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# Macroscopic Polarization Enhancement Promoting Photo- and Piezoelectric-Induced Charge Separation and Molecular Oxygen Activation

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Abstract: We report that both efficient photo- and piezoelectricinduced molecular oxygen activation are achieved via polarization macroscopic enhancement on а noncentrosymmetric piezoelectric semiconductor BiOlO3. The replacement of  $V^{5+}$  ions for  $I^{5+}\,\text{in}\,$  IO\_3 polyhedra gives rise to strengthened macroscopic polarization of BiOIO<sub>3</sub>, which facilitates the charge separation in the photocatalytic and piezoelectric-catalytic process, and renders largely promoted photo- and piezoelectric induced reactive oxygen species (ROS) evolution, such as superoxide radicals (•O2-) and hydroxyl radicals (•OH). The present work advances piezoelectricity as a new route to efficient ROS generation, and also discloses macroscopic polarization engineering on improvement of multiresponsive catalysis.

Reactive oxygen species (ROS), such as superoxide ( $\bullet O_2^{-}$ ), hydroxyl ( $\bullet OH$ ), singlet oxygen ( $^{1}O_2$ ), peroxyl (RO<sub>2</sub> $\bullet$ ), and alkoxyl (RO-) as well as hypochlorous acid (HOCI), as highly-active and green oxidants, are of great significance for environmental chemistry and biochemistry.<sup>[1]</sup> Currently, the ROS are basically produced in photocatalytic process. E.g., the photogenerated electron can reduce  $O_2$  to  $\bullet O_2^{-}$ , and  $\bullet OH$  are created via a hole oxidative process on H<sub>2</sub>O and/or -OH.<sup>[2]</sup> Particularly,  $\bullet OH$  is the most powerful and nonselective oxidant, which can damage all types of organic/biomolecules.<sup>[3]</sup> As the fast carrier recombination (~several ps) occurred in photocatalytic process, ROS evolution efficiency through photocatalysis is limited.<sup>[4]</sup> Recently, pyroelectrically driven  $\bullet OH$  generation was achieved by synergism of ferroelectric BaTiO<sub>3</sub> and superficial Pd

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nanoparticles, but its efficiency is still low.<sup>[5]</sup> Thus, promoting photocatalytic ROS evolution as well as exploration of new channels to production of ROS, particularly realized by a single material, are of significance and challenge. Piezoelectrics reversibly converting stress into electricity, are widely applied in optoelectronics. The stress-induced polarization potential can act as alternating built-in electric field to separate photoinduced carriers.<sup>[6]</sup> BiOIO<sub>3</sub> as a noncentrosymmetric (NCS) polar material presents strong second-harmonic generation (SHG, ~12.5 KDP) and piezoelectricity (d\_{33} ~26 pm/V).^{[7]} The large macroscopic polarity is mainly attributed to the alignment of the lone-pair containing IO<sub>3</sub> polyhedra. Recently, BiOIO<sub>3</sub> was investigated for diverse photocatalytic applications.<sup>[8]</sup> Fan et al and our group demonstrated that large macroscopic polarity can induce efficient charge separation, contributing to high photocatalytic activity.<sup>[9]</sup> Considering the large polarity of BiOIO<sub>3</sub> from IO<sub>3</sub> polyhedra, decoration on IO<sub>3</sub> may adjust the polarity, and thus improve photocatalytic molecular oxygen activation. Importantly,  $BiOlO_3$  is piezoelectric. It is worth surveying its performance for piezoelectric-catalytic ROS generation.

Herein, we describe the synthesis and photo- and piezoelectric-induced molecular oxygen activation of vanadium doped BiOIO<sub>3</sub>. V is selected for replacing I in BiOIO<sub>3</sub> for the following two reasons: The similar bond length of V-O and I-O (~1.6-1.9 Å) allows the replacement of V for I. Besides, the equivalent substitution of I<sup>5+</sup> with V<sup>5+</sup> can keep the charge conservation in BiOIO<sub>3</sub>. The results revealed that V replacement of BiOIO<sub>3</sub>. It significantly promotes the charge separation in both the photocatalytic and piezoelectric catalysis process, which renders strengthened photo- and piezoelectric induced molecular oxygen activation for producing •O<sub>2</sub><sup>-</sup> and •OH.

