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On-Demand Synthesis of H₂O₂ by Water Oxidation for Sustainable Resource Production and Organic Pollutant Degradation

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Abstract: H₂O₂ is a versatile and environmentally friendly chemical involved in water treatment, such as advanced oxidation processes. Anthraquinone oxidation is widely used for large-scale production of H_2O_2 , which requires significant energy input and periodic replacement of the carrier molecule. H_2O_2 production method should be customized considering the specific usage scenario. Electrochemical synthesis of H_2O_2 can be adopted as alternatives to traditional method, which avoids the concentration, transportation and storage processes. Herein, we identified Bi₂WO₆:Mo as a low-cost and high-selectivity choice from a series of Bi based oxide electrodes for H₂O₂ generation via 2-electron water oxidation reaction. It can continuously provide H₂O₂ for in situ degradation of persistent pollutants in aqueous. Simultaneously, clean energy of H₂ can be produced at the cathode. This kind of water splitting producing sustainable resources of H_2O_2 and H_2 presents an advance in environmental treatment and energy science.

Introduction

Worldwide H_2O_2 production is approximately 3 million tons per year. 60% is used for bleaching in the pulp, paper and textile industry. Anthraquinone oxidation (AO) has been considered as the mainstream production method for H_2O_2 since it was firstly introduced in the 1940s.^[1] It involves sequential hydrogenation and oxidation steps of the anthraquinone, H_2O_2 extraction and treatment of the working solution.^[1-2] However, this method has three main drawbacks: 1) the regeneration of anthraquinone solution and hydrogenation of Pd catalysts make AO an energydemanding and resource-consuming process; 2) it requires large infrastructures and impurity removal processes; 3) the concentration process is required to reduce transportation costs. The storage and transportation of concentrated H_2O_2 also encounter security issues.

Various production methods should be developed to meet the use of H_2O_2 in different occasions. For example, for the advanced oxidation processes (AOPs), onsite preparation of H_2O_2 is much more attractive than transporting concentrated H_2O_2 . AOPs only require the concentration of H_2O_2 to be about 1–10 wt.%, which can be achieved by onsite production.^[3] Electrochemical synthesis is considered as a promising route for the onsite production of H_2O_2 . Portable electrochemical devices can generate H_2O_2 avoiding the cost of plant building and the transportation of concentrated H_2O_2 , which is suitable for water purification in remote areas. The widely studied way for the electrochemical generation of H_2O_2 is two-electron oxygen reduction reaction (ORR, Eq. 1).^[4]

In our opinion, electrochemical two-electron water oxidation (Eq. 2) process provides a straightforward route for H₂O₂ production. $2H_2O \rightarrow H_2O_2 + 2(H^+ + e^-) E^0 = +1.76 V vs. RHE$ Ea. 2 This electrochemical reaction offers an economical and practical way for H_2O_2 generation. It only requires water as the reactant. Therefore, it can avoid the gas bubbling process, which lowers the production cost. Compared with oxygen reduction that requires cathode materials, electrochemical two-electron water oxidation is on the base of anode materials. Most of anode materials used for oxidative production are metal oxides, which are much cheaper than cathode materials of noble metal catalysts. More importantly, metal oxides are often proved to be stable within a large potential window. This is of great significance to environmental remediation because it often requires the electrode to operate for a long time.^[6] Therefore, two-electron water oxidation is a promising strategy for environmental remediation.

