A Tandem Reaction System for Inactivation of Marine Microorganisms by Commercial Carbon Black and Boron-Doped Carbon Nitride

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ABSTRACT: The Pureballast system, based on photocatalytic technology, can purify ships’ ballast water. However, the efficiency of photocatalytic sterilization still needs to be improved due to the shortcomings of the photocatalyst itself and the complex components of seawater. In this work, a tandem reaction of electrocatalytic synthesis and photocatalytic decomposition of hydrogen peroxide (H₂O₂) was constructed for the inactivation of marine microorganisms. Using seawater and air as raw materials, electrocatalytic synthesis of H₂O₂ by commercial carbon black can avoid the risk of large-scale storage and transportation of H₂O₂ on ships. In addition, boron doping can improve the photocatalytic decomposition performance of H₂O₂ by g-C₃N₄. Experimental results show that constructing the tandem reaction is effective, inactivating 99.7% of marine bacteria within 1 h. The sterilization efficiency is significantly higher than that of the single way of electrocatalysis (52.8%) or photocatalysis (56.9%). Consequently, we analyzed the reasons for boron doping to enhance the efficiency of g-C₃N₄ decomposition of H₂O₂ based on experiments and first principles. The results showed that boron doping could significantly enhance not only the transfer kinetics of photogenerated electrons but also the adsorption capacity of H₂O₂. This work can provide some reference for the photocatalytic technology study of ballast water treatment.

1. INTRODUCTION

The Pureballast water treatment system was the world’s first ballast water treatment system to be approved by the International Maritime Organization.¹² It works by using photocatalytic technology to generate hydroxyl radicals, which are then used to inactivate marine microorganisms.⁵⁻⁷ The first is that photocatalytic efficiency is low. In particular, salt can deactivate the catalyst or consume the photogenerated carrier, leading to undesirable side reactions on the catalyst surface and severely limiting the industrialization of daylight production of H₂O₂.¹⁰,¹¹ Both conditions limit the effectiveness of microorganisms in ballast water. The addition of hydrogen peroxide (H₂O₂) to the photocatalytic reaction system is an efficient way of improving the effectiveness of photocatalytic inactivation of ballast water. However, the large-scale H₂O₂ stored directly in the ship poses a possible safety risk to the vessel hull.¹³ It is more cost-effective to manufacture H₂O₂ in ships through the two-electron oxygen reduction reaction (ORR) of electrocatalysis, using seawater and air as raw ingredients. As a result, it is critical to develop an electro-catalyst capable of producing H₂O₂ in seawater. Some reports have demonstrated that commercial carbon black is an effective catalyst for electrocatalytic H₂O₂ production,¹³⁻¹⁶ with benefits such as high yield and low unit cost, which has some potential for future uses in ballast water management systems.

Moreover, decomposing H₂O₂ in a green way to generate hydroxyl radicals is an urgent problem that must be solved. Photocatalytic technology has become the primary choice with its environmentally friendly advantages. Since some studies have shown that unsaturated boron can effectively decompose H₂O₂ to produce hydroxyl radicals,¹⁷,¹⁸ we attempted to synthesize boron-doped g-C₃N₄ which not only has excellent optical properties and low cost but also can be used as a boron attachment site for the carbon vacancies generated during the preparation process.¹⁹⁻²³

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In this paper, electrocatalytic production and photocatalytic decomposition of \( H_2O_2 \) were connected in tandem, with commercial carbon black as an electrocatalyst and boron doped \( g-C_3N_4 \) as a photocatalyst, in order to efficiently inactivate microorganisms in seawater. The experimental results indicate that carbon black in seawater may manufacture \( H_2O_2 \). The concentration of \( H_2O_2 \) may reach \( 5634 \, \mu M \) after 1 h electrocatalytic reaction at potential 0.35 V (vs RHE). \( g-C_3N_4 \) shows an \( H_2O_2 \) decomposition performance at such a concentration, greatly improving the \( H_2O_2 \) decomposition and sterilization performance of boron doped \( g-C_3N_4 \). According to dynamic studies and adsorption energy calculations, the performance enhancement is mainly attributable to an increase in the lifetime of photogenerated carriers. On the other hand, it results from the enhancement of the adsorption energy of \( H_2O_2 \). This research proposes the possibility of combining electrocatalytic production and photocatalytic decomposition of \( H_2O_2 \) in succession for the treatment of ballast water.

