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Oxygen Reduction Reaction for Generating H₂O₂ through a Piezo-Catalytic Process over Bismuth Oxychloride

Dengkui Shao,^[a, b] Ling Zhang,^[a] Songmei Sun,^[a] and Wenzhong Wang^{*[a]}

Oxygen reduction reaction (ORR) for generating H₂O₂ through green pathways have gained much attention in recent years. Herein, we introduce a piezo-catalytic approach to obtain H₂O₂ over bismuth oxychloride (BiOCl) through an ORR pathway. The piezoelectric response of BiOCl was directly characterized by piezoresponse force microscopy (PFM). The BiOCl exhibits efficient catalytic performance for generating H₂O₂ (28 mmol h⁻¹) only from O₂ and H₂O, which is above the aver-age level of H₂O₂ produced by solar-to-chemical processes. A piezo-catalytic mechanism was proposed: with ultrasonic waves, an alternating electric field will be generated over BiOCl, which can drive charge carriers (electrons) to interact with O₂ and H₂O, then to form H₂O₂.

H₂O₂ is widely used in pulp bleaching and disinfection,^[1] furthermore, it has been explored as a green fuel for fuel cells in recent years.^[2] However, the current industrial process of producing H₂O₂ involves anthraquinones in organic solvents and the H₂O₂ extracted from this system may be contaminated by organic impurities: Moreover, the direct synthesis of H₂O₂ from the reaction of H₂ and O₂ catalyzed by Pd or Pd/Au alloy is an alternative with risk of explosion.^[3] The sustainable production of H₂O₂ from H₂O and O₂ through a solar-to-chemical process is therefore investigated owing to the sufficient and endless sunlight.^[4] Small kinetic energies^[5] such as those from sound, water waves, and vibrations are everywhere as well as solar energy, and they may be considered as other appealing driving forces for generating H₂O₂ through the oxygen reduction reaction (ORR).

With the rapid development of piezoelectric materials,^[6] growing interest has been devoted to the conversion of mechanical energy into electricity or even chemical energy.^[7] Numerous studies about nanogenerators that could harvest mechanical forces have been reported since Wang and Song reported a ZnO nanogenerator.^[8] Moreover, there are increasing

research works reporting the direct conversion of mechanical energy into chemical energy, which is termed as the piezo-electrochemical effect^[7] or piezo-catalytic effect.^[9] In a typical piezo-catalytic process, piezoelectric materials generate an electric field with external mechanical force, which can drive charge carriers (electrons and holes) participating in redox reactions such as water splitting^[7,10] or elimination of pollutants.^[9, 11, 12] Mechanistic analysis showed that H₂O₂ could be generated in situ in the electrochemical process.^[13] However, in the process of pollutant degradation through the piezo-cata-lytic effect, H₂O₂ is overlooked or only regarded as one of the active species to remove the pollutants and the mechanism of generating H₂O₂ is unclear.

BiOCl has a layered structure and the [Bi₂O₂]²⁺ and Cl⁻ layers are stacked together by van der Waals force along the c-axis, and the structure provides a space large enough to induce a dipole along this direction.^[14] It was verified that the internal electric field along <001> was the intrinsic driving force for the spatial separation and transport of carriers in BiOCl.^[15] Herein, we report that H₂O₂ was obtained by an ORR pathway over BiOCl with ultrasonic waves. The piezoelectric response of BiOCl was directly characterized by piezoresponse force microscopy (PFM). The controlled experiments under different atmospheres indicated that H₂O₂ originated mainly from the interaction of O₂ and H₂O. Reduction of Au³⁺ in the suspension of BiOCl with ultrasonic waves proved the existence of elec-trons. The addition of scavengers confirmed that the H₂O₂ was obtained from O₂ reduction by induced electrons. This work proposes a mechanism to explain the piezo-catalytic genera-tion of H₂O₂ and provides a clean and sustainable strategy for the production of H₂O₂ owing to the inorganic and safe pro-cess, and freely available O₂ and H₂O.

