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Synergetic effects by Co\textsuperscript{2+} and PO\textsubscript{4}\textsuperscript{3−} on Mo-doped BiVO\textsubscript{4} for an improved photoanodic H\textsubscript{2}O\textsubscript{2} evolution

Lele Yang\textsuperscript{a}, Hong Chen\textsuperscript{a}, Yuntao Xu\textsuperscript{a}, Rong Qian\textsuperscript{b}, Qiao Chen\textsuperscript{c*} and Yuanxing Fang\textsuperscript{a*}

\textsuperscript{a}State Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry, Fuzhou University, Fuzhou 350116, P. R. China

\textsuperscript{b}National Center for Inorganic Mass Spectrometry in Shanghai, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, P. R. China

\textsuperscript{c}Department of Chemistry, School of Life Sciences, University of Sussex, Brighton, BN1 9QJ, United Kingdom.

Email: Qiao.Chen@sussex.ac.uk; yxfang@fzu.edu.cn.
Abstract

The efficiency of hydrogen peroxide evolution reaction (H$_2$O$_2$ER) by photoanodic water oxidation is normally limited by low yield and poor selectivity. In this work, the surfaces of Mo doped BiVO$_4$ are modified by Co$^{2+}$ and PO$_4^{3-}$ ions (CPMB), which were used as the photoanode with improved H$_2$O$_2$ yield and selectivity. The optimal evolution rate of the CPMB is ca. 0.23 µmol·min$^{-1}$·cm$^{-2}$, corresponding to 2.5 times to the pristine BiVO$_4$ photoanode, and the faradaic efficiency of CPMB photoanode for H$_2$O$_2$ER is ca. 26%. In this study, the mechanism for the improved H$_2$O$_2$ evolution performance of CPMB has been investigated, indicating that PO$_4^{3-}$ ions mainly promote the formation of the •OH by dissociation of H$_2$O, while Co$^{2+}$ ions accelerate the conversion of the •OH for the subsequent H$_2$O$_2$ evolution. This study offers the strategy for designing an efficient photoelectrochemical system with optimized solar conversion efficiency for H$_2$O$_2$ production.

Keywords: hydrogen peroxide, photoanode, water oxidation, BiVO$_4$, photoelectrochemical system.
1. Introduction

Hydrogen peroxide (H₂O₂) is an important industrial raw material for a variety of chemical processes, such as propylene and alkane oxidation reactions [1-2], cyclohexanone oxime production [3], aromatic hydroxylation [4], and others [5]. H₂O₂ is currently produced by the anthraquinone method developed by Badische Anilin-und-Soda-Fabrik (BASF) company, which involves the catalytic reduction and oxidation of anthraquinone using H₂ and O₂ as the raw materials at 40-70 °C under the pressure of 4 atmospheric pressure [6]. The involvement of explosive hydrogen gases and the subsequent separation of H₂O₂ makes the process hazardous and expensive [7].

Alternatively, the H₂O₂ evolution reaction (H₂O₂ER) can be realized by photocatalysis at room temperature and atmospheric pressure using the photocatalytic water oxidation reaction (WOR) [8]. The reaction involves a two-electron process by equation 1 (Eq. 1) on the anode at the cost of the thermodynamic energy of 354 kJ/mol, corresponding to 1.76 V versus the reversible hydrogen electrode (vs. RHE) [9-11].

\[
2\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \quad E = 1.76 \text{ V vs. RHE (Eq. 1)}
\]

This WOR can be readily realized via a photoelectrochemical (PEC) approach [12-13], using photogenerated holes at the surface of the anode without any sacrificial agent [14-17]. Kinetically, this reaction will compete with the oxygen evolution reaction (OER) described in Eq. 2 [18-20].

\[
2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \quad E = 1.23 \text{ V vs. RHE (Eq. 2)}
\]

The OER standard potential is 1.23 V vs. RHE, which is sufficiently lower than that for H₂O₂ production [21-23]. As such, the anode materials and PEC reaction conditions
have to be optimized to limit the OER and to improve the selectivity towards the excellent performance of two-electron WOR for H₂O₂ production [24-26].