2. EXPERIMENTAL SECTION

2.1. Materials. The materials used in this work include melamine (\( C_6H_6N_6 \)), cyano acid (\( C_2H_3NO_2 \)), boric acid (\( H_3BO_3 \)), epoxy resin (\( C_{11}H_{12}O_3 \)), \( H_2O_2 \), isopropanol (\( C_3H_8O \)), EDTA-2Na (\( C_{10}H_{14}N_2O_8 \)), and boron doped \( g-C_3N_4 \). According to the high-temperature polycondensation method, the typical high-temperature polycondensation method is used to obtain \( g-C_3N_4 \). Cyanuric acid and melamine are mixed in a mass ratio of 1:1 in 130 mL of deionized water, followed by 20 mL of isopropanol. After 30 min of ultrasonic treatment, it is completely dissolved. The solution was stirred continuously in a 70 °C water bath until the solvent completely evaporated, then it was removed, placed in a crucible, covered, and heated to 600 °C for 3 h at a rate of 10 °C/min. A light yellow powder was produced after cooling to ambient temperature.

2.2. Synthesis. 2.3.1. Preparation of \( g-C_3N_4 \). The typical high-temperature polycondensation method is used to obtain \( g-C_3N_4 \). Cyanuric acid and melamine are mixed in a mass ratio of 1:1 in 130 mL of deionized water, followed by 20 mL of isopropanol. After 30 min of ultrasonic treatment, it is completely dissolved. The solution was stirred continuously in a 70 °C water bath until the solvent completely evaporated, then it was removed, placed in a crucible, covered, and heated to 600 °C for 3 h at a rate of 10 °C/min. A light yellow powder was produced after cooling to ambient temperature.

2.3.2. Preparation of Boron Doping \( g-C_3N_4 \). The typical high-temperature polycondensation method is used to obtain \( g-C_3N_4 \). Cyanuric acid and melamine are mixed in a mass ratio of 1:1 in 130 mL of deionized water, followed by 20 mL of isopropanol. After 30 min of ultrasonic treatment, it is completely dissolved. The solution was stirred continuously in a 70 °C water bath until the solvent completely evaporated, then it was removed, placed in a crucible, covered, and heated to 600 °C for 3 h at a rate of 10 °C/min. A light yellow powder was produced after cooling to ambient temperature.

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The electrode was a 1×1 cm² platinum sheet, and H₂O₂ was produced using the constant potential polarization technique. Throughout the experiment, O₂ was supplied to maintain the seawater’s O₂ saturation. Before and following the experiment, 25 μL of liquid was pipet-injected onto the surface of the solid medium (see Supporting Information for medium preparation), put in a biochemical incubator, and incubated at 28 °C for 36 h. Following extraction, a colony counter (LC-JLQ-1, Lichen) was used to count the colonies. Each sample corresponded to three media, and the final resulting sterilization efficiency was the average of the three media, and the standard deviation was calculated. All essential experimental equipment was sanitized by UV before the sterilization tests. The following equation was used to get the sterilization rate:

\[
\text{sterilization rate (\%) } = \left( \frac{S_0 - S_t}{S_0} \right) \times 100\%
\]

where \(S_0\) is the initial colony count in the seawater medium and \(S_t\) is the colony count in the medium following the sterilizing experiment.24

2.5. H₂O₂ Synergistic Photocatalytic Sterilization Experiment. 30 mL of fresh seawater was filtered and placed in a clear quartz container, to which a solution of 30% H₂O₂ was added and mixed well, and the produced film was applied using a 300 W Xe light source (with a 420 nm cutoff filter) with a light power of 20 mW/cm². For bacterial culture, samples were collected before and after the light exposure, and the culture procedure was as mentioned before.

2.6. Determination of H₂O₂ Content. The H₂O₂ content was determined using cerium titration.25−27 H₂O₂ can convert Ce⁴⁺ to Ce³⁺ and discolor the yellow solution, making it measurable to a UV spectrophotometer at a characteristic absorption wavelength of 318 nm. Before the quantitative analysis, a standard solution of cerium sulfate was prepared to evaluate a standard curve for measuring the H₂O₂ concentration, which is shown in Figure S4.