An SEM image of the hydrothermally synthesized BiOCl is shown in Figure 1 a. BiOCl exhibits a square-like morphology. The width of the as-prepared BiOCl is about 2–5 mm and the thickness is about 200–300 nm. Figure 1 b shows the crystal structure of BiOCl. All the peaks of BiOCl could be well indexed to the tetragonal phase of BiOCl with the lattice parameters of $a = b = 0.3891$ nm and $c = 0.7369$ nm (JCPDS No. 06-249).^[16] These results show that the as-prepared BiOCl is well crystal-lized.

The piezoelectric response of BiOCl was characterized by an atomic force microscope (AFM) with a ferroelectric test system. Figure 2 shows the AFM and PFM images of the BiOCl micro-plates. The AFM image shows that the width of as-prepared BiOCl is about 3 mm and the thickness is about 200 nm, which is consistent with the result from SEM. Although some studies have reported the internal polar field in BiOCl,^[14,15] the piezo-electric response of BiOCl has not been characterized. The PFM

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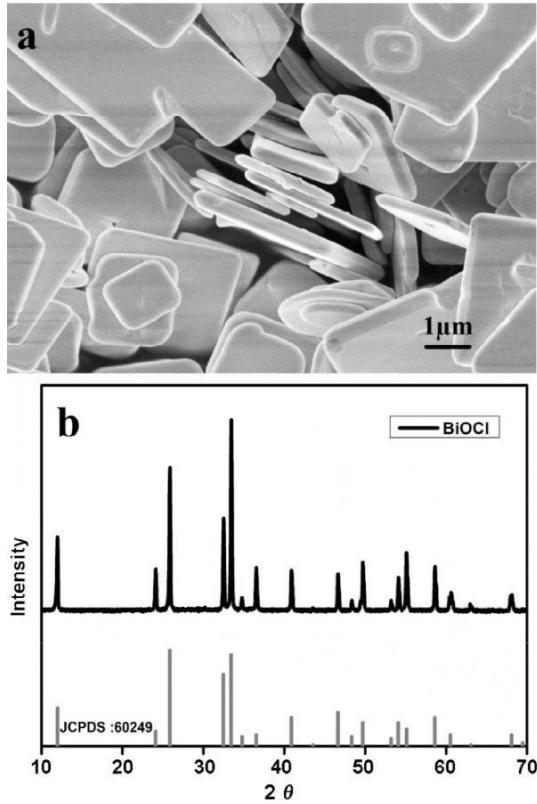


Figure 1. a) SEM image and b) XRD patterns of as-synthesized BiOCl.

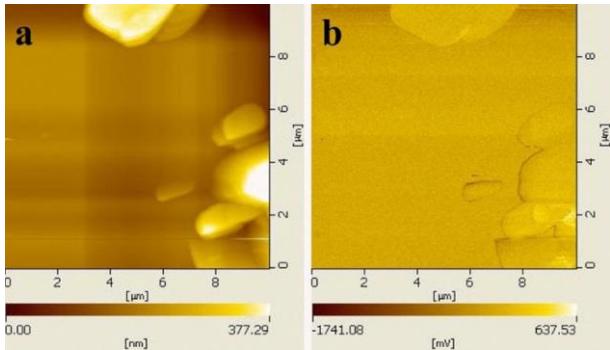


Figure 2. a) AFM and b) PFM images of as-synthesized BiOCl.

image of BiOCl revealed the piezoelectric response was indeed created from BiOCl microplates at an external load.