Metal oxides, including BiVO₄ [27], TiO₂ [28], WO₃ [29] and their hybrids have been studied as the anode materials for the PEC H₂O₂ER [11, 30-31]. However, the faradaic efficiencies (FE) for H₂O₂ER by these metal oxide photoanodes are generally lower than 15% [13, 32]. Therefore, it is necessary to develop cocatalysts to improve the performance further [28, 33-35]. In the recent work, PO₄³⁻ ion could improve the H₂O₂ production when it is deposited on the surface of BiVO₄ (BVO) with the FE improved from 15% to 46% [34], by improving the desorption of H₂O₂ molecules on the surface of the photocatalyst [35]. Meanwhile, Co₃O₄ particles deposited on the surface of TiO₂ photoanode could also improve the H₂O₂ production with the FE increased from 8% to 26.8% by improving the oxidation of water to hydroxyl radicals (•OH) and facilitating the conversion of •OH to H₂O₂ [28, 36]. We recognize that the formation of •OH and the desorption of H₂O₂ are the two most important steps in the H₂O₂ER process. Hence, the synergetic effects of Co²⁺ and PO₄³⁻ can potentially improve the H₂O₂ER efficiency dramatically.

Herein, we developed Mo-doped BiVO₄ (MB) coral-like nanostructures used as the substrate of the photoanode material. It is expected that the doping of Mo⁶⁺ in the V⁵⁺ framework can improve the conductivity with reduced charge recombination [37]. Meanwhile, the porous coral-like morphology will maximize the contact between the electrolyte and the hole to facilitate efficient WOR reaction. The synthesized Co²⁺ and PO₄³⁻ ions modified Mo-doped BiVO₄ (CPMB) has achieved the optimal H₂O₂
production rate of 0.23 µmol·min⁻¹·cm⁻² under the illumination of air mass 1.5 globe
(AM 1.5G, 100 mW/cm²) at the voltage bias of 1.7 V vs. RHE. This result is 2 and 2.5
times those of MB and the pristine BVO photoanodes, respectively. In-situ electron
paramagnetic resonance spectrometer (i-EPR) was acquired to study the roles of Co²⁺
and PO₄³⁻ ions for H₂O₂ER, which confirms that PO₄³⁻ mainly promotes the dissociation
of H₂O and the formation of the •OH, while Co²⁺ increases the conversions of the •OH.
This work presents two different types of ionic cocatalyst in the PEC system for an
efficient H₂O₂ER with the potential of facilitating photocatalytic •OH mediated water
oxidation reactions [38-39].

2. Experimental

2.1 Synthesis of BVO, MB, CPMB photoanodes

The BVO films were prepared on fluorine-doped tin oxide (FTO) glass substrate
by electrochemical deposition method [40]. Typically, nitride acid is added into 50 mL
deionized water to adjusted pH to 1.7, and 0.97 g Bi(NO₃)₂·5H₂O (99%, Sinopharm
Chemical Reagent) and 3.32 g KI (99%, Sinopharm Chemical Reagent) were dissolved
into the as-prepared acidic solution. 0.5 g p-benzoquinone (98%, Alfa Aesar) was
dissolved into 20 mL ethanol before being added into the stock solution. It was used as
the electrolyte solution for electrochemical deposition of a BiOI layer on the FTO glass
with a Pt foil (2.0 × 2.0 cm²) as the counter electrode and KCl saturated Ag/AgCl
electrode as the reference. The BiOI films were formed at -0.7 V vs. RHE for 3 minutes.
0.2 M vanadyl acetylacetonate (98% Aladdin) was produced by dissolving into
dimethyl sulfoxide (DMSO) as a precursor for coating onto BiOI (50 µL/cm²), before obtaining the BVO film by calcinating at 450 °C in a Muffle furnace for 2 hours. The BVO film was washed with 1.0 M NaOH to remove excess V₂O₅. To prepare MB, Na₂MoO₄·2H₂O (99%, Sinopharm Chemical Reagent) was used as the dopant by adding 2 µL of 0.1 M Na₂MoO₄ aqueous solution into the 0.2 M vanadyl acetylacetonate DMSO solution, followed by depositing on the BiOI before calcination at 450 °C to form the MB film.

\[ \text{Co}^{2+} \text{ and PO}_4^{3-} \text{ ions were deposited on MB by electrochemical deposition.} \]