The two-electron oxidation reaction of water has been examined over some metal oxides ^[4f, 7]. For example, BiVO₄ has been identified as a suitable compound for H₂O₂ generation.^[8] BiVO₄ can achieve a Faraday efficiency (FE) above 70% at around 3.1 V vs. RHE.^[4g, 9] However, the BiVO₄ suffered from high overpotential (~ 400 mV) and poor durability due to the dissolution of VO₄³⁻ anions, which renders it not suitable for AOPs that need to last for a certain period.^[9] Therefore, catalyst design should meet the requirements for both aspects: the selectivity towards

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Figure 1 a) Scheme diagram for the preparation process for five Bi-based oxide electrodes. b) XRD pattern of the as-prepared FTO/Bi₂WO₆:Mo electrode(pink pattern) as well as the pattern of FTO and the standard diffraction of Bi₂WO₆ for comparison. c) and d) Top-view SEM images of hierarchical flower-like structures of Bi₂WO₆:Mo. e) TEM image, f) HRTEM image and g) SAED for Bi₂WO₆:Mo nanosheet.

H_2O_2 generation and the stability.

In this contribution, from a series of Bi based oxide electrodes, we discover that Bi_2WO_6 was a satisfying electrode for 2-electron water ocidation reaction in terms of the FE, overpotential and durability. Then, the current density was enhanced by Mo-doping and enlarging the surface area. This FTO/Bi₂WO₆:Mo electrode achieves a peak FE of around 79% at 3.2 V vs. RHE, and can keep a current density of 10 mA cm⁻² for at least 6 hours. Clean energy H₂ was generated at the cathode with high current efficiency. This work also provides a new strategy for *in situ* AOPs on the base of H₂O₂ produced by via electrochemical water oxidation. Persistent pollutants of norfloxacin (NFX) and methyl blue (MB) can be effectively removed in the electrolytic cell as continuous H₂O₂ generated from Bi₂WO₆:Mo anode.

Results and Discussion

Firstly, a series of Bi-based oxide electrodes were prepared (details can be found in Supporting Information). The schematic

diagram of the preparation was shown in Figure 1a, which started from the bismuth metal electrode. We then investigated the activity trend of five electrodes towards oxidative H_2O_2 generation. From the current-voltage curves (*J-V* curves, Figure S1a), the current density of water oxidation reaction increases in the sequence of FTO/Bi₂O₃, FTO/Bi₂WO₆, FTO/BiVO₄, FTO/Bi₂MoO₆, FTO/BiFeO3. We identified that OER is the dominant reaction over the surface of FTO/BiFeO3 since the current rose below the thermodynamic potential 1.76 V vs. RHE for 2-electron oxidation of $H_2O.^{[4e,\ 5]}$ The FE and H_2O_2 yield of these electrodes were quantified and compared after operation at 2.6 V vs. RHE for several minutes (Figure S1b): only FTO/Bi₂O₃, FTO/Bi₂WO₆, FTO/BiVO₄ show preference toward H₂O₂ formation. Overall, considering the low production rate of FTO/Bi2O3 and the instability of FTO/BiVO₄ (I-T curve shown in Figure S2) in this alkaline condition, Bi₂WO₆ achieves the best H_2O_2 electrosynthesis in terms of selectivity, H₂O₂ yield and stability among all the Bi-based ternary oxides. Next, morphology optimization and Mo-doping were adopted to further increase the current density of Bi₂WO₆. Bi₂WO₆:5%Mo nanosheet with large

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Figure 2. a) Current density versus potential curves for electrodes FTO/Bi₂WO₆ and FTO/Bi₂WO₆:5%Mo. b) FE measurements collected at various constant applied potentials for FTO/Bi₂WO₆:5%Mo. c) Stability test of *J*-*T* curves under different biases. d) Accumulated H₂O₂ concentration at 2.4 V vs. RHE. e) *In situ* Raman spectra recorded during the potentiostatic current-time tests at the potential from 2.0 V to 2.6 V vs. RHE. f) The FE of H₂ evolution at cathode at different cell voltage.

