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# Journal of Materials Chemistry A

Materials for energy and sustainability

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Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/



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Photocatalytic water splitting to produce hydrogen and hydrogen peroxide are the core issue of photocatalysis. Thought they are both water-based reactions, it's extremely troublesome to conduct the two processes on one catalyst. Herein, a function-switchable metal-free catalyst was design and synthesized through the polycondensation of procyanidin and 4methoxybenzaldehyde. Impressively, the catalyst developed here not only was expected to split water to produce hydrogen by four-electron reaction process in air free, but also to generate hydrogen peroxide by preferentially reducing oxygen with two-electron pathway in air. The production rates of hydrogen and hydrogen peroxide reached 252.02 and 1385.42  $\mu$ mol h<sup>-1</sup>g<sup>-1</sup>, respectively. Through in-situ transient photovoltage tests and kinetic analysis, a clear and fundamental understanding on the highly efficient and switchable functions was acquired over this photocatalyst. This study highlights a unique behavior, and provides an insight into the design of function-switchable catalyst and the regulation of catalytic reactions.

# 1. Introduction

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Environmental pollution and the energy crisis spur the exploitation of clean and renewable energy sources<sup>1-3</sup>. Hydrogen ( $H_2$ ), a green and carbon-free energy source, has been shown to be an ideal candidate for replacing fossil fuels<sup>4</sup>. Generating hydrogen directly from water through photocatalysis is one of the most promising and scalable ways<sup>5</sup>. On the other hand, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) widely used in field of medicine, chemical industry and other aspects is also a powerful alternative to conventional fuels if it can be prepared by simply, clean and cheap approaches, such as photosynthesis method<sup>6,7</sup>. The most satisfactory situation is that, in the photocatalytic system, solar energy is converted directly into stored chemical energy  $(H_2 \text{ and } H_2O_2)$  through a water-based reaction without releasing any by-products, and the H<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> generation only needs light, water and oxygen<sup>8,9</sup>. However, the mechanism and free energy of hydrogen produced by water splitting are different from that of hydrogen peroxide by oxygen reduction<sup>10-12</sup>. Generally, in virtually all photocatalytic researches, the focus was placed on the single-functional catalytic reactions, in which photocatalyst could only achieve a single reaction, such as just splitting water to produce hydrogen or oxygen reduction to synthesize hydrogen peroxide<sup>13-16</sup>. It is significant to regulate hydrogen and hydrogen peroxide production on one photocatalyst for both high efficiency photocatalyst design as well as the wide application of photocatalytic technology.

Recent reports have demonstrated some bifunctional properties of photocatalysts, such as hydrogen production and olefin hydrogenation<sup>17</sup>, hydrogen production and organic degradation<sup>18</sup>, hydrogen production and reduction of carbon dioxide<sup>19</sup>. However, bifunctional catalysts that can both produce hydrogen and hydrogen peroxide are few reported. Due to the low yields of hydrogen peroxide product, an intermediate in water splitting, and it is easily decomposed<sup>20</sup>. Notably, in photocatalysis, catalytic material with low-cost, safety, high efficiency and functionswitchable, is considered as one of the most ideal photocatalysts. Very recently, the resorcinol-formaldehyde resin was reported as a low-bandgap metal-free photocatalyst for the synthesis of hydrogen peroxide by a single function way<sup>21</sup>. In this field, the most challenging obstacle is the design and synthesis of efficient bifunctional metal-free photocatalysts, based on water splitting, for both hydrogen evolution and hydrogen peroxide artificial synthesis.

We aim to fabricate a function-switchable metal-free photocatalyst for efficient and selective production of hydrogen and hydrogen peroxide. In this work, a metal-free polymer catalyst procyanidin-methoxy-benzaldehyde (PC-MB) was prepared by polymerization of light-sensitive dye procyanidin (PC) and 4-methoxybenzaldehyde (MB). Impressively, these catalysts exhibit excellent light absorption and function-switchable catalytic characteristics, that is, hydrogen or hydrogen peroxide could be selectively generated by controlling the reaction atmosphere. The material PC-MB possesses the ability of overall water splitting only in the absence of air, in which, the H<sub>2</sub> evolution was coupled with

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0TA03974H

DOI:

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

the O<sub>2</sub> formation via a one-step 4e<sup>-</sup> pathway. The efficiency of H<sub>2</sub> evolution is 252.02  $\mu$ mol h<sup>-1</sup>g<sup>-1</sup> and the conversion efficiency from solar to hydrogen (STH) can be up to 0.85% at the illumination intensity of 1.75 mW cm<sup>-2</sup>. After switching the function, only hydrogen peroxide was detected when catalyst is in air, by which, this sole product was obtained via a two-channel pathway (water oxidation reaction and oxidation reduction reaction). The yield of hydrogen peroxide can reach 1385.42  $\mu$ mol h<sup>-1</sup>g<sup>-1</sup> in air (illumination intensity is 31.27 mW cm<sup>-2</sup>). With evidence from electrochemical experiments, in-situ transient photovoltage (TPV) tests and kinetic analysis, a clear and fundamental understanding was acquired on the highly efficient and selective production of hydrogen and hydrogen peroxide over the function-switchable photocatalyst.

## 2. Experimental section

#### 2.1 Materials.

All chemicals were used without any further purification.  $Na_2CO_3$  (AR, 98%) and HNO<sub>3</sub> (AR, 98%) were purchased from Aladdin. Procyanidins (AR, 98%) was purchased from Yuanye. 4methoxybenzaldehyde (AR, 98%) was purchased from Sinopharm Group chemical Reagent Co., Ltd.