Typically, 3.13 mM Co(NO₃)₂·6H₂O (98.5%, Sinopharm Chemical Reagent), 31.25 mM NaH₂PO₂·H₂O (98%, Sinopharm Chemical Reagent) and 6.25 mM CH₃COONa (99%, Sinopharm Chemical Reagent) were dissolved in water as the electrolyte solution. The MB coated FTO glass was used as the working electrode, a Pt foil and a KCl saturated Ag/AgCl were used as the counter electrode and reference electrode, respectively. The loadings of the Co²⁺ and PO₄³⁻ ions were controlled by cycling the potential between -0.4 and 0.3 V vs. RHE at a scan rate of 50 mV/s. The optimal quantity was obtained after five cycles of loadings. For comparison, Co²⁺ or PO₄³⁻ ions were also deposited on the MB films independently following the same procedure, and corresponding materials were named as CMB or PMB, respectively. In addition, we have studied the performance of H₂O₂ER by adjusting the Co²⁺ ion concentration on PMB photoanode. The concentration of Co(NO₃)₂·6H₂O were used as 1.56 mM, 3.13 mM and 6.26 mM for the preparations of 0.5CPMB, 1CPMB and 2CPMB.
2.2 Characterizations

The structure and morphology of the films were studied by a scanning electron microscope (SEM, SU8010, Hitachi). The crystallinity of the films was studied by a powder X-ray diffractometer (XRD, MiniFlex 600, Rigaku). High-resolution transmission electron microscopy (HRTEM, FEI Talos) with an FEI super-X energy dispersive spectroscopy (EDS) was performed to examine the chemical composition of the photoanodes. The elemental composition and valence states of the catalysts were characterized by high-resolution X-ray photoelectron spectroscopy (XPS, ESCALB 250, Thermofisher Scientific). The spectra were fitted by the Gauss-Lorentz function with the Sherry function after removing the background signal. The C 1s binding energy of 284.8 eV was used as the reference. Ultraviolet-visible diffusion reflector spectrometers (UV-Vis DRS, Cary 500, Varian) with a small integrating sphere was used to measure the diffuse reflection absorption of the films. An electrochemical workstation (VSP-300, Bio-Logic) was used to study the PEC performance. A calibrated solar simulator with AM 1.5G filter (LCS-100, Newport, USA) was used as the light source. The probability of charge recombination was measured using the time-resolved photoluminescence (TRPL) spectroscopy (F-7000, Hitachi). The colorimetric data was measured in Ultraviolet-visible (UV-Vis) spectrophotometer (UH5300, Hitachi). The radical components were monitored by an in-situ electron paramagnetic resonance (i-EPR) spectrometer (A300 ESR, Bruker). The powder samples of BVO, MB, CMB, PMB and CPMB were used for the i-EPR measurements. Typically, 0.6 mg of the catalyst powder was suspended in 0.5 mL KHCO₃ solution (2.0 M). The
evolution of the •OH concentration under light illumination was measured by adding 5 µL of 5,5-dimethyl-1-pyrroline N-oxide (DMPO) to form DMPO-•OH adduct.

2.3 Photoelectrochemical studies for H₂O₂ production

The PEC study was conducted in a three-electrode system, where the catalyst coated FTO glass was used as the photoanode and the test area is 0.5 cm² (0.5 cm×1 cm). A KCl saturated Ag/AgCl electrode and a Pt foil were used as the reference and counter electrodes, respectively. The experiment was operated in an electrochemical cell with two chambers separated by a Nafion membrane. The electrolyte solution for the working electrode (photoanode) is 2.0 M KHCO₃ (pH~8.3) and for the counter electrode (cathode) is 0.2 M Na₂SO₄ (pH~7). The temperature of the anode reaction chamber is kept at 5℃. Before PEC measurement, the electrolyte solutions were bubbled by CO₂ for 20 mins to remove the O₂. The photoanodic H₂O₂ production was realized with voltage bias of 1.7 V vs. RHE and illumination of AM 1.5G.

The quantity of H₂O₂ was determined by the Fe²⁺ colorimetric method based on Eq. 3 [41-42].