3. RESULTS AND DISCUSSION

3.1. Characterization. The XRD and FT-IR spectra of the samples are shown in Figure 1. Here, the XRD and FT-IR data of all samples are normalized. Figure 1a shows that all samples exhibit the typical peaks of g-C₃N₄, with the peak at 12.7° corresponding to the (100) plane of the conjugated aromatics in-plane and interlayer stacking in the triazine ring unit (JCPDS-87-1526).28 The peak at 27.3° corresponds to the interlayer stacking reflection’s (002) plane. Except for the 5% B-gCN sample, the typical peak at 12.7° of the other boron-doped samples showed a slight shift to the right, around 0.2°, indicating that boron doping may cause structural alterations in g-C₃N₄.29 The chemical bonding vibrational modes of g-C₃N₄ are depicted in Figure 1b. The peak at 810 cm⁻¹ corresponds to the triazine ring unit’s respiration mode, and the 1200–1650 cm⁻¹ wide gap corresponds to the usual stretching vibrational mode of the CN heterocycle. Additionally, the wide

Figure 1. (a) XRD of gCN and B-gCN. (b) FT-IR of gCN and B-gCN.
absorption band between 3000 and 3450 cm$^{-1}$ corresponds to the functional group $\text{−NH}_2$ and water molecules adsorbed in the sample. In the FT-IR pattern, g-C$_3$N$_4$ does not appear to be considerably different from the boron-doped sample, which may be due to the doped boron element’s low concentration.$^{30-32}$ To confirm the presence of boron in the catalyst, XPS analysis of g-CN and 10% B-g-CN was performed, with the findings given in Figure 2. The total elemental spectra (Figure 2a) of both samples revealed C 1s, N 1s, and O 1s. The low boron doping induced a negligible B 1s signal in the 10% B-g-CN samples, and the appropriate boron signal was reflected in the subsequent high-resolution XPS spectra. The comparison of the high-resolution C 1s spectra of the samples is depicted in Figure 2b. The binding energies of 288.3 and 284.7 eV correspond to the C=\text{N} and C−N bonds in the tri-s-triazine structure, respectively.$^{33,34}$ The high-resolution N 1s spectrum of the sample is shown in Figure 2c, where the peaks at 398.8, 400.5, and 404.6 eV correspond to the N−C bond, N=\text{C} bond, and \pi-excitations in the heterocycles in g-CN, respectively, whereas the peaks representing the N−C bond (399.1 eV) and N=\text{C} bond (400.9 eV) in 10% B-g-CN are shifted toward the high binding energy, indicating that boron has affected the tri-s-triazine structure.$^{35,36}$ This result is also in response to the previous XRD data. Furthermore, B−N bonds were identified in the N 1s and B 1s (Figure 2d) high-resolution spectra of 10% B-g-CN by signals of 398.2 and 191.7 eV, indicating that boron-doped g-CN was produced in this work and that the boron element partially replaced the carbon in g-CN.$^{22,32,37}$ To further describe the boron distribution, we performed SEM and TEM experiments, the results of which are presented in Figure 3. The morphology of g-CN did not change considerably following boron doping (Figure 3a,b). However, the elemental mapping of 10% B-g-CN clearly shows the distribution of boron, nitrogen, and carbon components, consistent with the TEM observations (Figure 3c,d), demonstrating the successful boron doping into g-CN once again.

A comparison of the UV−vis DRS plots of g-CN and B-g-CN is shown in Figure 4a, which indicates that boron doping does not affect the light absorption characteristics of g-CN.$^{38}$ According to the Kubelka–Munk method, the DRS plot may be converted into Tauc plots (Figure 5S), and the prohibited bandwidth is between 2.78 and 2.83 eV. The Mott–Schottky method was used to investigate the flat-band (FB) potentials of g-CN and 10% B-g-CN samples to calculate their valence band

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**Figure 2.** (a) XPS spectra of g-CN and 10% B-g-CN. (b) High-resolution C 1s and (c) N 1s XPS spectra of g-CN and 10% B-g-CN. (d) High-resolution B 1s XPS spectra of 10% B-g-CN.
(VB) and conductive band (CB). The result shows that the FB values of these two samples are $-1.01$ and $-0.90$ V (vs RHE), respectively (Figure 4b). When coupled with the result of Tauc plots, the VB and CB for gCN are $-1.01$ and 1.77 V (vs RHE) and for 10% B-gCN are $-0.90$ and 1.88 V (vs RHE), respectively.