# 2.2 Preparation of PC-MB cross-linked organic semiconductor photocatalyst.

The interconnected organic semiconductor PC-MB was synthesized by using Na<sub>2</sub>CO<sub>3</sub> as the catalyst, through a sol-gel process, crosslinking polymerization and freeze-drying technique. Typically, 0.5 g of procyanidins (PC) and 0.1 g of Na<sub>2</sub>CO<sub>3</sub> were dissolved in 10 mL deionized water, and then 0.9 mL of 4-methoxybenzaldehyde (MB) was added. Next, different amounts of HNO<sub>3</sub> (4 mol L<sup>-1</sup>) were added to adjust the pH values of the mixture solution, which are 1, 3, 5 are 7, respectively. After stirring for 30 min at room temperature, the reactors were sealed to prevent the volatilization of the solution. The precursor was heated at 80 °C for 48 h to form PC-MB gel. After that, the PC-MB gel was washed with ethanol and water to remove the residual organic solvent. Finally, the PC-MB gel was frozen in liquid nitrogen (-196 °C) for 15 minutes, and transferred to the vacuum chamber of the freeze-drying device (operating at -53 °C and 0.113 mbar) for at least 60 h to obtain PC-MB cross-linked organic semiconductor photocatalyst. The samples synthesized at different pH values were labeled as PC-MB-1, PC-MB-3, PC-MB-5, and PC-MB-7, respectively.

#### 2.3 Materials characterization.

Powder X-ray diffraction (XRD) was carried out to characterized the crystal structure of the as-prepared products by using a PIXcel3D X-ray diffractometer (Empyrean, Holland Panalytical) with Cu K $\alpha$  radiation ( $\lambda$ =0.154178 nm). The scanning electron microscope (SEM) was applied to characterize the surface morphology of the samples. Transmission electron microscopy (TEM) was measured by using a FEI-Tecnai F20 transmission electron microscope with an accelerating voltage of 200 kV. The Fourier transform infrared (FTIR) spectra were collected by using a Hyperion spectrophotometer (Bruker) at the scan range of 400-4000 cm<sup>-1</sup>. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a KRATOS Axis ultra-DLD X-ray photo-electron spectroscope with a

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monochromatic Mg K $\alpha$  X-ray source (hv=1283.3 eV). <u>Dynamic light</u> scattering (DLS) was employed to determine the samples of the samples. Organic element analyzer (Vario MACRO cube) was used for the combustion elemental analysis (EA).

UV/VIS/NIR spectrophotometer (Lambda 750, Perkinelmer) was employed to acquire the UV-vis absorption spectra. Ultraviolet photoelectron spectroscopy (UPS) measurements were performed with He I (21.22 eV) as the monochromatic light source and a total instrumental energy resolution of 100 meV.

All the electrochemical measurements were conducted on a CHI 920C workstation (CH Instruments, Shanghai, China), using a standard three-electrode system, of which a carbon electrode is used as the reference electrode, a saturated calomel electrode (SCE) as the counter electrode and a glass carbon (GC) electrode as working electrode. The photoresponse-time curves were obtained at open circuit potential (OCP) in 0.1 M sodium sulphate (Na<sub>2</sub>SO<sub>4</sub>) with a 100 W light-emitting diode (LED) lamp as the light source. Electrochemical impedance spectra (EIS) measurements were carried out at open circuit potential as well, with a frequency range from 1 MHz to 0.01 Hz and Ac voltage amplitude of 5 mV in ultrapure water.

TPV was measured on a home-made system. The TPV was excited with a nanosecond laser radiation pulse (wavelength of 355 nm and the repetition rate is 5 Hz) from a third harmonic Nd:YAG (Beamtech Optronics Co., Ltd). The signal of the TPV was amplified by the amplifier and recorded by the oscilloscope. All the measurements were performed at room temperature and under ambient pressure.

#### 2.4 Photocatalytic activity exploration.

The production and detection of hydrogen peroxide (H2O2). The photocatalytic hydrogen peroxide production properties of the asobtained samples were evaluated using a multichannel photochemical reaction system (PCX50A, Beijing Perfectlight Co. Ltd, China) with a visible light source ( $\lambda \ge 420$  nm). No sacrificial or cocatalysts were needed. In a typically process, 40 mg photocatalyst was dispersed in 20 mL ultrapure water (in a 40 mL reaction bottles), and then the photocatalytic reactions were exposed to visible light for 12 h in air. A series of conditions were changed to explore the optimal activity and mechanism of the reaction, such as changing the amount of catalyst, lighting time, excitation wavelength, adding sacrificial agent, pH value of the reaction environment and reaction atmosphere (air, N<sub>2</sub>, O<sub>2</sub> and air free), etc. At the end of each reaction, the catalyst was centrifuged, washed, dried, and then used for the cycle reactions. To detect the amount of H<sub>2</sub>O<sub>2</sub> generated during the photocatalytic process, potassium permanganate titration was employed. 10 mL of the supernatant with 5 mL H<sub>2</sub>SO<sub>4</sub> (4 M) was titrated by KMnO<sub>4</sub> (0.1 M) to calculate the amount of the hydrogen peroxide produced.

The evolution and test of hydrogen (H<sub>2</sub>). The activity of photocatalytic hydrogen was investigated in a vacuum adaptive reactor with a xenon lamp as the light source ( $\lambda \ge 420$  nm). 40 mg as-prepared catalyst was dispersed in 80 mL of ultrapure water, then vacuumed for 30 min to reach an air-free environment, and finally added visible light for 12 h. The collected gas was detected by a gas chromatograph (GC-7890) set up with 5A molecular sieves column and a thermal conductivity detector (TCD) was utilized.