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + 2\text{OH}^- \quad \text{(Eq. 3)}
\]

Specifically, 0.9 mL HCl solution (3.0 M) was added into 1.0 mL of electrolyte solution containing produced H₂O₂. Then, 0.2 mL of FeSO₄·7H₂O (0.1 M, 99%, Sinopharm Chemical Reagent) was added to the solution. The concentration of the produced H₂O₂ was determined by the UV-Vis spectrophotometer.
The electrochemical impedance spectroscopy (EIS) measurements were acquired with and without light illumination. The flat band potentials of the materials were derived by Mott-Schottky plots [43].

The FE for H$_2$O$_2$ production was calculated using Eq. 4 [44]:

$$\text{FE} \% = \frac{2 \times N_{\text{H}_2\text{O}_2} \times 96485}{Q} \times 100 \quad (\text{Eq. 4})$$

where $N_{\text{H}_2\text{O}_2}$ and $Q$ refer to the amount of produced H$_2$O$_2$ (mol) and the total amount of charges involved in the reaction (C), respectively.

Incident photon-to-electron conversion efficiency (IPCE) was obtained under light irradiation at different wavelengths generated by a Xenon (300 W) lamp equipped with a monochromator (Newport, USA). IPCE was calculated using Eq. 5 [45]:

$$\text{IPCE}(\lambda) = \frac{1240 \ j_p(\lambda)}{\lambda \ E_\lambda(\lambda)} \quad (\text{Eq. 5})$$

where $\lambda$ and $E_\lambda(\lambda)$ are the wavelength (nm) and the incident light energy density at a certain wavelength (mW·cm$^{-2}$), respectively with the corresponding photocurrent density (mA·cm$^{-2}$), $j_p(\lambda)$.

3. Results and discussion

3.1 Physiochemical properties of the photoanodes

The morphologies of BVO, MB and CPMB photoanodes were investigated by SEM with the top-view images shown in Figures S1, 1a and 1b, respectively, while the cross-sectional view images are presented in Figures S2 and 1c. The BVO and MB samples have similar coral-like morphology with connected nanoparticles. The surface-modified CPMB sample maintained the porous coral-like morphology. The crystal
structures of BVO, MB and CPMB were studied by XRD (Figure S3). Specifically, for the BVO sample, the peaks at 18.67°, 28.95° and 30.55° correspond to the (110), (121) and (040) crystal faces of BVO (JCPDS No. 14-0688), respectively. The other peaks were assigned to FTO (JCPDS No. 46-1088). Noted that the low level of surface modification with Co²⁺ and PO₄³⁻ ions did not result in any phases from XRD measurement.

![Figure 1](image)

**Figure 1.** SEM of (a) MB and (b) CPMB. (c) SEM cross-section images of CPMB. The elements mapping of (d) Bi, (e) V, (f) O, (g) Mo, (h) Co and (i) P for the CPMB, and the inset of (d) is the high angle annular dark-field image accordingly.
Subsequently, HRTEM accompanied with EDX was acquired to study the element distributions. The inset of Figure 1d is the high angle annular dark-field (HAADF) image, and correspondingly Figure 1d to 1i present elemental distributions of Bi, V, O, Mo, Co and P. All the element distributions closely match the morphological image, indicating that the Mo doping and Co$^{2+}$ and PO$_4^{3-}$ ions coating was homogeneously distributed within the BVO.

![Graph](Image)

**Figure 2.** The high-resolution XPS spectra of (a) Co 2p, (b) P 2p for the MB, CMB, PMB and CPMB photoanodes, respectively.

The high-resolution XPS spectra were acquired to study the chemical state of the elements. From the survey XPS spectrum (Figure S4a), the elements of C, Bi, V, O, Mo, Co and P can be observed, indicating the presence of Co and P species on the MB photoanode. As shown in Figure 2a, high-resolution Co 2p XPS spectra confirm its presence in the CMB and CPMB samples, but not in the MB and PMB samples. The peaks centring at 780.4 eV and 796.6 eV are attributed to Co 2p$_{3/2}$ and Co 2p$_{1/2}$, respectively, and the peaks at 802.7 eV and 786.1 eV are the satellite peaks [46]. The high-resolution P 2p XPS spectra (Figure 2b) show the signal in the PMB and CPMB
samples, but not in the CMB and MB samples. The two peaks at 132.6 eV and 133.7 eV are assigned to the 2p$_{3/2}$ and 2p$_{1/2}$ of phosphorus atoms in phosphate species, confirming the successful deposition of PO$_4^{3-}$ ions [47-48]. As shown in Figure S4b, the peaks of binding energy at 529.1 eV and 530.8 eV in the XPS spectra of O 1s correspond to lattice oxygen species and adsorbed oxygen species, respectively [34]. The signals of V 2p (Figure S4c) are located at 523.6 eV and 516.0 eV, corresponding to V 2p$_{1/2}$ and V 2p$_{3/2}$ respectively, referring to V$^{5+}$ species [49]. The high-resolution Mo 3d XPS spectra are shown in Figure S4d. The peaks at 231.78 eV and 234.90 eV, assigned to the Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$, were observed from the MB, CPMB, PMB and CMB samples with similar intensities. This confirms the successful doping of Mo$^{6+}$ in the BVO.