XRD demonstrates that V-BiOIO<sub>3</sub> keeps both the phase and crystallization orientation unchanged (Fig. S1). XPS was conducted to reveal the V doping. It is evident that a new peak at 529.9 eV appears for V-BiOIO3, which is attributed to V 2p (Fig. 1a). The peaks at 530.4, 164.4, 159.1, 635.4 and 623.8 eV observed for BiOIO3 correspond well to O 1s, Bi 4f<sub>5/2</sub>, Bi 4f<sub>7/2</sub>, I  $3d_{3/2}$ , and I  $3d_{5/2}$ , respectively (Fig. S2). In contrast, the above-peaks of V-BiOIO3 all show distinct shift, which means the chemical environment change of related atoms. From Raman spectra (Fig. 1b), one can see an obvious band around 850 cm<sup>-1</sup> appeared for V-BiOIO<sub>3</sub>, which can be ascribed to V-O vibration.<sup>[10]</sup>

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**Fig. 1.** (a) XPS of O 1s and V 2p and (b) Raman spectra of  $BiOIO_3$  and V-BiOIO<sub>3</sub> (BiOI<sub>0.926</sub>V<sub>0.074</sub>O<sub>3</sub>). (c) XRD Rietveld refinement of V-BiOIO<sub>3</sub>. (d) Fourier transform (FT) curves of XAFS data of BiOIO<sub>3</sub> and V-BiOIO<sub>3</sub>. TEM images of (e,g) BiOIO<sub>3</sub> and (f,i) V-BiOIO<sub>3</sub>. (h) Unit cell illustration of BiOIO<sub>3</sub>.

To deeply understand the crystal structural evolution and the V action in BiOIO<sub>3</sub> structure, Rietveld refinement was carried out via the computer software General Structure Analysis System (GSAS). The result show that V-BiOIO<sub>3</sub> also crystallizes in orthorhombic-Pca21 space group, and I<sup>5+</sup> and V<sup>5+</sup> ions with ratio of 0.925(3)/0.074(7) co-occupy in the same site (Fig. 1c). Namely, the final V-BiOIO<sub>3</sub> is  $BiI_{1-x}V_xO_4$ : x = 0.074(7). The corresponding crystallographic data are summarized in Table S1-3. The unit cell parameters undergo slight changes resulting from the substitution of  $I^{5+}$  with  $V^{5+}$  according to Vegard's rule. For confirmation, XAFS data on the I K-edge (33.179 keV) of pristine BiOIO3 and BiOI<sub>0.926</sub> $V_{0.074}O_3$  were collected at room temperature. The Bi L-edge oscillation curves of BiOIO3 and  $BiOI_{0.926}V_{0.074}O_3$  display obvious difference in the energy range of 33160-33260 eV, which suggests their different local atomic arrangements (inset of Fig. 1d). Fig. 1d presents the Fourier transform (FT) curves of XAFS data. The strong peak between 1 and 2 Å is attributed to I-O bond. Remarkably, the I-O radial distance shows an evident shift (0.08Å) to smaller value, which is resulted from the replacement of  $V^{5+}$  for  $I^{5+}$ . It is in accordance with the fact that V-O has a slightly shorter bond length than I-O. The replacement of  $V^{5+}$  would induce a distortion of  $IO_3$ polyhedron.

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SEM and TEM revealed that the morphology of BiOIO<sub>3</sub> undergoes great change after V replacement. The original 2D square nanoplates transform into 1D nanostrips (Fig. 1e,f and Fig. S3a-d). HRTEM showed that the interplanar spacing of lattice fringe for BiOIO3 and BiOI0.926V0.074O3 is ~0.287 nm, corresponding to (002) and (200) planes. Their FFT patterns are also well assigned to the [010] zone-axis diffraction spots of orthorhombic BiOlO<sub>3</sub> or  $BiOl_{0.926}V_{0.074}O_3$  (Fig. S3e and f). Namely, the exposing facet for both samples is the {010} facet (Fig. 3g and i). It is perpendicular to the  $[Bi_2O_2]^{2+}$  layer stacking direction (Fig. 3h), where the internal electric field favors charge separation. Besides, the specific surface area of BiOIO<sub>3</sub> and  $BiOI_{0.926}V_{0.074}O_3$  is determined to be 3.1 and 8.7  $m^2/g,$ respectively, fitting the nonporous characteristic (Fig. S4). Namely, the V replacement in BiOIO<sub>3</sub> causes a 2.5-fold increase in surface area.