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## 3. Results and Discussion

#### 4. Characterization and Band Structure of Photocatalysts.

As shown in Fig. 1a, the postulated schematic of the procyanidinmethoxy-benzaldehyde (PC-MB) polymer, formed by the polycondensation of PC and MB, was demonstrated briefly. Under acidic condition, MB with aldehyde group was activated by hydrogen proton (Fig. S1a, ESI<sup>+</sup>)<sup>22</sup>, and then the activated MB was connected to PC containing the resorcinol group through catechol group, forming a phenolic resin chain by electrophilic substitution (Fig. S1b and S1c, ESI<sup>+</sup>)<sup>23-25</sup>. The phenolic resin chains are further cross-linked to form macromolecular polymers PC-MB (Fig. S1d, ESI<sup>+</sup>)<sup>22,26</sup>, which has a cross-networked structure. Here we mainly introduce the PC-MB-3, which was formed by polymerization at a pH value of 3 and exhibits the optimal photocatalytic performance.

The X-ray diffraction (XRD) patterns in Fig. S2, ESI<sup>+</sup> exhibit the similar broad diffraction peaks for different PC-MB catalysts, at 19° and 45° respectively, indicating the amorphous structure of PC-MB polymer. It has been reported that the diffraction peak of 19° represents the  $\pi$ -stacked aromatics<sup>21</sup>. Full X-ray photoelectron spectroscopy (XPS) spectra of PC-BM are available in Fig. S3a, d, g, and j ESI<sup>+</sup>, which indicate that the catalysts consist only of C and O. High-resolution XPS spectra of C 1s (Fig. S3b, e, h, and k, ESI<sup>+</sup>) can be divided into three peaks, in which the positions at 284.6, 286.3 and 288.8 eV are assigned to graphitic carbon, C-O and C=O bonds, respectively<sup>19,27</sup>. The XPS monitored at O 1s level (Fig. S3c, f, i, and l, ESI<sup>+</sup>) also reveals three components assigned to C-O, C=O and adsorbed O<sup>28</sup>. The content analysis of PC-MB catalysts was further confirmed by combustion elemental analysis (EA, Table S1, ESI<sup>+</sup>). The surface functional groups of the reactants and photocatalysts were further confirmed by Fourier transform infrared (FT-IR, shown in Fig. S4, ESI<sup>+</sup>). The comparison between the reactants and the polymerization reveals that the characteristic peaks of polymer PC-MB-3 are all derived from the two reactants. The polymer resin shows distinct bands from PC, linker, BM and residual groups, including phenyls and their substituents, methyl and methylene groups, C-O, C=C, etc<sup>29</sup>.

The morphology of the catalyst was observed by scanning electron microscopy (SEM). As can be seen from Fig. S5a, ESI<sup>+</sup>, the PC-BM-3 is mainly composed of microspheres with a particle diameter of about 0.5-5  $\mu$ m, which is confirmed by dynamic light scattering (DLS, Fig. S5b, ESI<sup>+</sup>) analysis (80-1000 nm). The magnified image of catalyst particles shows that the microspheres have rough surface (inset in Fig. S5a, ESI<sup>+</sup>), exposing more specific surface area, which is more conducive to the catalytic reaction. The transmission electron microscopy (TEM, Fig. S6, ESI<sup>+</sup>) offers more surface details, showing clearly that the microspheres are polymerized by irregular fragments.

As indicated in Fig. 1b, the ultraviolet-visible (UV-Vis) diffuse reflection spectrum reveals that the prepared polymer photocatalyst PC-MB-3 has strong absorption in the both the ultraviolet and visible light regions. Its absorption range can be extended to the near infrared region ( $\lambda \ge 700$  nm), which assigns to the charge transfer transition of the polymerized monomer pair<sup>21,30</sup>, indicating that the catalyst could more effectively improve the utilization of solar energy. The optical band gap of the catalyst was calculated by the Tauc plot that derived from the UV-Vis

absorption spectrum. The curve of  $(\alpha hv)^2$  versus hv obtained by LMe Vis spectrum conversion is illustrated in Fig. DB; in which at h, and hvare correspond to the absorption coefficient, Planck's constant, and frequency of the incident light, respectively. In the ordinate, r=2 denotes the directed band gap of a material, while r=1 represents the indirect band gap of a material<sup>31,32</sup>. The curve in Fig. 1b illustration fits well linearly at r=2, indicating that the photocatalyst PC-BM-3 is a direct band gap material. A low Eg value of PC-BM-3, which may be caused by  $\pi$ -stacking according to the previous report<sup>21</sup>, could be calculated as 1.88 eV by measuring the x-axis intercept of the extrapolated line from the linear state of the curve. The UV-Vis absorption diagrams of other catalysts are accessed in Fig. S7, ESI<sup>+</sup>.



**Fig. 1** Postulated schematic and the band structure of PC-MB-3. (a) Reaction process of catalyst PC-MB-3 in an acidic environment. (b) UV-Vis absorption spectrum of PC-MB-3 (Inset is the corresponding Tauc plot). (c) UPS spectrum of PC-MB-3. The horizontal dashed red line marks the baseline, and the other red dashed lines are tangent to the curve. (d) CV curve of PC-MB-3 modified glassy carbon (GC) electron in N<sub>2</sub>-saturated anhydrous acetonitrile (0.1 M BMIMPF6) with ferrocene as the internal standard. A carbon electrode and an Ag/AgCl (3 M KCl) electrode were used as the counter electrode and the reference electrode with a scan rate of 50 mV s<sup>-1</sup>. (e) The band structure diagram of PC-MB-3 with respect to the redox potential of  $H_2O$  and  $H_2O_2$ .