### 3.2. Catalytic Performance

In this section, we used EC600 as an electrocatalyst in a photoelectric tandem system to generate H$_2$O$_2$. A tandem of tests was done to understand the performance of H$_2$O$_2$ generation better. All the potential units were converted into reversible hydrogen electrodes (RHE) in the following figures. The findings of the cyclic
Figure 4. (a) UV-vis DRS plot of g-CN and B-g-CN. (b) Mott–Schottky plots of g-CN and 10% B-g-CN.

Figure 5. Electrochemical ORR performance of EC600 in O$_2$ saturated seawater pH = 7.9. (a) LSV at 1600 rpm (red line) and the simultaneous H$_2$O$_2$ detection current density (after N correction) at the ring electrode (pink line). (b) Calculated electron transfer number and H$_2$O$_2$ selectivity. (c) H$_2$O$_2$ productive rate and Faradaic efficiencies for the ORR at different potentials. (d) Time-dependent current density curves of EC600 at different potentials.
voltammetric (CV) curve tests, which were conducted under N₂ and O₂ saturation circumstances, are described in Figure S6. The redox peak of the sample was not seen at the N₂ saturation condition, suggesting that the sample does not react in seawater.

In comparison, under O₂ saturated conditions, a significant oxygen reduction peak was observed at 0.41 V (vs RHE) for the negative sweep curve. No significant current change was observed for the positive sweep curve, indicating that the sample can reduce oxygen without being oxidized by it.²⁰,²¹ Earlier studies demonstrated the limits of the Koutechy–Levich method in estimating the oxygen reduction selectivity and transfer electron number,²² thus the current work applied a RRDE to assess the oxygen reduction performance of the catalyst, with a catalyst loading of 0.1 mg cm⁻² at 1600 rpm and fresh seawater as the electrolyte (pH = 7.9). The collection coefficient (N) of the Pt ring was tested using the redox reaction \([\text{Fe(CN₆)}_4]^-/[\text{Fe(CN₆)}_3]^-\) to make the RRDE
The equation below:\textsuperscript{43}
\[ N = \frac{I_d[Fe(II)(CN)]^-}{-I_d[Fe(II)(CN)]^+} \]
(2)
where \( I_r \) is the current of the ring, and \( I_d \) is the current of the disk. The result is shown in Figure S7. Figure 5a shows the linear scanning voltammetric curve measured using RRDE, with the ring current calibrated by the collection coefficient (0.30) in the upper half and the disk current in the lower half. The limiting current plateau of the catalyst occurs at 0.4 V. Therefore, we calculated the number of electrons transferred and the \( \text{H}_2\text{O}_2 \) selectivity of the catalyst at potentials of 0.3, 0.35, 0.4, and 0.45 V (vs RHE), respectively, according to the following equations for the number of electrons transferred\textsuperscript{44} and the \( \text{H}_2\text{O}_2 \) selectivity:\textsuperscript{45}
\[ n = \frac{4I_d}{I_r + (I_d/N)} \]
(3)
\[ \% \text{H}_2\text{O}_2 = \frac{2I_d/N}{I_d + I_r/N} \times 100\% \]
(4)
where \( I_r \) is the current of the ring, \( I_d \) is the current of the disk, and \( N \) is the collection coefficient of the Pt ring (\( N = 0.30 \)). The results are summarized in Figure Sb and Table S2.