Diffuse reflectance spectra reveal that  $BiOI_{0.926}V_{0.074}O_3$ shows visible light absorption with a long absorption tail extending to 550nm compared with  $BiOIO_3$  (Fig. S5), corresponding to the color change from white to yellow. This would allow  $BiOIO_3$  visible-light active photo-reactivity. The band gap was determined as 3.07 and 2.95 eV for  $BiOIO_3$  and  $BiOI_{0.926}V_{0.074}O_3$ , respectively (Fig. S7a). DFT calculation<sup>[111]</sup> demonstrated that the narrowed band gap and visible-light absorption of  $BiOI_{0.926}V_{0.074}O_3$  are mainly resulted by the downshift of conduction band (Fig. S6a and Fig. S7b), which is contributed by the V 3d orbital (Fig. S6c-e).

Photo-induced molecular oxygen activation was studied under visible light ( $\lambda$  > 420 nm) and UV light. DMPO-assisted ESR inspects the spin-trapped paramagnetic oxygen species •O2<sup>-</sup> and •OH.<sup>[2c]</sup> BiOIO3 shows no signal under visible light, confirming no visible-light activity of BiOIO<sub>3</sub> (Fig. 2a and b). Whereas, evident six identical peaks are observed for BiOI<sub>0.926</sub>V<sub>0.074</sub>O<sub>3</sub>, which is assigned to DMPO-•O<sub>2</sub><sup>-</sup> adduct derived from O<sub>2</sub> reduction by electrons.<sup>[12]</sup> Meanwhile, four peaks with intensities of 1:2:2:1 attributing to DMPO-•OH also appear.<sup>[2c]</sup> •OH should originate from the OH<sup>-</sup>/H<sub>2</sub>O oxidation in water by holes. It demonstrates that V replacement endows BiOIO<sub>3</sub> with the visible-light molecular oxygen activation ability with generation of the above two powerful oxidative species. This is understandable because BiOI<sub>0.926</sub>V<sub>0.074</sub>O<sub>3</sub> exhibit photoabsorption in visible region. However, it is significant to find that this property is also greatly enhanced with irradiation of UV light. BiOI<sub>0.926</sub>V<sub>0.074</sub>O<sub>3</sub> shows a stronger six-line spectrum than BiOIO<sub>3</sub> under UV light (Fig. 2c,), meaning a higher •O<sub>2</sub><sup>-</sup> production. Remarkably, a significantly strengthened seven-line spectrum was generated by BiOI<sub>0.926</sub>V<sub>0.074</sub>O<sub>3</sub> (Fig. 2d). This type of peaks with intensity of 1:2:1:2:1 represents the appearance of DMPOX, resulting from the oxidation of DMPO by two •OH radicals.<sup>[13]</sup> As the amount of free radical is approximately proportional to the square of the height of signal,<sup>[14]</sup> the  $\cdot O_2^-$  and  $\cdot OH$  amounts for BiOI<sub>0.926</sub>V<sub>0.074</sub>O<sub>3</sub> is calculated to be ~ 3.5 and 95.5 times that of BiOIO3. This observation clearly states that a more powerful UV-light driven ROS evolution ability was achieved for BiOI<sub>0.926</sub>V<sub>0.074</sub>O<sub>3</sub> than the pristine BiOIO<sub>3</sub> compared to visible-light-activity enhancement, and the enormously intensified activity is not associated with photoabsorption.

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**Fig. 2.** ESR signals for (a,c) DMPO-•O<sub>2</sub><sup>-</sup> and (b,d) DMPO-•OH over BiOIO<sub>3</sub> and V-BiOIO<sub>3</sub> (BiOI<sub>0.926</sub>V<sub>0.074</sub>O<sub>3</sub>) under visible light ( $\lambda$  > 420 nm) and UV light illumination for 5 min, respectively.