In addition to the appropriate band gap, for photocatalyst, it's also important to properly match the conduction band and valence band level with the redox potential of photocatalytic reaction. Therefore, other characterizations have been carried out to further

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explore the band structure of the sample. As shown in Fig. 1c, the ultraviolet photoelectron spectroscopy (UPS) was conducted to determine the ionization potential (equivalent to the valence band energy Ev) of catalyst PC-MB-3. By subtracting the width of the He I UPS spectrum from the exciting energy (21.22 eV), the valence band (Ev) of -5.98 eV will be obtained. Thus, the conduction band (Ec) is determined to be -4.1 eV by calculating from (Ev-Eg).

In order to study the band structure of the catalyst more accurately, furthermore, the cyclic voltammetry (CV) experiment (shown in Fig. 1d) was employed to identify the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) positions of the sample PC-MB-3, in which the ferrocene redox system was used as the external standard. It is clearly seen from the CV curve that there are two pairs of redox peaks, where one is from the commercial ferrocene and the other is from the catalyst itself. According to the formulas (mentioned in the method<sup>33,34</sup>), the HOMO and LUMO levels of PC-MB-3 were calculated from the onset of oxidation ( $E_{onset}^{ox}$ ) and reduction ( $E_{onset}^{red}$ ) potential with the energy level of ferrocene (4.8 eV below the vacuum level) as a reference, which are -6.07 and -4.17 V, respectively. To better demonstrate the relationship between CB and VB of the catalyst and the redox potentials of  $H_2O$ , electron volts are converted to electrochemical energy potentials in volts according to the reference standard, where 0 V versus RHE is equal to -4.44 eV versus evac. As shown in Fig. 1e, the CB of PC-MB-3 is above the reduction level for H<sub>2</sub>O to H<sub>2</sub>, while the VB is lower than the oxidation level from water to oxygen, but it cannot reach the oxidation level from water to hydrogen peroxide. Therefore, the catalyst could realize the direct decomposition of water to hydrogen and oxygen. On the other hand, the CB is far lower than the reduction level from oxygen to hydrogen peroxide, so the oxygen reduction will be achieved theoretically.

#### 3.2 Photocatalytic Properties of Catalysts.

Photocatalytic activity in hydrogen evolution. The photocatalytic activity of as-prepared catalysts for overall water splitting was evaluated under visible-light irradiation ( $\lambda \ge 420$  nm, light intensity = 3.85 mW cm<sup>-2</sup>) and vacuum condition without any sacrificial agent and cocatalyst. Fig. 2a presents the hydrogen and oxygen productions by different catalysts after 12 h under light irradiation. Obviously, the polymer PC-MB-3 produces the largest amount of gases in these catalysts, where  $H_2$  and  $O_2$  production rates are 120.97 and 56.82 µmol, respectively. It's roughly twice as much as PC-MB-7, which produced the least amount of hydrogen and oxygen, 56.43 and 24.30  $\mu mol,$  respectively. The further analysis of PC-MB-3 shows that the molar ratio of hydrogen to oxygen production is 2.1, which is effectively consistent with the approximately stoichiometric vale of 2 for overall water splitting. And the hydrogen evolution rate of PC-MB-3 could be up to 10.08 µmol h<sup>-1</sup> (252.02 µmol h<sup>-1</sup>g<sup>-1</sup>). The cyclic stability experiments (Fig. 2b) were carried out to investigate the stability of PC-MB-3, which exhibits favorable stability with hardly reduced hydrogen production after reusable irradiated under visible light ( $\lambda \ge 420$  nm) for 5 times (each time is 12 h).



**Fig. 2** Photocatalytic overall water splitting of the photocatalysts. (a) Gases productions of different PC-MB photocatalysts. (b) Typical time course of  $H_2$  production for the stability of PC-MB-3. (c) Hydrogen evolution and the conversation efficiency from solar energy to hydrogen energy (STH) of PC-MB-3 at different incident light intensity. (d) Wavelength course of  $H_2$  evolution and corresponding UV-vis spectrum of PC-MB-3.

In the following experiments, the photocatalytic performance of the optimum sample PC-MB-3 for water decomposition was studied. Fig. 2c shows the amount of hydrogen produced and the conversation efficiency from solar energy to hydrogen energy (STH) under different incident light intensity (12 h visible light irradiation), indicating that hydrogen production gradually increased with the increased light intensity through the experiment range. Note that the STH value shows an inverse trend to hydrogen yield when light intensity increases, and the STH could reach as high as 0.85% at the light intensity of 1.75 mW cm<sup>-2</sup>, much higher than the previously reported values<sup>1,35</sup>. This is most likely because low light intensity reduced the loss of solar energy, which in turn increases the utilization of solar energy. Next, we researched the dependence of the hydrogen evolution rate on incident wavelength of the catalyst PC-MB-3 (Fig. 2d). As the incident wavelength increases, the produced hydrogen will gradually decrease, indicating that the catalytic activity is positively correlated with the photo-absorption by the catalyst.

**Photocatalytic activity of producing hydrogen peroxide.** The photocatalytic activity of as-prepared PC-MB for photocatalytic reduction of oxygen to hydrogen peroxide was carried out at room temperature and pressure by visible light irradiation ( $\lambda \ge 420$  nm, illumination intensity = 31.27 mW cm<sup>-2</sup>), and the generated hydrogen peroxide was detected by potassium permanganate titration (KMnO<sub>4</sub>, 0.1M). Fig. 3a displays the hydrogen peroxide yield of PC-MB after 12 h of photocatalytic reaction, revealing that PC-MB-3 shows the best catalytic activity, with the evolution of hydrogen peroxide reaching 665 µmol (1385.42 µmol h<sup>-1</sup>g<sup>-1</sup>), while PC-MB-7 shows the worst catalytic activity. This result is likely to that of photocatalytic overall water splitting, which further proves that catalyst PC-MB-3 has higher catalytic activity than other PC-MB catalysts under the excitation of visible light. Similarly, PC-MB-3 was

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tested the stability of photocatalytic reduction of oxygen to produce hydrogen peroxide. As seen from Fig. 3b, the catalyst PC-MB-3 could be used for drying and recycling at least 4 times to produce hydrogen peroxide via photocatalysis under the same condition (exposure in visible light for 12 h). Certainly, the amount of recovered catalyst and hydrogen peroxide produced was decreasing in each cycle, notwithstanding, but the evolution rate remained essentially the same while only decreased for the fourth time. During the process of centrifugation, filtration and drying, part of the catalyst will be absorbed on the surface of the container and difficult to recover due to the small particle size. In addition, repeated drying may destroy the structure of the catalyst and then reduce its activity.



