉, BDD₁.₂, BDD₁.₅ and BDD₁.₈ in that order. The gas flow rate of the incoming H₂ was 97 sccm, and 3 sccm for CH₄, the deposition pressure was 3 kPa, the deposition time was 12 h and the deposition temperature was 850°C.

2.2. Reagents

Analytically pure RB-19 dye (Shanghai No. 8 Dye Chemical Factory) was used as the target contaminant and analytically pure Na₂SO₄ (Sinopharm Chemical Reagent Co., Ltd.) was used as the supporting electrolyte. The solutions were all prepared with deionized water (UPT-I-10T, Accexp company, China) with a resistance value of 18.25 MΩ at room temperature.

2.3. Physical and chemical characterization methods of BDD electrodes

SEM (Nova nanosem 230, FEI, Netherlands) was used to analyze the surface morphology and grain size of the BDD films; Raman spectroscopy (labram HR800) was used to examine the carbon phase composition and boron doping of the BDD films; and an electrochemical workstation (Model CHI660E, Shanghai) was used to test the electrochemical properties of the BDD films. The oxidation capacity and reversibility of the electrodes were characterized by cyclic voltammetry (CV) through a three-electrode system (working electrode, counter electrode and reference electrode), with the working electrode being the BDD electrode, the counter electrode being the Pt electrode and the reference electrode being the Ag/AgCl electrode.

2.4. Electrochemical degradation experiments

For the RB-19 degradation experiments, the prepared BDD electrode was used as the anode material and the cathode was a 20 mm × 25 mm sheet of 304 stainless steel (requires ultrasonic shock in ethanol solution to remove greasy dirty). The power supply used for this experiment was a DC regulated power supply (Model RD-3020) and a 500 ml glass beaker was used as the electrolytic bath.
The beaker was placed on a magnetic stirrer (MS7-H550-Pro) and the speed was adjusted to 200 r/min.

2.5. Analysis of degradation effect

The total organic carbon (TOC) in solution was tested using a total organic carbon analyzer (TOC-L type, Shimadzu, Japan). The degree of mineralization of the dye solution can be assessed by the TOC value and the TOC removal rate can be expressed by calculating Equation (1) [18]:

\[
\text{TOC removal} \% = \left( \frac{\text{TOC}_0 - \text{TOC}_t}{\text{TOC}_0} \right) \times 100 \quad (1)
\]

TOC₀ (mg L⁻¹) is the initial TOC value of the wastewater and TOCₜ (mg L⁻¹) is the TOC value at time t of degradation.

The degradation of the dye solution was tested using an ultraviolet-visible spectrophotometer (UV-8000S, Metash, Shanghai). The absorbance of the dye at the maximum absorption wavelength in the visible region was recorded and the chromaticity removal rate was calculated using the following equation, as expressed in Equation (2):

\[
\text{Chromaticity removal} \% = \left( \frac{A_0 - A_t}{A_0} \right) \times 100 \quad (2)
\]

A₀ and Aₜ indicate the absorbance of the dye at the maximum wavelength in the visible region initially and after t time of degradation, respectively.

Finally, the energy consumption of the experimental process is calculated as in Equation (3):

\[
\text{Energy consumption} = EI\Delta t / V \quad (3)
\]

E (V) is the average voltage during the degradation; I (A) is the current value during the degradation; Δt (h) is the degradation time; V (L) is the volume of the dye [18].

3. Effect of boron concentration

3.1. Microstructural characterization of BDD electrodes

Figure 1 shows the SEM images of BDD electrodes with different boron concentrations. It can be seen from the figure that the boron concentration has a significant effect on the morphology of the BDD films. The difference in grain size among BDD₀.₁₀.₆ is not significant and the diamond grain size is not uniform at all concentrations which is about 4–8 μm. BDD₁.₈ has a uniform grain size of approximately 5 μm. Secondary nucleation generated in BDD₁.₂ and BDD₁.₅, and the grain got finer with a small size variation, which is approximately 2 μm. The surface of BDD₁.₈ is covered by a layer of cauliflower-like material and the original diamond grain shape disappears. In summary, as the boron source flux increases, the general trend is towards a decrease in grain size, an increase in secondary nucleation and an incomplete crystal shape [19,20], due to the fact that the doping of B introduces renucleation, resulting in smaller grains on the primary crystal [16]. When the B-source flux reaches 1.8 sccm, the film surface changes from a crystalline phase to an amorphous phase, which is attributed to the formation of borohydride depriving the gas phase of its carbon-to-hydrogen ratio, which in turn affects the grain size and morphology [21].