3.2 Photoanodic H$_2$O$_2$ evolution reaction

The photoanodic H$_2$O$_2$ER was performed by a three-electrode configuration in the electrolyte of 2.0 M KHCO$_3$ solution. Linear sweep voltammetry (LSV) curves were received under the illumination of the AM 1.5G, presented in Figure 3a. It is generally understood that the pathway of H$_2$O$_2$ by water oxidation reaction can be described as Eq. 6 and 7 [50].

\[
2\text{H}_2\text{O} + \cdot \rightarrow \cdot\text{OH} + \text{H}_2\text{O}^+ + \text{H}^+ + e^- \tag{Eq. 6}
\]

\[
\cdot\text{OH} + 2\text{H}_2\text{O} + \text{H}^+ + e^- \rightarrow \text{H}_2\text{O}_2 + \text{H}^+ + e^- \tag{Eq. 7}
\]

Therefore, the fact indicates that this reaction is favoured to be proceeded in basic electrolyte solution. As such, the photoanodic H$_2$O$_2$ER is also acquired in phosphate
buffer (Figure S5). Though the photocurrent density obvious, we cannot detect any H$_2$O$_2$, revealing in phosphate buffer OER is the only reaction.

Among the samples as shown in Figure 3a, CPMB photoanode achieved the highest photocurrent density at all bias voltages. Meanwhile, MB offered a higher photocurrent density than BVO, attributed to improved charge transport by replacing V with Mo. More importantly, both PMB and CMB photoanodes presented higher photocurrent densities than MB, confirming the positive effects of surface modification with Co$^{2+}$ or PO$_4^{3-}$. Since the thermodynamics for H$_2$O$_2$ER is 1.76 V vs. RHE (Eq. 1), the corresponding chronoamperometry (CA) curve was acquired with a voltage bias of 1.7 V vs. RHE, shown in Figure 3b. Stable photocurrent densities of 1.72, 2.25, 2.83, 2.49 and 2.96 mA $\cdot$ cm$^{-2}$ were achieved from the BVO, MB, CMB, PMB and CPMB photoanodes, respectively. No rapid decay of the performance was observed for all samples.
Figure 3. (a) Photocurrent densities of the photoanodes for H$_2$O$_2$ER under AM 1.5G illumination with CO$_2$ gas bubbling in cooling bath. (b) CA curve of photoanodes for H$_2$O$_2$ER with the applied voltage of 1.7 V vs. RHE. (c) The H$_2$O$_2$ER of the photoanodes. (d) FE diagram for H$_2$O$_2$ER.

Moreover, the H$_2$O$_2$ production performances were investigated by measuring the H$_2$O$_2$ evolution rate and the corresponding FE values, shown in Figures 3c and 3d. The production of H$_2$O$_2$ was determined by the calibrated colorimetric method with the calibration shown in Figure S6 [41-42]. As shown in Figure 3c, the best H$_2$O$_2$ production performance was achieved by CPMB photoanode with a production rate of 0.23 µmol·min$^{-1}$·cm$^{-2}$. This performance is better than CMB or PMB photoanode and is almost 2 times than that of the MB photoanode. These results further reveal the
importance of the Co$^{2+}$ and PO$_4^{3-}$ surface deposition for the H$_2$O$_2$ER. Correspondingly, among all the samples, CPMB photoanode has achieved the highest FE of 26% (Figure 3d), which is 1.6 times than that of the MB photoanode. The proportional increase in the H$_2$O$_2$ production rate and the FE value with respect to those of MB suggests that the Co$^{2+}$ and PO$_4^{3-}$ ions on surface adsorption effectively promoted the H$_2$O$_2$ production. On the other hand, the FE for H$_2$O$_2$ER of CMB photoanode (Figure 3d) is similar to those of BVO and MB, indicating that when only Co$^{2+}$ ion is deposited, it promotes the OER and H$_2$O$_2$ER kinetics. Hence, the selectivity for H$_2$O$_2$ not improved in CMB photoanode. However, the co-deposition of PO$_4^{3-}$ ions significantly improves the H$_2$O$_2$ selectivity. As such, there is a synergetic effect for promoting the H$_2$O$_2$ER by loading both Co$^{2+}$ and PO$_4^{3-}$ ions.