**Fig. 3** Photocatalytic oxygen reduction of the photocatalysts. (a) Comparison of  $H_2O_2$  evolutions among PC-MB-1, PC-MB-3, PC-MB-5 and PC-MB-7. (b) Stability of photocatalytic production of hydrogen peroxide by PC-MB-3. (c) Typical photocatalyst weight course of  $H_2O_2$  production from  $O_2$  under visible light irradiation. (d) Wavelength-dependent apparent quantum yield (AQY) of oxygen reduction by PC-MB-3.

An addition experiment was performed likewise to demonstrate the relevance between the concentration and photocatalytic activity property of PC-MB-3. The controls were experimented under the same condition except for the concentration of the catalyst. The result in Fig. 3c suggests that the initial increase of the catalyst concentration promote the formation of hydrogen peroxide until reaching a maximum, but the production of hydrogen peroxide remains relatively stable when the weight of the catalyst PC-MB-3 is further increasing. On the contrary, the catalytic efficiency is proportional to catalyst content when it rises to 40 mg PC-MB-3 in 20 mL ultrapure water, yet when the concentration of PC-MB-3 is higher than 40 mg, the activity turns to a gradual decline process, which is probably due to the fast recombination of the electronhole pairs and the low light absorption at high concentrations. In fact, there was no significant difference in catalytic activity at the weight below 60 mg, and the difference in activity (Fig. 3c) is mainly due to the error caused by the low weight of catalytic. Apparent quantum yield (AQY) values as a function of the incident light wavelengths (365, 420, 535 and 630 nm) are illustrated in Fig. 3d, indicating a desirable consistent with UV-Vis-spectrum AQV value decreases with the increase of incident wavelength, and it could still reach to 1.44 % with the longest wavelength at 630 nm in photocatalytic oxide reduction.

After the photocatalytic reactions, the collected catalyst was performed by FT-IR and XPS measurements to detect the stability of the sample. As shown in Fig. S8, ESI<sup>+</sup>, the FT-IR spectra of the sample before and after the catalytic reactions were similar, and the characteristic peaks show no obvious change, indicating that the structure of the catalyst was stable before and after reaction. In the XPS patterns of PC-MB-3 (Fig. S9, ESI<sup>+</sup>), although the contents of C-O and  $O_{ads}$  were relatively increased after the catalytic reactions, the total composition did no significantly changes. Therefore, the PC-MB-3 catalyst expresses a good photostability.

#### 3.3 Study on the Photocatalytic Mechanism and Process.

Investigated the photocatalytic process by photocatalytic experiments. For the sake of studying the mechanism and the favorable conditions for the photocatalytic reaction of PC-MB-3, a series of experiments were carried out. Fig. 4a compares the reactivity of PC-MB-3 in different gas atmospheres, and it was found that, with respect to the reaction in air, the produced hydrogen peroxide increased slightly under oxygen saturation condition, while the evaluated hydrogen peroxide significantly decreased under nitrogen saturation. When the photocatalytic reaction took place in vacuum, only hydrogen but no hydrogen peroxide was detected, indicating that photocatalytic water splitting is a four-electron reaction process, which can directly decompose water into hydrogen and oxygen. These results further certify that the production of hydrogen peroxide is a photocatalytic oxygen reduction process. Above all, the PC-MB-3 catalyst has the characteristics of functional and selective regulation. That is to say, photocatalytic reactions produce hydrogen peroxide in the presence of oxygen and hydrogen in the absence of oxygen. Then the variation trend of hydrogen peroxide evolution over time was investigated (Fig. 4b), suggesting that the production of hydrogen peroxide increased with the duration of light, while no hydrogen peroxide was detected without light exciting. However, due to the gradual inactivation of the catalysis and the reaction of oxygen in the water, the total production of hydrogen peroxide began to decline after 72 h of photocatalytic reaction. Comparing the curves (continuous light and light off after 72 h) in Fig. 4b, the thermal effect (from the continuous irradiate) and the degradation of hydrogen peroxide by the catalyst itself are also non-negligible reasons for the decrease in hydrogen peroxide evolution. The degradation curve of hydrogen peroxide (Fig. S10, ESI+) further proves the ability of the catalyst to degrade hydrogen peroxide.