Figure 2a shows the Raman spectra of BDD electrodes with different boron concentrations. Compared with the conventional diamond characteristic peak (1332 cm⁻¹), the diamond peaks of the BDD films prepared in this paper undergo a small shift to the left, and the intensity of this peak decreases with increasing boron source flux, indicating that the BDD film prepared in this paper are heavily doped [19]. A distinct broad band appears in the 400–600 cm⁻¹ and 900–1250 cm⁻¹ regions, which is due to boron doping defects in the BDD layer [22,23]. The peak at ~450 cm⁻¹ shifts to the left, indicating an increase of boron concentration in the diamond.
grains. The Raman peak at 1280–1300 cm\(^{-1}\), which corresponds to the vibration of the first-order phonon of the diamond [24], shifts to the left with increasing boron concentration, suggesting that the stresses generated by lattice distortion due to boron doping within the diamond lattice are increasing [25]. Thus, as the B-source flux increases, distinct graphite peaks gradually appear near 1350 cm\(^{-1}\) and 1580 cm\(^{-1}\), demonstrating an increase in the \(sp^2\) hybridization state of the films.

For a clearer comparison, the Raman curves for different [B]/[C] ratios were fitted with a Lorentz-Gauss fit after subtracting the backbone, and then the Raman curves at 400–600 cm\(^{-1}\) were subjected to a Lorentz-Gauss decomposition, where the wave values corresponding to the Lorentz part at 400–600 cm\(^{-1}\) can be used to calculate the actual number of boron atoms inside the doped diamond film grains [26,27]. The amount of actual boron atoms doped within a unit cubic centimeter can be calculated from Equation (4):

\[
[B] = 8.44 \times 10^{10} \times \exp\left(-0.048W\right) \left(\text{cm}^{-3}\right)
\]

(4)

\(W\) is the wave number corresponding to the peak of the Lorentzian component of the Raman spectrum at 400–600 cm\(^{-1}\).

In addition, the ratio of the Raman peak intensities at 1350 cm\(^{-1}\) (D peak) and 1580 cm\(^{-1}\) (G peak), known as the \(I_D/I_G\) ratio, was calculated to assess the degree of graphitization of the diamond film with increasing boron concentration; the higher the \(I_D/I_G\) ratio, the lower the degree of graphitization and the better the diamond quality [28].

The calculated boron atom concentrations and the corresponding \(I_D/I_G\) ratios for the BDD films with different boron doping concentrations are presented in Figure 2b. It is clear from the calculated results that the boron concentration gradually increases with increasing B-source flux and is significantly higher than \(10^{21}\) cm\(^{-3}\), indicating that the BDD electrode is in a heavily doped state.

### 3.2. Electrochemical characterization of BDD electrodes

The CV curves of the BDD electrodes with different B-doped concentrations in 1 M H\(_2\)SO\(_4\) are shown in Figure 3, with data on the OEP displayed on the right. The higher the OEP of the BDD electrode, the less likely it is that side reactions such as oxygen precipitation will occur, and the more conducive it is to produce the strongly oxidizing \(\cdot\)OH for the electrochemical
degradation of organic matters [29,30]. The oxidation potential of most organic pollutants is among 1.0 V–2.0 V, while the OEPs of the BDD electrodes prepared in this paper are among 2.166 V–2.728 V, thus they have strong oxidative degradation capacity for pollutants. All of BDD0.1–BDD1.5 have high OEO and share only minor variation (2.565–2.728 V). The OEP of BDD1.8 (2.166 V) is significantly lower than the other electrodes, which is consistent with the SEM results that the grains of BDD1.8 lose their diamond shape and become amorphous due to the small sp³/sp² ratio.

Figure 4 shows the CV curves of BDD electrodes with different B-doped concentrations obtained in 1 mM K₃Fe(CN)₆ + 0.1 M KCl solution at scan rates of 20 mV s⁻¹, 50 mV s⁻¹ and 100 mV s⁻¹. Each BDD electrode showed good symmetry of redox peaks at different scan rates and the ratio of anode peak current to cathode peak current was close to 1, indicating good reversibility. A linear fit of the square root of the scan rate to the peak current shows a good linear relationship, indicating that the electrochemical reaction process at the BDD electrode is a diffusion-controlled transfer process.

EASA is an important parameter to measure the electrochemical performance of an electrode. The larger the EASA of the electrode, the more active reaction sites on the electrode surface during the electrocatalytic process and the higher the spatiotemporal yield of strong oxidizing active substances such as hydroxyl radicals, which is conducive to improving degradation efficiency [31]. The Randles-Sevcik formula was used to calculate EASA [32]:

\[
Ip = 2.69 \times 10^5 \times n^{1/2} \times A \times D^{1/2} \times C \times v^{1/2}
\]

(5)

Ip (mA) is the peak current, n is the number of electrons transferred, D (cm² s⁻¹) is the diffusion coefficient, C (mol L⁻¹) is the electrolyte concentration, v (V s⁻¹) is the sweep speed and A (cm²) is the electrochemical active surface area.

The EASA of the electrodes from BDD0.1 to BDD1.8 are shown in Figure 4h. BDD1.5 has the highest EASA (9.366 cm²) while BDD1.8 has the smallest (5.968 cm²). The EASA of the electrode is related to the number of active sites on the electrode surface. Boron doping defect sites [13], sp² impurities [10] etc. can be active

![Figure 4](image-url)
sites for electrocatalytic reactions. From BDD 0.1 to BDD 0.6, the EASA decreases, which may be due to the decrease of impurity phases and the low number of active sites on the electrode surface at this stage. From BDD 0.9 to BDD 1.5, the BDD grain size decreases and the number of grain boundaries increases, so that more \( sp^2 \) impurity phases evolve at the grain boundaries and become active sites and adsorption sites, which is conducive to the increase of the EASA [10].