### 3.3 The role of the Co$^{2+}$ and PO$_4^{3-}$ ions on photoanodes for H$_2$O$_2$ER

To elucidate the mechanism of the synergetic effect, we attempted to identify three determining factors for the H$_2$O$_2$ER, namely light absorption, photoexcited charge separation and transfer, and surface reaction. As shown in Figure S7, the UV-Vis DRS spectra were acquired to study the light absorption of the photoanodes. The bandgap energies were retrieved from the corresponding Kubelka-Munk plots (Figure S8). The surface deposition of Co$^{2+}$ and PO$_4^{3-}$ ions and the doping of Mo have minor effects on their band structures with similar bandgap energy around 2.50 eV [40]. The flat band potentials of the photoanodes can be determined by the Mott-Schottky plots from the
EIS measurements (Figure S9). Similarly, there is no significant change in the flat band potentials (Figure S10) [40, 51].

Photoexcited charge separation and transfer have studied by TRPL. As expected, TRPL spectra show that the lifetime of the photoexcited charge is reduced once Mo is doped into BVO (Figure S11), implying the Mo acts as an electron donor in the BVO lattice to enhance the mobility of photoanode. However, the deposition of Co$^{2+}$ or PO$_4^{3-}$ ions has no effect on the fluorescence lifetime of MB, indicating that the adsorptions of ions cannot affect the manners of photoexcited charge transfer.

IPCE were measured operando at the voltage bias of 1.7 V vs. RHE under light irradiation (Figure 4a). Although there is no change in the spectrum profile, the relative intensities were all enhance once BVO was doped or surface modified. The IPCE value was increased by doping Mo into the BVO crystal. With the surface deposition of Co$^{2+}$ or PO$_4^{3-}$ ions, the IPCE value was further increased, while the highest quantum efficiency from the incident wavelength from 300 nm to 520 nm was achieved by depositing Co$^{2+}$ and PO$_4^{3-}$ ions simultaneously. This result also confirmed the positive synergetic effects of co-deposition of Co$^{2+}$ and PO$_4^{3-}$ ions.

To investigate the electron transfer between the semiconductor/electrolyte interface of photoanodes, Nyquist plots were generated from the EIS measurements with the modulation in the frequency range of 200 kHz to 100 mHz with the illumination on or off. In comparison with the dark condition, Figure S12 reveals that the charge transfer resistance at the electrolyte interface was significantly reduced under
the illumination condition for all samples. This observation is due to the effective surface reaction with the photoexcited holes and electrons. Furthermore, the CPMB photoanode showed the smallest interface resistance representing by the smallest semicircle under light illumination. This confirmed that the surface modification with Co$^{2+}$ and PO$_4^{3-}$ ions can improve the rate for the surface WOR. Such surface modifiers could be the dominant mediates for the high-efficiency H$_2$O$_2$ER.

![Figure 4](image)

**Figure 4.** (a) IPCE plots, and (b) $i$-EPR spectroscopy of BVO, MB, CMB, PMB and CPMB photoanodes under light illumination and dark. (c) Illustration of the possible mechanism of CPMB photoanode for H$_2$O$_2$ER.