To determine the mechanism of photocatalytic hydrogen peroxide generation of as-prepared PC-MB-3, active species capturing experiments were conducted. In this exploration, AgNO<sub>3</sub>, EDTA-2Na, and benzoquinone (BQ) were used as the electron (e<sup>-</sup>), hole (h<sup>+</sup>), and superoxide radical ( $\cdot$ O<sub>2</sub><sup>-</sup>) scavengers, respectively. Fig. 4c shows the data characterizing the produced amount of hydrogen peroxide in the presence of different scavenger agents (1 mmol L<sup>-1</sup>), exemplifying that the addition of AgNO<sub>3</sub> reduces the photocatalytic activity while the addition of EDTA-2Na increases it. The reason is that the trapping of electrons impedes the reaction, while the

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capture of holes promotes the use of electrons. Surprisingly, the produced hydrogen peroxide hardly changes with the addition of BQ. Thus, as previously reported in the literature<sup>36</sup>, hydrogen peroxide was formed by a one-step two-electron direct reduction  $(O_2 + 2H^+ + 2e^- \rightarrow H_2O_2)$  pathway. In this mechanism, the existence of oxygen enhanced the production of hydrogen peroxide (as analyzed in Fig. 4a) and the protons are favorable for the coupled electron transfer. Therefore, we investigated the relationship between catalyst activity and concentration of hydrogen protons in the reaction solution (Fig. 4d). Comparing the photocatalytic activity of PC-MB-3 from pH 3 to 5, it is noted that PC-MB-3 was sensitively affected by the concentration of protons. This is probably because it is much facilitated for PC-MB-3 framework to conduct proton, and higher proton conductivity should favor the production of hydrogen peroxide. However, when the proton concentration reaches a certain level (pH  $\leq$  3), the overall production of hydrogen peroxide would be much less affected by the pH value. The following theoretical calculations have also proved this claim.



**Fig. 4** Experimental investigation of photocatalytic reaction process. (a) Comparison of  $H_2$  and  $H_2O_2$  by photocatalytic reaction in different gas environment. (b) The production of hydrogen peroxide changes with time (blue curve: continuous irradiated by visible light; red curve: remove the light after irradiated 72 h). (c) The amount of photocatalytic hydrogen peroxide production by adding different sacrificial agents. (d) The relationship between the concentration of H<sup>+</sup> in the reaction solution and the photocatalytic  $H_2O_2$  evolution rate.

In the air environment, the reaction process of two-electron oxygen reduction is as mentioned above. Thus, we can get the relationship between hydrogen proton concentration and hydrogen peroxide production (detailed derivation in supporting information).

$$r_{H_2O_2,min} = \frac{3\sqrt{2}}{2} k_1 k_2^{0.5} (p_{O_2}^0)^{0.5} [e^{-1}]^2 K_{water}^2 [h^+]^2$$
(1)

As shown in formula 1, the high or low solubility of  $[H^+]$  is beneficial to the formation of  $H_2O_2$ , however, the hydrogen peroxide is unstable under alkaline condition. Thus, the higher the

acidity of the reaction solution, the higher production efficiency of hydrogen peroxide, which is consistent with the septemental results in Fig. 4d.

**Research the photocatalytic mechanism by photoelectrochemistry tests.** To further study the photocatalystic mechanism of the polymer catalyst PC-MB, a series of electrochemical tests were characterized. The time-current (i-t) curves from PC-MB-1 to PC-MB-7 were collected to estimate the photo-response properties through an intermittent light on-off way under open circuit potential. As shown in Fig. 5a, all the PC-MB samples show an elevated mutation of photocurrent once exposed to light, which reveals very quickly separated electron-hole pairs.



**Fig. 5** Photo-electrochemical exploration of photocatalytic reaction mechanism. (a) Photo-response curves and (b) EIS Nyquist plots of PC-MB-1, PC-MB-3, PC-MB-5, PC-MB-7. (c) TPV patterns of PC-MB-1, PC-MB-3, PC-MB-5, and PC-MB-7. (d) Comparison of the in-situ TPV with PC-MB-3 in different reaction conditions (wavelength of 355 nm and pulse width of 5 ns). (e) The RRDE collection experiment for PC-MB-3 with a rotating speed of 1600 rpm in N<sub>2</sub>-saturation water. (f) The RRDE collection experiment for PC-MB-3 with a rotating speed of 1600 rpm in  $N_2$ -saturation water.

And then the photocurrent decays smoothly to a stable value, which is mainly caused by the redistribution of charges between the interfaces during illumination. What's more, the photocurrent generated by light excited of PC-MB-3 is higher than others, which also explains why PC-MB-3 emerges higher photocatalytic activity. Next, the ability of the transfer generated charge carries was investigated by electrochemical impedance spectra (EIS) in ultrapure water. Fig. 5b depicts the EIS Nyquist plot of the samples, Published on 20 May 2020. Downloaded on 5/23/2020 1:41:01 AM

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where a smaller semicircle is considered to a faster interfacial electron transfer speed. It can be easily observed that PC-MB-3 displays the smallest semicircle, demonstrating that the charge recombination is more steadily inhibited. The TPV tests of the samples (Fig. 5c) were carried out to demonstrate the action of different catalysts (from PC-MB-1 to PC-MB-7) under light excitation. It's clearly to point out that more charges were excited on PC-MB-3 than others, which is more favorable for the photocatalytic reactions. A more detailed observation in the illustration shows that the attenuation of the TPV curves is not the prime-type attenuation, indicating a redistribution of surface charge after photo-excitation, which is consistent with the i-t curves in Fig. 5a. According to the above data and analyses, PC-MB-3 has both great light absorption and surface photovoltage due to the appropriate degree of polymerization crosslinking, which eventually improve the separation efficiency and charge transfer speed to enhance catalytic performance.