On the basis of the piezoelectric response of BiOCl microplates, we performed the experiment of generating H₂O₂ over BiOCl with ultrasonic waves. Without any scavengers, the ultrasonic energy-driven generation of H₂O₂ in the presence of BiOCl was realized. As shown in Figure 3, the generation rate of H₂O₂ could reach 28 mmol h⁻¹, which is above the average level achieved by powdered water splitting photocatalysts (summary of representative experiments for generating H₂O₂ through a solar-to-chemical process is shown in the Supporting Information, Table S1). The amount of H₂O₂ continuously increased with time without a noticeable decay. The X-ray diffraction (XRD) and UV/Vis diffuse reflectance spectra of BiOCl

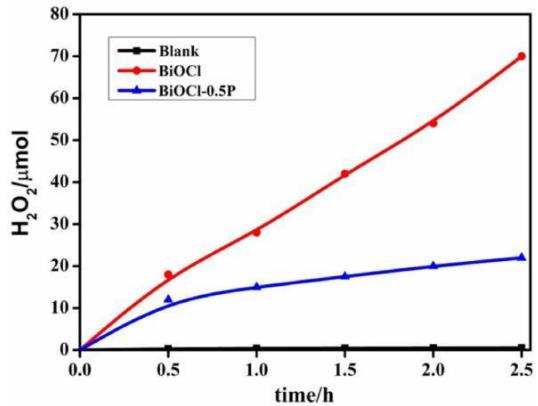


Figure 3. H₂O₂ generation upon irradiation of ultrasonic waves. The black line represents no addition of BiOCl; red line represents applying the 100 % power of ultrasonic machine; blue line represents applying the 50 % power of ultrasonic machine.

before and after use remain unchanged, indicating the stability of BiOCl (as shown in the Supporting Information, Figure S1). It was found that the generation rate of H₂O₂ was negligible (0.5 mmol h⁻¹) in the absence of BiOCl. Such phenomena indicated that BiOCl was necessary for generating H₂O₂. When the power of ultrasonic waves was adjusted to 50 % of the full power, the generation rate of H₂O₂ decreased to 3 mmol h⁻¹ except for the initial 30 min. The lower power contributed to much lower generation rate of H₂O₂, indicating that the amplitude of ultrasonic waves was a key factor for the generation of H₂O₂, because for piezoelectric materials the voltage output is proportional to the amplitude of external ultrasonic waves.^[17]

We obtained H₂O₂ from the suspension of BiOCl with ultra-sonic waves, but the mechanism is not clear. There are two possible reactions for generating H₂O₂. One consists of O₂ re-acting with H₂O and finally transforming into H₂O₂ [Eq. (1)] and the other consists of H₂O decomposing into H₂ and H₂O₂ [Eq. (2)].



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To ascertain the role of O₂ for generating H₂O₂, we performed an experiment of controlling the atmosphere in a sealed double-deck glass vessel with ultrasonic waves for 5 h. The results are shown in Figure 4: when the atmosphere was high-purity N₂, a small amount of H₂ showing a linear relationship with time could be detected and the amount of H₂O₂ was 1.68 mmol; when the atmosphere was high-purity O₂, H₂ could not be detected and the amount of H₂O₂ was 28.5 mmol. When BiOCl was absent, H₂ and H₂O₂ could not be detected in any atmosphere. In view of the amount of H₂O₂ produced with BiOCl in the atmospheres of high-purity N₂ and O₂, it could be concluded that the O element of the obtained H₂O₂ was mainly from O₂. The competition of generation of H₂O₂ and H₂ may be attributed to the different reduction potentials, because the redox potential of H₂O₂/O₂ (0.68 V, pH 0)^[4b] is more positive than that of H₂/H⁺ (0.00 V, pH 0)^[16] and electrons