In order to study the roles of the ion modifiers for the H$_2$O$_2$ER, we used $i$-EPR to test the changes of •OH as intermediates (Figure 4b). DMPO was added to couple with
•OH to present quartet peaks with the intensity ratio of 1:2:2:1 in EPR under the light illumination. This peak intensity in EPR is proportional to the concentration of photogenerated •OH near the photoanode. The EPR intensity of CPMB photoanode is similar to that of PMB photoanode, but larger than that of MB photoanode, indicating that PO₄³⁻ ion promotes the formation of the •OH by dissociation of H₂O. In addition, the intensity of CMB is significantly lower than that of MB, indicating that Co²⁺ ion improves the consumption of the •OH. The consumption can be either H₂O₂ER or OER, and this result is accordance with the performances. With respect to MB, despite the photocurrent density of CMB increases (Figure 3b and 3c), the selectivity of H₂O₂ was reminded (Figure 3d).

To further understand the role of Co²⁺ in the system, we acquired a control experiment the investigate the performance by loading different quantity of the Co²⁺ on PMB (Figure 13). It is obvious that the photocurrent density increases by increasing the loading quantity of Co²⁺ ions till the formation of CMPB (Figure 13a). Correspondingly, the production rate of H₂O₂ also increases by increasing of the photocurrent density (Figure S13b). As such, FEs of them were close to each other by loading Co²⁺ ions on the surface of the photoanode. The results implied that both pathways for H₂O₂ER and OER are promoted. Noted that when the Co²⁺ ion loading is increased to 2CPMB, the photocurrent still increases, but the production of H₂O₂ is lower than CPMB. This observation can be accounted as the rate of H₂O₂ leaving is lower than the production, and therefore the selectivity turns to O₂ production. The
result indicates that again the loading of Co\(^{2+}\) promote the water oxidation reaction for the productions of both H\(_2\)O\(_2\) and O\(_2\).

Combining all the experimental results, we propose the efficient H\(_2\)O\(_2\)ER process in Figure 4c. Generally, PO\(_4^{3-}\) ion promotes the formation of the •OH by dissociation of H\(_2\)O, which is considered as intermediate state (TS1) after injecting the photoexcited hole. Subsequently, •OH is proceeded either to couple with together to form H\(_2\)O\(_2\) (TS2) or to dehydrogenate for OER (TS3). Literatures have reported that Co species can promote both reactions owing to the redox cycles among Co(II), Co(III) and Co(IV) [36, 52], and this understanding is consistent with our results. Furthermore, the PO\(_4^{3-}\) ion was also likely to improve the desorption of H\(_2\)O\(_2\) molecules on the surface of the photocatalyst [35]. As such, the overall performance for H\(_2\)O\(_2\)ER improves by promoting the surface reaction with loading Co\(^{2+}\) and PO\(_4^{3-}\) ions as co-catalyst.

4. Conclusions

In summary, photoanodic H\(_2\)O\(_2\)ER was realized by BVO based photoanodes. Since the surface reaction is the main obstacle for photoanodic H\(_2\)O\(_2\)ER, we have attempted to load PO\(_4^{3-}\) and Co\(^{2+}\) ions on MB films as CPMB photoanode to improve both selectivity and yield for H\(_2\)O\(_2\)ER. As such, the optimal evolution rate and FE are ca. 0.23 \(\mu\)mol·min\(^{-1}\)·cm\(^{-2}\) and ca. 26%, respectively. This H\(_2\)O\(_2\)ER performance is ca. 2.5 times that of pristine BVO photoanode. More importantly, we have studied the role of the Co\(^{2+}\) and PO\(_4^{3-}\) for the improved performance. It has been found that PO\(_4^{3-}\) ion mainly promotes the formation of the •OH by dissociation of H\(_2\)O and inhibit the
adsorption of H₂O₂ and its subsequent decomposition on the catalyst surface, while 
Co²⁺ ion improves the consumption of the •OH for subsequent H₂O₂ER or OER. This 
investigation demonstrated the role of the ions on the surface of photoanode to improves 
the H₂O₂ER selectivity and pave the strategy to design the PEC system for H₂O₂ 
production by green approach.

Credit author statement

Lele Yang: Investigation, Methodology, Formal analysis, Data curation, Writing–original draft. Hong Chen, Yuntao Xu: Formal analysis, Data curation, Visualization.
Rong Qian: Investigation, Writing- review & editing. Qiao Chen: Investigation, Supervision, Writing- review & editing. Yuanxing Fang: Conceptualization, Methodology, Formal analysis, Investigation, Resources, Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare no competing financial interest.

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