To better understand the catalytic functional selection of PC-MB-3 with  $H_2$  and  $H_2O_2$  production via two-channel pathway, the in-situ TPV tests were measured under different conditions (Fig. 5d). Obviously, PC-MB-3 shows a high photovoltage intensity in nitrogen-saturated ethyl acetate, indicating that no reaction occurs in this case and no photogenic charge is consumed. With the addition of water, the photovoltage decreased as the holes is consumed in the process of water oxidation. Compared with the photovoltage in nitrogen-saturated ethyl acetate and water condition, the optical-voltage has a large attenuation under the oxygen-saturated ethyl acetate, meaning that, in the present reaction system, the oxygen reduction rate is higher than that of water oxidation process. To determine the electron changes in the catalytic reactions in the two pathway (with and with oxygen), the electron transfer number (n) of PC-MB-3 was characterized via rotating ring-disk electrode (RRDE) curves. As depicted in Fig. 5e, the ring current (red line) does not change while the disk current saliently improves when the light is applied to the ultrapure water without oxygen. Therefore, according to the formula mentioned in supporting information, the electron transfer number of PC-MB-3 was calculated to be 4 for the water splitting. Fig. 5f shows the electron transfer number in photocatalytic oxygen reduction process. The test was performed at the potential of 0.3 V (vs RHE), which avoids electrochemical oxygen reduction. After the irradiation of visible light, there are relatively strong saltation in both disk and ring disk, and the electron transfer number was calculated to be 1.98, indicating the photocatalytic oxygen reduction reaction is a two-electron process.

Based on the above exploration and analysis, a reasonable mechanism of PC-MB-3 was explained, as illustrated in Fig. 6. Under the illumination of visible light ( $\lambda \ge 420$  nm), PC-MB-3 can easily absorb visible light to produce photogenic electron-hole pairs. In the absence of oxygen, the electrons generated by conduction band and the holes generated by valence band work together to decompose water directly to produce hydrogen and oxygen (shown in the red part). In the presence of oxygen, however, the oxidation of water is completely inhibited, and the photogenic electrons will combine with the oxygen in water, reducing the oxygen to hydrogen peroxide (shown in the black part). Therefore, by controlling the change of oxygen in the reaction process, the

functional selectivity of photocatalyst for producing hydrogen and hydrogen peroxide can be realized.



Fig. 6 The mechanism diagram of hydrogen or hydrogen peroxide produced over the PC-MB-3 through photocatalytic reaction in different environments.

## 5. Conclusions

In this paper, we successfully designed and synthesized the bifunctional metal-free catalyst PC-MB-3 by phenolic condensation, and realized precise regulation for H<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> production on one catalyst. The catalytic reaction pathway of the catalyst PC-MB-3 can be controlled by adjusting the reaction atmosphere, which exhibits the characteristics of switchable function and excellent catalytic activity. The in-situ TPV and photoelectrochemical experiments show that the case of redox reactions of water, a four-electron process, occurs to produce H<sub>2</sub> and O<sub>2</sub> in the absence of air. In case of the air, oxygen preferentially participates in the reaction, and  $H_2O_2$  is generated through two-electron reduction. The apparent reaction kinetics analysis of hydrogen proton concentration ([H<sup>+</sup>]) and reactivity further demonstrated that the influence of acidic condition is conducive to hydrogen peroxide production. The conversion efficiency from solar to hydrogen (STH) can be up to 0.85% at the illumination intensity of 1.78 mW cm<sup>-2</sup>, and the yield of  $H_2O_2$  can reach 1385.42 µmol  $h^{-1}g^{-1}$  at the illumination intensity of 31.27 mW cm<sup>-2</sup>. Our study on the switch function of water-based catalytic reactions is of great significance in catalytic design, catalytic reaction regulation and other aspects, and it may lay a foundation for industrialization process of photocatalytic hydrogen and hydrogen peroxide production. This field of function-switchable metal-free photocatalyst is one that continues putting much emphasis by both experimentalists and theoreticians.

## **Conflicts of interest**

There are no conflicts to declare

# Acknowledgements

This work is supported by National MCF Energy R&D Program (2018YFE0306105), Innovative Research Group Project of the National Natural Science Foundation of China (51821002), National Natural Science Foundation of China (51725204, 21771132, 51972216, 52041202), Natural Science Foundation of Jiangsu

Published on 20 May 2020. Downloaded on 5/23/2020 1:41:01 AM

Province (BK20190041, BK20190828), Key-Area Research and Development Program of GuangDong Province (2019B010933001), Collaborative Innovation Center of Suzhou Nano Science & Technology, the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), and the 111 Project.