To further understand the drastically promoted ROS activity, photodegradation on a dye model RhB is performed (Fig. S8-S11). The photocatalytic activity of BiOl<sub>0.926</sub>V<sub>0.074</sub>O<sub>3</sub> is ~10.1 and 21.1 times that of BiOlO<sub>3</sub> under visible and UV light, respectively (Fig. 3a). Active species trapping test shows that  $\cdot$ O<sub>2</sub><sup>-</sup> and  $\cdot$ OH are the main reactive species and take crucial roles in the photocatalytic oxidation regardless of light source (Fig. S12 and 13).<sup>[15]</sup> These results well confirmed the highly enhanced molecular oxygen activation of BiOl<sub>0.926</sub>V<sub>0.074</sub>O<sub>3</sub>.



**Fig. 3.** Reaction rate constant for RhB degradation over BiOIO<sub>3</sub> and V-BiOIO<sub>3</sub> (BiOI<sub>0.926</sub>V<sub>0.074</sub>O<sub>3</sub>) under (a) visible light ( $\lambda > 420$  nm) and (b) UV light. (c) Transient photocurrent response and (d) surface photovoltage spectra over BiOIO<sub>3</sub> and V-BiOIO<sub>3</sub> under UV light.

For exploring the origin for the enormously enhanced photoreactivity, several factors that predominantly affect the photochemical reaction, e.g. photoabsorption, surface area and charge separation efficiency, are considered. As revealed by the above data, the extended photoabsorption in visible region of  $BiOI_{0.926}V_{0.074}O_3$  is not responsible for the improved UV-light activity. Their surface area difference (~2.5 times) is also far small to contribute to huge enhancement on ROS generation and photodegradation. Therefore, charge separation as the most possible factor is investigated by transient photocurrent and SPV spectroscopy.<sup>[16]</sup> BiOl<sub>0.926</sub>V<sub>0.074</sub>O<sub>3</sub> produces a markedly increased current density under UV light (Fig. 3c), beyond 5 times that of BiOlO<sub>3</sub>, indicating a higher charge separation in BiOl<sub>0.926</sub>V<sub>0.074</sub>O<sub>3</sub>. SPV spectroscopy can reveal the surface potential barrier and charge separation extent of excited states generated by absorption. It is demonstrated that the SPV signal generated by BiOl<sub>0.926</sub>V<sub>0.074</sub>O<sub>3</sub> far exceeds that of BiOlO<sub>3</sub> in the range of 310-390 nm, with enhancement degree of over 10-fold (Fig. 3d). These results illuminates that the V replacement endues BiOlO<sub>3</sub> with significantly promoted charge separation, accounting for the robust molecular oxygen activation performance. In view of that BiOl<sub>0.926</sub>V<sub>0.074</sub>O<sub>3</sub> and BiOlO<sub>3</sub> have the same exposing {010} facet there must exist some other reasons for the dramatically strengthened charge separation.

Porlarization engendered in NCS crystal structure can cause a large intrinsic polarization effect, promoting charge separation.<sup>[9]</sup> The polarity of BiOIO<sub>3</sub> mainly originates from alignment of IO<sub>3</sub> polyhedra along [001] direction. Along the a and b axis, the polarity of IO3 polyhedra is offset due to the completely opposite arrangement of IO3 groups (Fig. 4a). While along the c-axis, namely [001] direction, the local dipolemoment of IO<sub>3</sub> polyhedra is additive, which results in a large macroscopic polarization (Fig. 4b).<sup>[7]</sup> As revealed by TEM, BiOI<sub>0.926</sub>V<sub>0.074</sub>O<sub>3</sub> crystal grows along the [001] direction. This crystallization orientation may be induced by the polarization. SHG performed by irradiation of a 1064 nm Nd:YAG laser confirms the enhanced macroscopic polarity in  $BiOI_{0.926}V_{0.074}O_3$ , which produces a superior SHG response, beyond 2 times that of BiOIO<sub>3</sub> (Figure 4c). It verifies that a larger macroscopic polarity is realized in  $BiOI_{0.926}V_{0.074}O_3$ , favorable for the separation of photogenerated electrons and holes.<sup>[9b]</sup> For in-depth understanding, the strengthened macroscopic polarization of  $BiOI_{0.926}V_{0.074}O_3$  is analyzed by polyhedral distortion index. The symmetry of coordination environment in crystal structure can be influenced by the polyhedral distortion. The polyhedral distortion index D can be calculated by Eq. (1)<sup>[17]</sup>