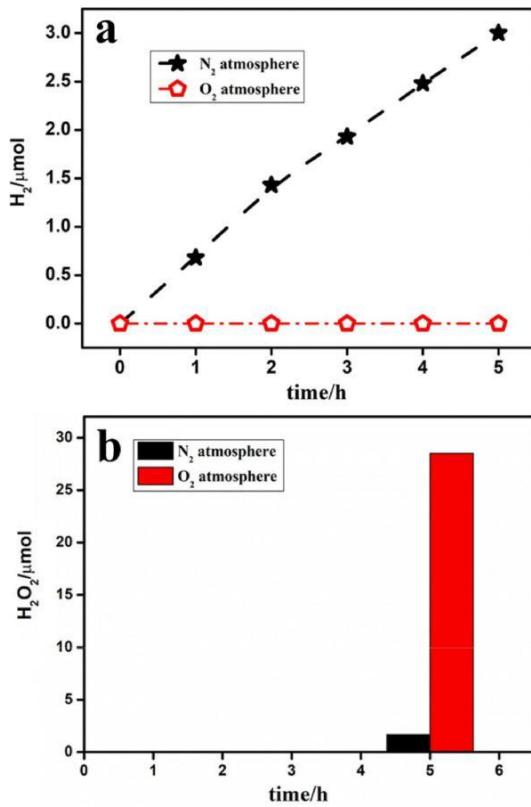


Figure 4. a) H₂ generation at high pure N₂ and O₂ atmosphere and b) H₂O₂ generation at high pure N₂ and O₂ atmosphere in suspension of BiOCl with ultrasonic waves.

prefer to reduce O₂. An experiment to determine the generation and diffusion of electrons was therefore needed.

To verify that the electrons induced by the piezoelectric effect over BiOCl with ultrasonic waves can transfer to the surface and participate in chemical reactions, a Au-deposition experiment was performed. In general, the deposition of noble metals is realized by the reduction reaction induced by photo-generated electrons or reducing agents. From a thermodynamics point of view, the potentials of ORR and the hydrogen evolution reaction are far more negative than the reduction potential of HAuCl₄, therefore, depositing Au on BiOCl in the suspension of BiOCl and HAuCl₄ through the piezo-catalytic effect should be feasible. With ultrasonic waves, the suspension of BiOCl and HAuCl₄ gradually turned to purple and finally to black, which was an indication of the presence of metallic Au. The UV/Vis diffraction spectrum showed the extended absorption edge of Au@BiOCl. An extra absorption peak at 550 nm in contrast to pure BiOCl was ascribed to the deposition of Au nanoparticles (Figure 5 b). An SEM image of Au@-BiOCl is shown in Figure 5 a. It clearly shows that Au nanoparticles were randomly deposited on the surface of BiOCl, and the size of Au nanoparticles ranges from 20 to 100 nm.

The suspension only contains BiOCl, H₂O, and O₂. Therefore, there are two possible pathways of consuming holes (charge carriers) induced by the piezoelectric effect: one is the oxidation of BiOCl and the other is the oxidation of H₂O. If the holes are consumed by decomposing BiOCl, the whole reaction for-

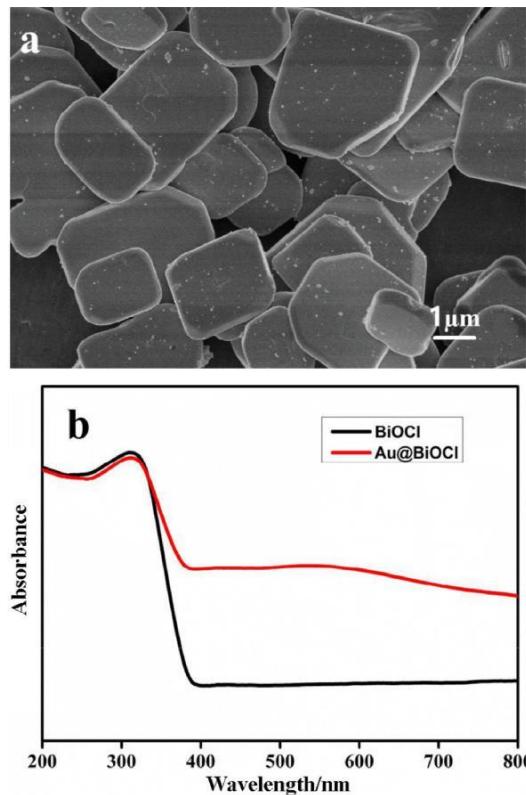


Figure 5. a) SEM image of Au@BiOCl and b) UV/Vis diffuse reflectance spectra of as-prepared sample.