To determine the quantity of \( \text{H}_2\text{O}_2 \) produced in a simple device, we put EC600 onto carbon paper (with a loading of 0.5 mg cm\(^{-2}\)) and tested it in an H-type electrolytic cell filled with fresh seawater. Figure 5c illustrates the \( \text{H}_2\text{O}_2 \) yields and Faraday efficiencies at various potentials. The corresponding time–current curve is shown in Figure 5d. At 0.45 V (vs RHE), the EC600 electrode has a maximum Faraday efficiency of 70.5%, equivalent to an \( \text{H}_2\text{O}_2 \) production rate of 2540 \( \mu \text{M} \text{h}^{-1} \). The highest yield of 5634 \( \mu \text{M} \text{h}^{-1} \) was obtained at 0.35 V (vs RHE) potential, but the Faraday efficiency was significantly lower at 47.5%. It is noteworthy that some white flocculent precipitates were produced during the reaction at each potential. Moreover, a large amount of white flocculent precipitates on the electrode surface during the reaction at a potential of 0.4 V (vs RHE). Eventually, it covered the electrode surface with the increase of reaction time. We collected and analyzed the white flocculent precipitation on the electrode surface and electrolytic cells, including SEM images, EDS (Figure S8), HRTEM images, corresponding EDS elements (Figure S9), and ICP-OES (Table S3). The results showed that the main elements of this white flocculent precipitation were Mg and O, with small amounts of Na, K, Ca, Cl, and S elements. This explains why the Faraday efficiency drops noticeably below or equivalent to 0.4 V (vs RHE). In the 0.3–0.45 V (vs RHE) potential interval, the corresponding \( \text{H}_2\text{O}_2 \) concentrations in the H-type electrolytic cell were 2540, 2116, 5634, and 2964 \( \mu \text{M} \text{h}^{-1} \), respectively. To test the inactivation performance of \( \text{H}_2\text{O}_2 \) concentration on marine bacteria, 25 \( \mu \text{l} \) of seawater from the H-type electrolytic cell was taken in the solid medium for incubation, and the sterilization efficiency is summarized in Figure 6a. The result reveals that the higher the concentration of \( \text{H}_2\text{O}_2 \), the higher the sterilization performance. When the concentration is 5634 \( \mu \text{M} \), the sterilizing efficiency is 52.8% (see Figure S10), insufficient for \( \text{H}_2\text{O}_2 \) decomposition alone. In order to test the stability of the EC600 electrode for \( \text{H}_2\text{O}_2 \) production, an additional 10 cycles of stability testing was performed on the same EC600 electrode. Before the test, the electrode surface was rinsed with deionized water to remove white flocculent precipitates. Each test was conducted for 1 h, and fresh seawater was replaced. As shown in Figure S11, the EC600 electrode showed a 49% decrease in \( \text{H}_2\text{O}_2 \) production rate after the first test and a relatively stable \( \text{H}_2\text{O}_2 \) production rate of 2627 \( \mu \text{M} \text{h}^{-1} \) (average) in the subsequent tests. Furthermore, as the \( \text{H}_2\text{O}_2 \) production rate decreased, the Faraday efficiency improved from 46% in the first test to 61% (average). This may be caused by the decrease of \( \text{H}_2\text{O}_2 \) production rate on the electrode surface, resulting in less white flocculent precipitation.

To further improve the sterilization efficiency, we utilized the photocatalyst to enhance the decomposition of \( \text{H}_2\text{O}_2 \) to generate hydroxyl radicals. Furthermore, we built a tandem reaction for electrocatalytic synthesis and photocatalytic decomposition of \( \text{H}_2\text{O}_2 \). First, we tested the sterilization performance of the photocatalytic system. The photocatalyst coating by combining the catalyst with epoxy resin painting was prepared. We then tested the sterilization performance of pure epoxy resin coating (EP) and photocatalyst coating under visible light-only conditions (\( \lambda > 420 \text{ nm} \)). The results indicated that pure epoxy resin coating (EP) had almost no sterilization effect, excluding the possibility of pure epoxy resin coating interference. All photocatalytic coatings exhibited quantified sterilization performance, and B-g-CN outperformed g-CN, with the best sterilization effect of 56.9% for 10% B-g-CN, which is summarized in Figure 6b. The corresponding photos of the media are shown in Figure S12. We then added \( \text{H}_2\text{O}_2 \) to the photocatalytic system. The \( \text{H}_2\text{O}_2 \) concentration here was the maximum for electrocatalytic \( \text{H}_2\text{O}_2 \) generation in the above experiment. After 1 h of photocatalytic sterilization, the sterilization performance of all samples was significantly improved, with the sterilization efficiency of 10% B-g-CN reaching 98.7%, which was significantly better than the sterilization efficiency of g-CN (Figure 6c and Figure S13). Photocatalytic decomposition of \( \text{H}_2\text{O}_2 \) sterilization efficiency was significantly higher than the sterilization efficiency of single way. Finally, we verified the performance of the tandem system. After electrocatalytic synthesis of \( \text{H}_2\text{O}_2 \) at 0.35 V vs RHE potential, the treated seawater was added directly to a reaction vessel containing a photocatalytic film. The results are shown in Figure 6d and Figure S14. The sterilization efficiency of the tandem system was similar to that of \( \text{H}_2\text{O}_2 \) photocatalytic decomposition (99.7%). The result indicates the feasibility of constructing a tandem system of electrocatalytic synthesis and photocatalytic decomposition of \( \text{H}_2\text{O}_2 \) for the inactivation of marine microorganisms.