surface area was converted from WO3:5%Mo plate-like array (Figure S3). The XRD result (Figure 1a) reveals that the asprepared FTO/Bi₂WO₆:5%Mo is in accordance with the orthorhombic bismuth tungstate (PDF#73 2020). This also indicates the conversion of Bi2WO6:5% from WO3:5% has been achieved by the second hydrothermal treatment. From SEM images presented in Figures 1b, c and Figure S4, both Bi₂WO₆ and Bi2WO6:5%Mo appears with hierarchical flower-like structures by self-assembly nanosheets with a thickness about 10 ~ 20 nm. The average diameter of the nanoflowers is determined to be 1-2 µm. Then exposed facet of Bi₂WO₆:5%Mo nanosheets was further determined by TEM technique (Figures 1d-f). A part of the well-dispersed nanosheet is displayed in Figure 1d, and the high-resolution TEM (HRTEM) image (Figure 1e) reveals two sets of lattice fringes with an interplanar spacing of 0.274 and 0.276 nm, which corresponding to the (020) and (200) planes, respectively. The selected area electron diffraction (SAED, Figure 1f) pattern confirms the orthorhombic structure with (001) oriented growth. Other diffraction spots are also indexed to corresponding planes indicated. The surface chemical composition and valence state were characterized by XPS and shown in Figure S5. From the XPS spectrum of Mo (inset of Figure S5a), the energy difference between $4f_{5/2}$ and $4f_{7/2}$ is about 3.2 eV, implying the chemical state of doped Mo is +6.^[10]

The current-voltage (*J*-V) curves were recorded to evaluate the electrocatalytic performance of pure Bi_2WO_6 , Mo doped Bi_2WO_6 and bare FTO (Figure 2a). Bi_2WO_6 shows a lower onset potential and a higher current density than FTO. The current density is further increased after Mo-doping and reaches 0.2 mA cm⁻² at 2.0 V vs. RHE. The substitution of W by Mo induces slight modification of the crystal structure and d electronic configuration, which affects the charge transfer property.^[11] The charge transfer

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resistance of electrodes with and without Mo-doping were evaluated according to electrochemical impedance spectroscopy (EIS) shown in Figure S6. The diameter of the semicircle in Nyquist plots becomes much smaller after Mo-doping, indicating a higher charge transfer rate, which contributes to higher current density.

The H_2O_2 production reaction must compete with the four-electron oxidation reaction (oxygen evolution, Eq. 3) and the one-electron oxidation reaction (•OH, hydroxyl radical generation, Eq. 4).

 $2H_2O \rightarrow O_2 + 4(H^+ + e^-)$ E^o = +1.23 V vs. RHE Eq. 3 $H_2O \rightarrow \cdot OH + (H^+ + e^-)$ $E^\circ = +2.38 \text{ V vs. RHE}$ Eq. 4 Our electrode can achieve a high selectivity and stability toward H₂O₂ generation. Then faradaic efficiency of FTO/Bi₂WO₆:5%Mo towards H₂O₂ generation is further quantified as a function of potentials. Figure 2b shows that the 2-electron-WOR is the predominant reaction in the bias window of 2.6 ~ 3.4 V vs. RHE in KHCO₃ electrolyte, and the peak of FE reaches 79% at 3.2 V vs. RHE over Bi2WO6:5%Mo surface. The FE for both FTO/Bi₂WO₆:5%Mo and bare FTO electrode shows a similar trend: increasing firstly to the maximum and then decreasing over the tested range. Also, the H₂O₂ generation rate as a function of bias was tested (purple curve in Figure 2b), and it achieves the maximum about 300 µmol h⁻¹ cm⁻² at 3.4 V vs. RHE.

The effect of electrolyte on the selectivity of water oxidation was also investigated in other electrolytes (1 M KH₂PO₄, 1 M K₂HPO₄ and 1 M K₂CO₃). We found Bi₂WO₆:Mo achieves the highest H₂O₂ generation in KHCO₃ (Figure S7), and higher concentration of KHCO₃ facilitates both the current density and FE (Figure S8). The role of HCO₃²⁻ has been discussed previously.^[7a, 12] It is proposed that adsorbed HCO₃²⁻ can be firstly oxidized to percarbonate intermediates (HCO₄⁻ or C₂O₆²⁻), which can further hydrolyzed in water to give H₂O₂.