mula should be as shown in Equation (3). However, producing 70 mmol H₂O₂ (as shown in Figure 3) will consume 280 mmol BiOCl, which is contradictory with the practical usage of BiOCl (50 mg, 191 mmol). The characterization of BiOCl before and after use also verified that BiOCl had good stability under ultrasonic waves (as shown in the Supporting Information, Figure S1). In view of the thermodynamics, H₂O has a more negative oxidation potential (1.23 V, pH 0) than Cl[⊖] (1.36 V, pH 0), so the holes prefer to oxidize H₂O. As a result, the induced holes were consumed by oxidizing H₂O.

ultrasonic



The mechanical-energy-driven generation of H₂O₂ may be derived from two pathways: one is the ORR [Eq. (4), Eq. (5)] and the other is both of ORR and the oxidation of H₂O [Eq. (6)].



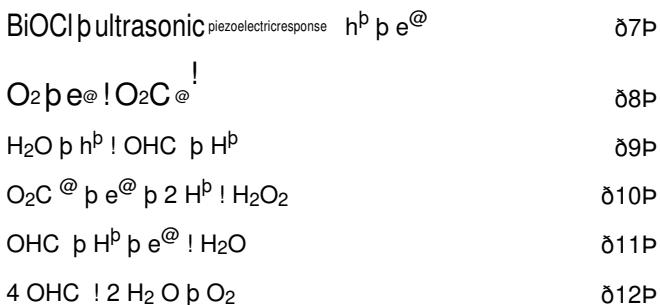
To confirm the intermediate products in the H₂O₂ generation, experiments of addition of scavengers were performed (Figure 6). Isopropanol (IPA) is a common OH[·] scavenger and benzoquinone (BQ) is a common O₂C[·] scavenger.^[18] With the addition of IPA, the amount of H₂O₂ increased about three

reach 28 mmol h⁻¹. The experiment of controlling the atmosphere indicated that H₂O₂ was mainly formed from O₂ and H₂O. Experiments of Au deposition and addition of scavengers confirm that the formed H₂O₂ was derived from ORR by the electrons induced by the piezoelectric effect. Based on these results and previous reports, a mechanism was proposed, with ultrasonic waves over BiOCl driving the electrons interact with H₂O and O₂ to generate H₂O₂. This research provides a safe and green method of generating H₂O₂ by harvesting ultrasonic energy and may facilitate the energy and avoid environmental issues.

Figure 6. H₂O₂ generation over BiOCl with addition of different scavengers.

times in contrast to the suspension of BiOCl without IPA, which indicated that the induced holes could oxidize H₂O into OHC and the formed H₂O₂ was not from the oxidation of H₂O. The existence of OHC was further confirmed by the degradation of the organic pollutant rhodamine B (RhB, for details, please refer to the Supporting Information, Figure S2) However, with the addition of BQ, the generation rate of H₂O₂ decreased to zero, which indicated that the electrons were the key for generating H₂O₂ and O₂C[•] was the intermediate of the formed H₂O₂. These results confirm that H₂O₂ was generated through the ORR by the electrons induced by the piezoelectric effect.