In order to analyze the sterilization mechanism, we performed a free radical capture experiment. The findings of free radical capture tests in seawater containing 5600 \( \mu \text{M} \text{H}_2\text{O}_2 \) are depicted in Figure 6e and Figure S15. When no photocatalyst was used, the sterilizing effectiveness was 45.2%. This result was comparable to the electrocatalytic sterilization efficiency only. EDTA and TBA were used as radical trapping agents for superoxide and hydroxyl radicals, respectively. With the addition of EDTA, the photocatalytic sterilization efficiency was maintained at 96.3%. Whereas with the addition of TBA, the photocatalytic sterilization efficiency fell dramatically to 48.9%. It implies that the primary mechanism by which marine bacteria are inactivated is the generation of hydroxyl radicals in the system. When combined...
with the analysis of DRS and Mott–Schottky data, it was determined that the VB of 10% B-gCN was insufficient to generate hydroxyl radicals. Thus, the hydroxyl radicals in the system originated from the decomposition of H$_2$O$_2$ by photocatalyst. Both electrocatalytic synthesis and photocatalytic decomposition of H$_2$O$_2$ played a significant role in the entire sterilization system, contributing to the system’s high efficacy.

To analyze the effect of boron doping on the electron transfer kinetics of g-C$_3$N$_4$, we performed EIS, transient photocurrent, photoluminescence and time-resolved fluorescence spectroscopy tests. As shown in Figure 7a-b, B-gCN resulted in a substantial decrease in the EIS arc radius and an increased in the transient photocurrent density. The equivalent circuit diagram was obtained by fitting EIS data. In the equivalent circuit diagram, R1 represents solution resistance $R_s$, and R2 represents charge-transfer resistance $R_{ct}$. 10% B-gCN shows the lowest $R_{ct}$ and this indicated that boron doping could improve the efficiency of electron transfer. The corresponding data are shown in Table S4. The photoluminescence intensity was substantially decreased after boron doping, and third-order exponential fitting was used to evaluate the time-resolved fluorescence lifetimes of the samples (Figure 7c,d). gCN and 10% B-gCN had fluorescence durations of 6.34 and 9.27 ns, respectively. The details fitting parameters are shown in Table S5. Additionally, the EIS and photocurrent results show that the presence of H$_2$O$_2$ may enhance the photogenerated carrier separation efficiency of the catalysts. Figure S16 and Table S4 illustrate the EIS plots and $R_{ct}$ of several catalysts in seawater with and without H$_2$O$_2$. When H$_2$O$_2$ is present in seawater, the EIS arc radii and $R_{ct}$ all decrease substantially, indicating that H$_2$O$_2$ may serve as an acceptor for photogenerated electrons, thus increasing the surface reaction efficiency of the catalysts. Photocurrent curves also confirm this conclusion, shown in Figure S17.

Numerous previous studies have established that g-C$_3$N$_4$ can synthesize H$_2$O$_2$ via two-step single electron transfer or one-step two electrons transfer in a photocatalytic system, but our results appear to contradict previous findings. One possible explanation is that when the H$_2$O$_2$ concentration in the solution exceeds a specific value, O$_3$ and H$_2$O$_2$ will compete for adsorption on the catalyst surface. When combined with DRS and Mott–Schottky data, it is demonstrated that boron doping can increase the efficiency of photogenerated carrier separation without altering the band structure of g-C$_3$N$_4$. B-gCN has a higher H$_2$O$_2$ decomposition and sterilization ability in a certain concentration of H$_2$O$_2$.