The electrochemical stability is vitally important for H₂O₂ production materials, especially for those used in degradation context for long-term service. A current-time (1-T) curve of FTO/Bi₂WO₆:5%Mo was tested up to 6 hours under different bias (Figure 2c). This electrode is quite stable at 2.4 V vs. RHE, while current densities only undergo slight decrease when bias increased to 2.8 V and even 3.4 V vs. RHE. To further quantify the H₂O₂ generation capacity of FTO/Bi₂WO₆:5%Mo, onsite H₂O₂ concentration was measured under 2.4 V vs. RHE in 40 mL electrolyte over 6 h as shown in Figure 2d. The accumulated concentration reaches around 25 ppm in 6 hours. Additionally, the J-V curve recorded after the stability test is very close to the previous one (Figure S9), indicating robust durability for FTO/Bi₂WO₆:5%Mo during H₂O₂ production. Additionally, Raman spectra were collected during the potentiostatic current-time experiments at different biases (2.0 V ~ 2.6 V vs. RHE) and shown in Figure 2e. Based on previous researches, Raman bands at 790 cm⁻¹ and 829 cm⁻¹ were associated with the antisymmetric and symmetric Ag modes of terminal O-W-O,[13] band at ~700 cm⁻¹ was associated with the W-O stretching modes for equatorial oxygens in WO₆ octahedra,^[14] bands at around 302 cm⁻¹ was ascribed to the bending vibration of WO₆ as well as the stretching and bending vibration of BiO₆ polyhedra^[15]. All Raman bands remain unchanged positions during the electrochemical test regardless of applied bias, indicating a stable structure characteristic of Bi₂WO₆:5%Mo in H₂O₂ generation.

While H_2O_2 was produced at the anode, a clean fuel H_2 was formed at the cathode simultaneously. As shown in Figure 2f, the FE of H_2 evolution at cathode exceeds 90% or even up to 100%

when the cell voltage above 2.3 V. Thus, clean energy of H_2 was produced simultaneously at the cathode. Therefore, this electrochemical system for water splitting can provide valuable chemical of H_2O_2 and H_2 simultaneously.

Then we try to understand mechanism for the high selectivity of water oxidation reaction over the surface of Bi2WO6:Mo. As reported before, a ΔG_{OH^*} between 1.6 and 2.4 eV is favorable to H_2O_2 production.^[4g] A small ΔG_{OH^*} often leads to weak OH* bonding energy and O₂ evolution is more likely to happen.^[9, 16] ·OH formation is more likely to occur on catalysts with strong OH* bonding free energy (ΔG_{OH^*}). By using density function calculation, we construct Bi_2WO_6 and Mo-doped Bi_2WO_6 as shown in a, b and c of Figure 3. In the model of Mo-doped Bi₂WO₆, the OH intermediate is located near the Mo or W sites for investigation (Figure 3b and c). They are denoted as $Bi_2W(Mo)O_6:Mo$ and $Bi_2W(W)O_6:Mo$. The ΔG_{OH^*} is calculated to 1.62 eV for Bi₂W(W)O₆, 1.41 eV for Bi₂W(Mo)O₆:Mo and 1.93 eV for $Bi_2W(W)O_6$:Mo. The ΔG_{OH^*} for $Bi_2W(W)O_6$ and $Bi_2W(W)O_6$:Mo are in the favorable range for H_2O_2 evolution,^[4g, 17] which is beneficial to the H_2O_2 evolution. However, compared with $Bi_2W(Mo)O_6:Mo$ with ΔG_{OH^*} of 1.41 eV, $Bi_2W(W)O_6:Mo$ shows a better ΔG_{OH^*} of 1.93 eV. The ΔG_{OH^*} of OH* locates in the middle of the H₂O₂ evolution range when the OH* is situated at the W sites. This indicates that the W atoms in the Mo-doped $Bi_2W(Mo)O_6$ should be the reaction center.