On account of the above results and previous reports of the piezo-catalytic effect,^[7, 9, 19–21] we propose a mechanism to illustrate the process H₂O₂ generation. When ultrasonic waves are applied to BiOCl, an electric field along <001> will be generated. The as-generated electric field can induce and separate the electron-hole pairs, as shown in Equation (7). Next, the O₂ traps the electron and forms O₂C[•], as shown in Equation (8). Simultaneously, the water will be transferred to OHC and H⁺ by interacting with holes, as shown in Equation (9). Then, protons and electrons interact with the O₂C[•] to form H₂O₂, as shown in Equation (10). One of the possible ways of consuming OHC is when it receives one electron and H⁺ to regenerate H₂O, as shown in Equation (11); another is when four OHC convert into H₂O and O₂, as shown in Equation (12).



In summary, the oxygen reduction reaction (ORR) for generating H₂O₂ through the piezo-catalytic effect was realized over BiOCl with ultrasonic waves. The piezoelectric response of BiOCl was first characterized by piezoresponse force microscopy (PFM). Under air atmosphere, the generation of H₂O₂ can

Experimental Section

Materials: All chemicals were of analytical grade purity obtained from Sinopharm Chemical Reagent Co. Ltd and used as received without further purification.

Synthesis of BiOCl: In a typical procedure, Bi(NO₃)₃·5 H₂O (2 mmol) and KCl (2 mmol) were added in distilled water (30 mL) at room temperature with continuous stirring. The suspension was stirred for 1 h and then poured into a 50 mL Teflon-lined stainless auto-clave. The autoclave was allowed to be heated at 160 °C for 24 h, and then air-cooled to room temperature. The resulting precipitates were collected and washed with ethanol and deionized water for several times to remove residual ions.

Au@BiOCl: The BiOCl (50 mg) and HAuCl₄ (1 mg) were added to pure water (100 mL) in a Pyrex glass of 500 mL and thoroughly mixed by stirring. After 10 min, the glass was placed in an ultrasonic cleaner (SK2200HP). With stirring, the suspension was treated by ultrasonic waves for 60 min. The purple-black resulting products were centrifuged and washed with pure water. The above sample was then dried at 60 °C for 4 h for further characterization.

Piezoelectric performance measurement: Normally, BiOCl (0.05 g) was dispersed in pure water (100 mL). The generation of H₂O₂ in air was done in a Pyrex glass of 500 mL in an ultrasonic cleaner (SK3200HP) with stirring by a power-driven stirrer of D2004W. The power of ultrasonic cleaner was 150 W and the frequency 53 KHz. The experiment in high-purity N₂ and high-purity O₂ atmosphere was performed, respectively in a sealed double-deck Pyrex glass of 600 mL in the ultrasonic cleaner. The amount of H₂O₂ in solution was determined by the titanium sulfate spectro-photometric method using a UV/Vis spectrophotometer (Hitachi 3010) equipped with an integrating sphere. Generated H₂ was detected by an online gas chromatograph (Tianmei, GC-7890, TCD, Ar carrier). For the experiment with addition of scavengers, IPA (10 mm) was selected as OHC scavenger, BQ (0.1 g) was selected as O₂C[•] scavengers. RhB was selected as a model pollutant. The concentration of RhB was 10 mg L⁻¹.

Characterization methods: The samples were characterized by XRD on a Rigaku powder diffractometer. The samples were scanned using CuK α radiation with an operating voltage of 30 kV and operating current of 100 mA. The scan rate of 48 min⁻¹ was applied to record the patterns in the range of 10–70°. UV/Vis diffuse reflectance spectra were recorded on an UV/Vis spectrophotometer (Hitachi 3010) equipped with an integrating sphere. The morphologies of the as-prepared samples were investigated by SEM (Hitachi S4800). The piezoelectric response of as-prepared sample was characterized by an AFM (SPA-300HV) equipped with a ferroelectric test system. In a typical procedure of sample preparation, for the

PFM test, a drop of the suspension of BiOCl dispersed on the Si substrate coated Pt by pulsed laser deposition (PLD).

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Conflict of interest

The authors declare no conflict of interest.

Keywords: bismuth oxychloride · hydrogen peroxide · oxygen reduction reaction · piezo-catalytic effect · piezoelectric response

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