Figure 7. (a) EIS Nyquist plots of gCN and B-gCN. (b) Transient photocurrent response spectra of gCN and 10% B-gCN. (c) PL spectra of gCN and 10% B-gCN. (d) Time-resolved fluorescence spectroscopy of gCN and 10% B-gCN.
3.3. Calculation. To seek a reasonable explanation for our conjecture, we finally used the first-principles calculations to compare the adsorption energies of O$_2$ and H$_2$O$_2$ on the catalyst surface. The calculations were carried out in Materials Studio using the CASTEP module with a cutoff energy of 630 eV and a k-point of $2 \times 2 \times 3$. Figure S18 illustrates the built adsorption model, and the total energy of cells was summarized in Table S6. The equation of adsorption energy is the following:

$$E_{ab} = E_{\text{total}} - E_{O_2/H_2O_2} - E_{\text{cat}}$$  (5)

where $E_{ab}$ is the adsorption energy, $E_{\text{total}}$ is the total cell energy after adsorption of the substance, $E_{O_2/H_2O_2}$ is the cell energy of O$_2$ or H$_2$O$_2$, and $E_{\text{cat}}$ is the cell energy of the catalyst. The calculated results revealed that the adsorption energies of H$_2$O$_2$ and O$_2$ on the g-CN surface are $-0.81$ eV and $-0.97$ eV, respectively, with a difference of 0.16 eV between them. When the H$_2$O$_2$ concentration in the solution system is low, the g-CN surface will preferentially adsorb O$_2$ to produce H$_2$O$_2$. After boron doping, the adsorption energies of H$_2$O$_2$ and O$_2$ on the B-g-CN surface were $-0.57$ eV and $-0.61$ eV, respectively, with a significant difference of just 0.04 eV, indicating that boron doping was more favorable for H$_2$O$_2$ adsorption on the catalyst surface. Furthermore, when the concentration of H$_2$O$_2$ in the solution system reaches a certain value, both H$_2$O$_2$ and O$_2$ compete for adsorption on the surface of the B-g-CN catalyst. As the concentration of H$_2$O$_2$ increases, the catalyst eventually exhibits significant H$_2$O$_2$ decomposition, which is consistent with the sterilization results. The surface’s differential charge density diagram (Figure S19) can see the electron transfer from the boron and nitrogen atoms to the H$_2$O$_2$, which indicates that the boron and nitrogen atoms can act as the decomposition center of H$_2$O$_2$.

Based on experimental results and theoretical calculation, the schematic diagram of electrocatalytic synthesis and photocatalytic decomposition of H$_2$O$_2$ tandem reaction is shown in Figure 8. As a first step, the electrocatalytic reaction can use O$_2$ and seawater as raw materials to synthesize H$_2$O$_2$ by the commercial electrocatalyst EC600 at a proper potential. The second step, photocatalysis can effectively decompose H$_2$O$_2$ and convert it into hydroxyl radicals. During the photocatalytic reaction, H$_2$O$_2$ acts not only as a source of hydroxyl radicals but also as an electron acceptor for the photocatalyst, which effectively improves the separation efficiency of photogenerated carriers. Effective inactivation of marine bacteria can be achieved by a two-step reaction in tandem. At the same time, sterilization efficiency is much lower when using the only electrocatalytic synthesis of H$_2$O$_2$ for sterilization or only photocatalytic reaction for sterilization.

4. CONCLUSIONS

This work developed a tandem reaction for the electrocatalytic production and photocatalytic decomposition of H$_2$O$_2$ using commercial carbon black (EC600) as an electrocatalyst and B-g-CN as a photocatalyst and applied it to the treatment of marine microorganisms. In seawater, EC600 demonstrated a two-electron ORR performance. After a 1 h of electrocatalytic reaction, the H$_2$O$_2$ concentration in seawater could reach 5634 μM, inactivating 52.8% of marine bacteria in the reaction system. While B-g-CN can decompose H$_2$O$_2$ into hydroxyl radicals in the photocatalytic system, 99.7% of marine bacteria can be inactivated within 1 h in the tandem reaction system. It suggests that creating a tandem reaction is a viable method. Moreover, based on experimental data and first-principles calculations, it can be inferred that following boron doping, the transfer kinetics of g-CN$_4$ photogenerated electrons can be considerably improved. In contrast, the adsorption capacity of the catalyst for H$_2$O$_2$ can be improved. When the concentration of H$_2$O$_2$ in the solution reaches a certain value, the B-doped g-CN$_4$ demonstrates efficient photocatalytic decomposition of H$_2$O$_2$.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c00679.

Detailed information on culture media production methods and some characterization equipment; characterization data of EC600; hydrogen peroxide standard curve; DRS, photocurrent, and EIS data of photocatalysts; characterization of white flocculent precipitates; details of the first-principles calculation; water quality parameters of fresh seawater; and culture media photos of the sterilization experiment (PDF)
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Notes
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