Figure 3. Structure of OH^{*} on a) Bi_2WO_6 , b) Mo- $Bi_2W(Mo)O_6$ and c) Mo- $Bi_2W(W)O_6$. Blue atoms are Bi, red are O, orange W and green is Mo. d) Energy diagram for H_2O_2 evolution on Mo-doped Bi_2WO_6 .

At 0 V on the surface of Bi₂W(W)O₆:Mo, the theoretical equilibrium potential for H_2O_2 is 1.76 V vs. RHE. As a two-electron reaction process, the free energy for H_2O_2 evolution situates at 3.52 eV.^[16] At the equilibrium potential of 1.76 V vs. RHE, the first step for the formation of OH* is uphill, and the second step is downhill. Hence, the first step of forming the OH* intermediate is a rate limiting step. Consequently, at the equilibrium potential, the H_2O_2 evolution is not spontaneous. When the applied bias increase to 2.2 V (red line in Figure 3d), as used in our experiments, the downhill in free energy is more obvious. This is consistent with our experiments that H_2O_2 is generated apparently at this bias.

The application of onsite produced H_2O_2 can be used for water remediation, disinfection, and pulp bleaching. In this work, we propose to use the onsite generated H_2O_2 to degrade persistent pollutants of NFX (25 ppm) and dye of MB (25 ppm). NFX is an antibiotic that belongs to the class of fluoroquinolone antibiotics, and 75% of NFX is excreted from the human body and induces the accumulation of antibiotics in aquatic ecosystems.^[18] Continuously accumulated NFX has been proved to interfere with bacterial DNA replication and thereby leading to bacterial genotoxicity.^[19] Whether the pharmaceutical group of NFX can be

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Figure 4. a) Comparison of NFX removal performance of FTO and FTO/Bi₂WO₆:5%Mo. b) NFX removal comparison of FTO/Bi₂WO₆:5%Mo at different biases. c) TOC removal over time using FTO/Bi₂WO₆:5%Mo as the working electrode at 3.0 V vs. RHE. d) The accumulative H_2O_2 concentration in the degradation system with and without the existence of NFX. e) Accumulative ·OH generated in the onsite H_2O_2 production system. f) Effect of IPA scavenger on NFX degradation performance using FTO/Bi₂WO₆:5%Mo as the working electrode.

attacked must be considered in assessing the efficiency of the degradation pathway.

During the NFX removal test, the soaked area of the working electrode was 2 cm², and a carbon rod was used as the counter electrode. We first tested the NFX degradation efficiency in this onsite H_2O_2 generation system. High performance liquid chromatography (HPLC) was used to test the residual NFX and other oxidation derivatives. Figure 4a shows the variation of residual NFX (appeared at ~10 min in the Chromatogram) as a function of time for the substrate FTO and electrode FTO/Bi₂WO₆:5%Mo at 2.4 V vs. RHE. It shows a much faster degradation rate for FTO/Bi₂WO₆:5%Mo compared with the FTO substrate. With the continuous generation of H_2O_2 , the NFX concentration decreased rapidly and it was no longer detected after 80 minutes for FTO/Bi₂WO₆:5%Mo. Meanwhile, the MB

decolorization test was conducted and shown in Figures S10a and b. Obvious color removal was observed with time when 2.4 V vs. RHE bias was applied to FTO/Bi₂WO₆:5%Mo electrode. MB polluted electrolyte becomes colorless after 2.5 h. Then bias dependent NFX degradation performance was also investigated as shown in Figure 4b. The faster NFX removal rate observed at higher potential should be closely related to the higher accumulated H₂O₂ concentration.From the HPLC chromatogram (Figure S11), the new appeared peaks in the total ion current indicate the newly formed intermediates transformed from NFX, and these results demonstrate that the NFX molecule was degraded into smaller molecules. These small molecules can be further degraded to CO₂ and water, as the final total organic carbon (TOC) removal reaches up to ~88% after 4 h of electrolysis of FTO/Bi₂WO₆:5%Mo at 3.0 V vs. RHE (Figure 4c).