### Notes and references

- M. Faraji, M. Yousefi, S. Yousefzadeh, M. Zirak, N. Naseri, T. H. Jeon, W. T. Choi, A. Z. Moshfegh, *Energy. Environ. Sci.* 2019, **12**, 59-95.
- B. Lin, G. D. Yang, L. Z. Wang, Angew. Chem. Int. Ed. 2019, 131, 4635-4639.
- Y. Zheng, Z. H. Yu, H. H. Ou, A. M. Asiri, Y. L. Chen, X. C. Wang, Adv. Funct. Mater. 2018, 28, 1705407.
- Y. Zhang, K. Sun, D. Wu, W. J. Xie, F. Z. Xie, X. L. Zhao, X. F. Wang, *ChemCatChem* 2019, **11**, 2546-2553.
- T. Morikawa, S. Sato, K. Sekizawa, T. Arai, T. M. Suzuki, ChemSusChem 2019, 12, 1807-1824.
- L. H. Zheng, H. R. Su, J. Z. Zhang, L. S. Walekar, H. V. Molamahmood, B. X. Zhou, M. C. Long, Y. H. Hu, *Appl. Catal. B* 2018, **239**, 475-484.
- 7. Y. Isaka, Y. Kawase, Y. Kuwahara, K. Mori, H. Yamashita, *Angew. Chem. Int. Ed.* 2019, **131**, 5456-5460.
- Z. J. Zhang, Y. F. Zhu, X. J. Chen, H. J. Zhang, J. Wang, Adv. Mater. 2019, **31**, 1806626.
- 9. S. Zhao, X. Zhao, Appl. Catal. B 2019, 250, 408-418.
- O. Elbanna, M. H. Zhu, M. Fujitsuka, T. Majima, ACS Catal. 2019, 9, 3618-3626.
- Z. W. Li, J. G. Hou, B. Zhang, S. Y. Cao, Y. Z. Wu, Z. M. Gao, X. W. Nie, L. C. Sun, *Nano Energy* 2019, **59**, 537-544.
- Z. D. Zhu, H. H. Pan, M. Murugananthan, J. Y. Gong, Y. R. Zhang, Appl. Catal. B 2018, 232, 19-25.
- X. B. Fan, S. Yu, X. Wang, Z. J. Li, F. Zhan, J. X. Li, Y. J. Gao, D. X. Xia, Y. Tao, X. B. Li, L. P. Zhang, C. H. Tung, L. Z. Wu, *Adv. Mater*. 2019, **31**, 1804872.
- 14. S. N. Xiao, W. R. Dai, X. Y. Liu, D. L. Pan, H. J. Zou, G. S. Li, G. Q. Zhang, C. L. Su, D. Q. Zhang, W. Chen, H. X. Li, *Adv. Energy Mater.* 2019, **9**, 1900775.
- C. H. Chu, D. H. Huang, Q. H. Zhu, E. Stavitski, J. A. Spies, Z. H. Pan, J. Mao, H. L. Xin, C. A. Schmuttenmaer, S. Hu, J. H. Kim, ACS *Catal.* 2018, **9**, 626-631.
- Z. Wei, M. L. Liu, Z. J. Zhang, W. Q. Yao, H. W. Tan, Y. F. Zhu, Energy Environ. Sci. 2018, 11, 2581-2589.
- 17. X. Fan, Y. L. Yao, Y. S. Xu, L. Yu, C. T. Qiu, *ChemCatChem* 2019, 11, 2596-2599.
- 18. G. Ge, M. Liu, C. Liu, W. Zhou, D. F. Wang, L. Q. Liu, J. H. Ye, J. Mater. Chem. A 2019, 7, 9222-9229.
- 19. Z. S. Luo, Y. X. Fang, M. Zhou, X. C. Wang, Angew. Chem. Int. Ed. 2019, 58, 6033-6037.
- J. Liu, Y. Liu, N. Y. Liu, Y. Z. Han, X. Zhang, H. Huang, Y. Lifshitz, S. T. Lee, J. Zhong, Z. H. Kang, *Science* 2015, **347**, 970-974.
- Y. Shiraishi, T. Takii, T. Hagi, S. Mori, Y. Kofuji, Y. Kitagawa, S. Tanaka, S. Ichikawa, T. Hirai, *Nat. Mater.* 2019, **18**, 985-993.
- 22. J. Drinkine, Y, Glories, C. Saucier, J. Agr. Food Chem., 2005, 53, 7552-7558.
- 23. N. E. Es-Safi, C. L. Guernev é , V. Cheynier, M. Moutounet, *Tetrahedron Lett.* 2000, **41**. 1917-1921.
- 24. L. Pilato, (Ed.). New York: Springer. 2010, 11, 41-56.
- 25. J. M. Kenny, G. Pisaniello, F. Farina, S. Puzziello, *Thermochimica Acta*, 1995, 269/270. 201-211.
- 26. R. L, Bindu, C. P. R. Nair, K. N. Ninan, J. Polym. Sci. Pol. Chem. 2000, 38. 641-652.
- 27. V. C. Nguyen, N. J. Ke, B. S. Nguyen, Y. K. Xiao, Y. L. Lee, H. S. Teng, *J. Mater. Chem.* A 2019, 7, 8384-8393.

- 28. V. R. Battula, S. Kumar, D. K. Chauhan, S. Samanta, K. Kailasam Appl. Catal. B 2019, 244, 313-319. DOI: 10.1039/DOTA03974H
- 29. C. Zhu, C. A. Liu, Y. J. Fu, J. Gao, H. Huang, Y. Liu, Z. H. Kang, *Appl. Catal. B* 2019, **242**, 178-185.
- T. Marszalek, M. M. Li, W. Pisula, ChemComm. 2016, 52, 10938-10947.
- Z. L. He, C. Kim, L. H. Lin, T. H. Jeon, S. Lin, X. C. Wang, W. Y. Choi, *Nano Energy* 2017, 42, 58-68.
- G. H. Moon, M. Fujitsuka, S. Kim, T. Majima, X. C. Wang, W. Y. Choi, ACS Catal. 2017, 7, 2886-2895.
- C. Zhu, M. M. Zhu, Y. Sun, Y. J. Zhou, H. Huang, Y. Lifshitz, S. T. Lee, J. Zhong, Z. H. Kang, *Appl. Catal. B* 2018, **237**, 166-174.
- 34. C. A. Liu, Y. J. Fu, Y. J. Xia, C. Zhu, L. L. Hu, K. Zhang, H. H. Wu, Y. Liu, T. F. Xie, J. Zhong, Z. H. Kang, *Nanoscale* 2018, **10**, 2454-2460.
- S. Sun, T. Hisatomi, Q. Wang, S. S. Chen, G. J. Ma, J. Y. Liu, S. Nandy, T. Minegishi, M. Katayama, K. Domen, *ACS Catal.* 2018, 8, 1690-1696.
- 36. S. Z. Hu, X. Y. Qu, P. Li, F. Wang, Q. Li, L. J. Song, Y. F. Zhao, X. X. Kang, *Chem. Eng. J.* 2018, **334**, 410-418.



View Article Online DOI: 10.1039/D0TA03974H

Function-switchable metal-free catalyst splits water to produce hydrogen in air free,

while hydrogen peroxide is generated preferentially in air.