3.3. Degradation properties of BDD electrodes

Figure 5 demonstrates the effect of different B-doped concentrations of BDD electrodes on the degradation efficiency of 100 mg L\(^{-1}\) RB-19 dye. At low boron concentrations (BDD 0.1 to BDD 0.6), as the boron concentration increased, the time required to degrade the RB-19 dye to transparency increased, the chromaticity removal rate and TOC removal rate both decreased and the energy consumption increased. At higher boron concentrations (BDD 0.9 to BDD 1.5), the time taken to clear the RB-19 solution decreased, the chromaticity removal rate and TOC removal rate increased, and the energy consumption decreased. Three hours degradation of RB-19 dye at the BDD 1.5 electrode did not result in a clear solution, with the lowest chromaticity removal rate and TOC removal rate and the highest energy consumption. The BDD 1.5 electrode showed the best electrocatalytic performance with nearly 100% dye chromaticity removal after 90 min, 74.48% TOC removal after 180 min and the lowest energy consumption.

The relationship between the degradation efficiency of the electrode and its OEP and EASA is further discussed. BDD 1.8 shows a sharp increase in boron concentration compared to the other electrodes. Its grains lose their diamond-like morphology due to the existence of an upper doping limit of boron concentration \( (5 \times 10^{21} \text{ cm}^{-3}) \) in the dense diamond lattice [33]. The overhigh boron concentration results in lower OEP and EASA than the other electrodes and therefore the worst electrocatalytic performance of BDD 1.8. Also, the highest energy consumption during degradation means that too high a boron doping does not lead to an improvement in the conductivity of the BDD films, but even to a decrease.

EASA and OEP are two important factors that determine the electrocatalytic performance of an electrode. The BDD 1.5 has the highest TOC removal rate, which is attributed to its significantly larger EASA than the other electrodes, and its high OEP. The EASA of BDD 1.2 and BDD 0.9 are similar, but the OEP of BDD 0.9 is obviously higher than that of BDD 1.2. However, in terms of degradation effect, BDD 0.9 is much worse than BDD 1.2. The reason may be that BDD 1.2 has a higher boron concentration and a higher number of carriers in the lattice. Thus, there is a larger surface electron transfer dynamic rate. BDD 0.3 to BDD 0.9 have similar OEP and EASA, so their electrocatalytic capacity is also similar.
However, it is worth noting that the degradation energy consumption of BDD$_{0.1}$-BDD$_{0.6}$ increases with the increase of boron concentration, which seems to be contrary to our traditional understanding that the increase of boron concentration will lead to the increase of electrode conductivity. P. Ashcheulov [34] found through hall effect tests that the concentration of holes was lower than that of boron atoms at high doping levels. Thus, it can be inferred that, for high doping levels, boron acceptors become more compensatory or boron incorporates into another form than conventional shallow acceptors, which explains the slight increase in electrode resistivity.

4. Conclusions

A series of BDD electrodes with small gradients of B-doping concentration in the high B-doping concentration range ($1.21 \times 10^{21}$ cm$^{-3}$ $\sim$ $9.11 \times 10^{21}$ cm$^{-3}$) were prepared and characterized for their microscopic morphology, electrochemical properties and degradation capacity. The BDD$_{1.5}$ electrode had the highest OEP (2.72 V), the largest EASA (5.32 cm$^2$) and the best degradation capacity. The chromaticity removal rate of RB-19 dye wastewater was nearly 100% after 90 min, and the TOC removal rate was 74.48% after 180 min, with the lowest energy consumption of 31.23 kWh m$^{-3}$.

The effect of boron concentration on the degradation capacity of the electrode is undoubtedly significant, which is related to a number of factors: firstly, the increase in boron concentration will affect the nucleation and growth process of diamond grains, within a certain range (BDD$_{0.1}$-BDD$_{1.5}$) the increase in boron concentration will lead to smaller grains and the phenomenon of secondary nucleation, accompanied by an increase in the sp$^2$ impurity phase, and an excess of boron doping (BDD$_{1.5}$) will destroy the crystalline morphology of the diamond, turning the film into a non-diamond phase. Both the OEP and EASA of BDD electrode show a non-linear variation with the increase of boron concentration, which is consistent with the change of degradation efficiency and energy consumption, higher OEP and larger EASA make the degradation efficiency show a more obvious increase.

Author contributions

Y. C., X. G. and Q. W. conceived and designed the study. Y. C. performed the research. R. Z., G. L., W. Y., Z. L., F. L., K. Z., L. M., and Z. Y. participated in the experimental research and discussions. Y. C., X. G., and G. L. analyzed the data and wrote the manuscript. Q. W. and G. L. supervised all aspects of the research. All authors have given approval to the final version of this manuscript.

Disclosure statement

No potential conflict of interest was reported by the authors.

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