$$= \frac{1}{n} \sum_{i=1}^{n} \frac{|l_i - l_{av}|}{v}$$
(1)

where  $l_i$  is the distance from the central atom to the *i*th ligands and  $l_{av}$  is the average bond length. The polyhedral distortion of IO<sub>3</sub> is determined to be 0.065 in BiOI<sub>1-x</sub>V<sub>x</sub>O<sub>3</sub>:x = 0.074(7), which is bigger than that of BiOIO<sub>3</sub> (0.063). Therefore, the superimposition of microscopic polyhedral distortion contributes to the large macroscopic polarization of BiOI<sub>0.926</sub>V<sub>0.074</sub>O<sub>3</sub>.

As BiOIO<sub>3</sub> is piezoelectric, polarization enhancement caused by V replacement may also result in an improved piezoelectric-induce molecular oxygen activation ability. Here, ultrasonic was employed as a stable irradiation source to provide press, and NBT was used as a probe to quantify the  $\cdot O_2$ concentration.<sup>[18]</sup> Sharp decrease in the absorbance of NBT centering at 259 nm is observed, demonstrating that both BiOIO<sub>3</sub> and BiOI<sub>0.926</sub>V<sub>0.074</sub>O<sub>3</sub> show robust pizeoelectric-catalytic activity for transforming  $O_2$  into  $\bullet O_2^-$  (Fig. S14). Based on the reacting relation between NBT and •O2<sup>-</sup> (1:4 in molar ratio),<sup>[18]</sup> the average •O2<sup>-</sup> evolution rate of BiOIO3 and BiOI0.926V0.074O3 is determined to be 6.5 and 11.1 µmol·L<sup>-1</sup>·h<sup>-1</sup>, respectively (Fig. 4e). To inspect if •OH was generated in the piezoelectric-induce process, terephthalic acid (TA)-photoluminescence (PL) method is employed, as •OH could react with TA in equal proportion to produce highly fluorescent 2-hydroxyterephthalic acid at 425 nm.<sup>[5]</sup> Drastic PL peak intensity increase occurs with increasing

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the ultrasonic time (Fig. S15), suggesting the continuous production of •OH. The plot of •OH concentration vs. ultrasonic irradiation time is illustrated in Fig. 4f. The •OH concentration generated by BiOl<sub>0.926</sub>V<sub>0.074</sub>O<sub>3</sub> far exceeds that by BiOlO<sub>3</sub>, and the average production rates are 1.2 and 3.9 µmol·L<sup>-1</sup>·h<sup>-1</sup> for BiOlO<sub>3</sub> or BiOl<sub>0.926</sub>V<sub>0.074</sub>O<sub>3</sub>, respectively. Therefore, BiOl<sub>0.926</sub>V<sub>0.074</sub>O<sub>3</sub> shows a much superior pizeoelectric-induce •O<sub>2</sub><sup>-1</sup> and •OH evolution, approximately 1.7- and 3.3-times of BiOlO<sub>3</sub>. Besides, no •O<sub>2</sub><sup>-1</sup> and •OH are detected under ultrasonic without BiOlO<sub>3</sub> or BiOl<sub>0.926</sub>V<sub>0.074</sub>O<sub>3</sub> (Fig. S16), further verifying the piezoelectric induced ROS evolution process.