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Figure 5. The proposed degradation pathway for NFX in the onsite H₂O₂ synthetic system.

Subsequently, the H₂O₂ concentration in the onsite degradation system was quantified with and without the addition of 25 ppm NFX (Figure 4d). The accumulative concentration of H₂O₂ increases as a function of time regardless of whether NFX is added. It reveals that almost half of the generated H₂O₂ was consumed by the degradation process of NFX. Moreover, the formation of OH in the degradation system generated by Bi₂WO₆:Mo was confirmed by the fluorescence method (Fiure S12, ESI†). Figure 4e shows that the amount of accumulative ·OH increases linearly. 2-propanol (IPA) was chosen as scavenger to studies the contribution of ·OH for degradation. Figure 4f shows the NFX removal efficiency was significantly affected by IPA, suggesting OH is crucial for the degradation of NFX. The FTO/Bi₂WO₆:Mo electrode continuously supplies H₂O₂ to degrade NFX molecules, resulting in NFX degradation and mineralization in this onsite H₂O₂ generation system.

Using the liquid chromatography-mass spectrometry (LC-MS) technique, the mass spectra and structural formulas of 6 intermediate molecules (IA, IB, IC, ID, IE, IF) in this system were analyzed in Figure S13. The structure of NFX consists of a fluorine atom, a piperazine ring and the basic pharmacophore quinolone group. The destruction of the quinolone group is the key step to prevent the spread of antibiotic-resistance gene. Then combining the LC-MS result and structural property of NFX, we analyzed the structure of intermediates and proposed the degradation pathways. As shown in Figure 5, the degradation mainly occurs through two paths: guinolone group transformation and piperazine ring cleavage. In pathway I, the guinolone was opened at the unsaturated bond by hemolytic reaction, producing m/z=352 through addition reaction. Followed by decarboxylation. decarbonylation and hydroxylation reactions, the m/z=352 is further oxidized to m/z=296. In pathway II, the piperazine ring is firstly attacked at the tertiary amine (site II) and causing a ringopening reaction. Then, two methylenes are lost and intermediate m/z=294 is generated. Subsequently, intermediate m/z=294 is further oxidized via the loss of functional group -NH-CH2-CH2 to produce intermediate m/z=251. Finally the m/z=233 is produced by defluorination.

Conclusion

In conclusion, we identified Bi_2WO_6 as a suitable electrode for H_2O_2 production through a 2-electron water oxidation route. The

H₂O₂ generation rate was further optimized by Mo-doping and enlarged specific surface area. The FE of electrode FTO/ Bi₂WO₆:Mo reaches peak 79% at 3.2 V vs. RHE, and it also shows good durability at least in 6 h. As revealed by DFT calculation, the ΔG_{OH^*} value for both Bi₂WO₆ and Bi₂WO₆:Mo is favorable for a 2electron water oxidation reaction, and W atoms should be the reaction center. As H₂ evolution occurs at the cothode, this electrolytic cell achieves a superior current efficiency with highvalue-added chemicals produced at both electrodes. Then the degradation performance of the onsite generated H₂O₂ was evaluated using NFX and MB as model pollutants. It gives satisfying results in terms of removal rate and mineralization ratio of NFX. Subsequently, the degradation intermediates were identified by using the LC-MS technique and the degradation routes were also analyzed based on the structure information on the intermediates. This on-demand production approach allows maximum utilization of H₂O₂ in a system.

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RESEARCH ARTICLE

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 H_2O_2 is synthesized by direct electrochemical oxidation of water on the surface of Bi_2WO_6 : Mo anode, which provides a straightforward route for the onsite need of H_2O_2 , such as advanced oxidation processes. Combined with the superior H_2 evolution efficiency at the cathode, this electrolytic cell enables sustainable resources produced at both electrodes.