**Fig. 4.** Crystal structure of V-BiOIO<sub>3</sub> (BiOI<sub>0.926</sub>V<sub>0.074</sub>O<sub>3</sub>) (a) along *a-b* and (b) along *b-c* planes (Black arrows indicate polarization direction of I<sub>1-x</sub>V<sub>x</sub>O<sub>3</sub>). (c) SHG generation for BiOIO<sub>3</sub> and BiOI<sub>0.926</sub>V<sub>0.074</sub>O<sub>3</sub>. (g)  $\cdot$ O<sub>2</sub><sup>-</sup> and (f)  $\cdot$ OH evolution curves over BiOIO<sub>3</sub> and BiOI<sub>0.926</sub>V<sub>0.074</sub>O<sub>3</sub> under ultrasonic irradiation (40 kHz, 300 W).

On the basis of the above results, the possible piezoelectriccatalytic molecular oxygen activation and enhancement mechanism is speculated. As BiOIO<sub>3</sub> is pizeoelectric, the ultrasonic-introduced press could induce the generation and asymmetrical distribution of positive and negative charges on two opposite sides of BiOIO<sub>3</sub>. According to the metal oxide anode radical production theory, the electro-catalytic effect would occur which is indued by the as-generated electric charges.<sup>[19]</sup>

 $BiOIO_3 + H_2O \rightarrow BiOIO_3 + \bullet OH + H^+ + e^-$  (2)

$$0_2 + e^- \rightarrow \bullet 0_2^- \tag{3}$$

During the electro-catalytic process, •OH, H<sup>+</sup> and e<sup>-</sup> were generated at anode. As the anode of BiOlO<sub>3</sub> nanostrips bears ultrasonic-induced polarization negative charges, and cathode is positively charged, the piezoelectric polarization field goes from cathode to anode. Due to charge interaction, the e<sup>-</sup> produced at anode would migrate to cathode, and reduce O<sub>2</sub> into •O<sub>2</sub><sup>-</sup>. In view of the much stronger polarity of BiOl<sub>0.926</sub>V<sub>0.074</sub>O<sub>3</sub> than BiOlO<sub>3</sub> along the [001] direction, higher charge separation occurs for BiOl<sub>0.926</sub>V<sub>0.074</sub>O<sub>3</sub>. Therefore, more •O<sub>2</sub> and •OH are produced from BiOl<sub>0.926</sub>V<sub>0.074</sub>O<sub>3</sub>. Besides, the nanostrip

morphology of  $BiOI_{0.926}V_{0.074}O_3$  strengthens the asymmetrical distribution of positive and negative charges on its surface, further contributing to the ROS production.

In summary, both photo- and piezoelectric- induced molecular oxygen activation are achieved on a NCS piezoelectric BiOIO<sub>3</sub>. More fascinatingly, the replacement of  $V^{5+}$ for I<sup>5+</sup> ions in IO<sub>3</sub> polyhedra resulted in a macroscopic polarization enhancement, which largely facilitates the charge separation, and thus resulting in highly promoted molecular oxygen activation in both the photocatalytic and ultrasonicassisted piezoelectric-catalytic process. Compared to pure BiOlO<sub>3</sub>, the  $\cdot$ O<sub>2</sub><sup>-</sup> and  $\cdot$ OH evolution rates for BiOl<sub>0.926</sub>V<sub>0.074</sub>O<sub>3</sub> increase separately ~ 3.5 and 95.5 fold for photocatalysis, and 1.7 and 3.3 times for piezoelectric-catalysis. Besides, the formation mechanism of reactive oxygen species in piezoelectric-catalytic process was speculated. This study exposes the promising prospect of macroscopic polarization enhancement on promoting photo/piezoelectric-catalysis, and may have potentials to be extended to other applications, e.g. supercapacitor, lithium-ion battery, etc.

#### **Experimental Section**

The experimental section part is provided in the supporting information.

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#### **Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** Macroscopic polarization • Photocatalysis Piezoelectric-catalysis • BiOIO<sub>3</sub> • Molecular oxygen activation

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# COMMUNICATION

### **Entry for the Table of Contents**

### COMMUNICATION

Macroscopic polarization V<sup>5+</sup> enhancement by replacement in piezoelectric BiOIO3 can semiconductor greatly facilitate the charge separation and render efficient photoand piezoelectricinduced molecular oxygen activation producing abundant for powerful superoxide and hydroxyl radicals.



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Macroscopic Polarization Enhancement Promoting Photo- and Piezoelectric-Induced Charge Separation and Molecular Oxygen Activation