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Preparation and Application of Visible Light Driven Bi₂O₃-Cu₂O

Dual Photoelectrode Photocatalytic Fuel Cell

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Abstract: Photocatalytic fuel cells can be used for organic waste treatment and power generation by combining photocatalytic technology with fuel cells. However, traditional photocatalytic fuel cells rely on UV-responsive TiO₂-based photocatalysts and noble metal platinum cathodes, and the utilization of visible light is low and the cost is high, which restricts practical applications. In this

study, high-performance and low-cost Cu_2O photocathode materials were explored to replace precious metal platinum cathodes. Bi_2O_3 photoanode materials and Cu_2O photocathode materials were successfully prepared by low-energy hydrothermal method. By optimizing the ratio of photocatalyst, Nafion solution and absolute ethanol, uniform and dense photoelectrodes were prepared by drop coating method, and Bi_2O_3 - Cu_2O heterojunction dual-photoelectrode photocatalytic fuel cell (PFC) was constructed. At the same time, a series of characterization methods were used to characterize the crystal structure, elemental composition, and photoelectrocatalytic properties of Bi_2O_3 photoanode and Cu_2O photocathode. The degradation mechanism, electricity generation performance and stability of the system were investigated by free radical capture, electrochemical test and cycle stability experiment. The results show that the battery exhibits excellent photocatalytic ability and power generation ability in the degradation of methylene blue (MB). The degradation rate of MB by Bi_2O_3 - Cu_2O PFC system was as high as 96.46% after 80 minutes. The maximum power density, short-circuit photocurrent density and open-circuit voltage were $10.08\mu\text{W}/\text{cm}^2$, $0.075\text{mA}/\text{cm}^2$ and 0.54V, respectively. The Bi_2O_3 - Cu_2O PFC still has good photocatalytic performance after 5 cycles, and the Cu_2O photocathode has no obvious phase structure change verified by XRD and XRS. The innovation of this study lies in the construction of heterojunctions by Bi_2O_3 -n-type and Cu_2O -p-type semiconductors to achieve efficient separation of photogenerated carriers. At the same time, non-precious metal Cu_2O is used instead of Pt cathode, which greatly reduces the system cost and has a good application prospect in the field of low-cost organic wastewater treatment and energy reuse.

Keywords : Photocatalytic fuel cell photoelectrode preparation of organic electricity generation wastewater degradation cycle stability

1 Introduction

With the rapid development of industrial manufacturing, organic wastewater discharged from dyes, pharmaceuticals and other industries has become a key problem in global water environment governance. Industrial wastewater containing refractory organic pollutants, such as methylene blue and rhodamine B, is characterized by its strong toxicity and tendency for bioaccumulation. These pollutants are typically challenging to treat due to their complex chemical structures and stable bonds, which make them resistant to conventional biological degradation. The traditional treatment technology faces many bottlenecks: the adsorption method needs to replace the adsorbent frequently, the operation cost is high and it is easy to produce secondary pollution. The membrane filtration method has the problem of membrane fouling and complex maintenance. The biodegradation method has poor adaptability to high concentration and high toxicity wastewater,

and the treatment cycle is up to several days^[1-3]. In this context, photocatalytic fuel cell (PFC) technology, which has the functions of pollutant degradation and energy recovery, has emerged as a research focus in the field of environmental engineering and energy due to its unique advantages of "treating waste with waste and recycling resources." In the operational mechanism of a PFC, organic pollutants, which act as fuel, are decomposed through photoactivation at the photoanode. The photogenerated electrons then undergo directed migration due to the potential difference between the two electrodes. This process effectively suppresses undesired electron-hole recombination, thereby significantly enhancing the photocatalytic activity of the system^[4,5].

Traditional photocatalytic fuel cell (PFC) systems usually include anodes, cathodes, electrolytes, and external circuits^[6]. Among them, photoelectrode materials mostly use semiconductor photocatalysts. According to the composition of the photoelectrode, if either electrode (anode or cathode) consists of semiconductor material, it is called a single photoelectrode PFC system; if both electrodes use semiconductor photocatalysts, a dual photoelectrode PFC system is formed^[7]. In recent years, to enhance the performance of PFC systems, researchers have combined photocatalytic advanced oxidation technology with it. The photoelectric conversion capability of the system has been significantly enhanced through the broadening of the visible-light response, facilitation of charge separation, and improvement of electron transport efficiency in semiconductor photocatalysts^[8-10]. At present, many scholars have optimized the performance and power generation efficiency of photocatalytic fuel cells from different perspectives such as semiconductor electrode materials, PFC reactor structure, reaction conditions, fuel, electrolyte, and pH value of PFC devices^[11-13]. As the core of efficient operation of PFC, semiconductor photocatalytic electrode^[14] can not only effectively degrade organic pollutants, but also transform chemical energy into electrical energy to achieve the dual goals of pollution control and energy recovery. It shows broad prospects in the field of wastewater treatment and resource utilization. The traditional TiO_2 ^[15-17]-based photocatalyst can only exert activity under ultraviolet light excitation, which limits its practical application. Researchers are focusing on developing visible-light-responsive photocatalytic materials to improve visible-light utilization efficiency^[18,19]. In addition, the high cost of noble metal Pt cathodes has also promoted the exploration of economical and high-performance visible light-responsive photocathode materials. From the initial UV-driven TiO_2 electrode to the widely studied visible-light-responsive photocatalytic materials, the light-harvesting ability has been continuously enhanced. At the same time, the Pt cathode is gradually replaced by a high-performance, low-cost photocathode, thereby reducing the system cost and enhancing the overall performance in electricity generation and organic wastewater degradation^[20-22]. Therefore, the development of stable, efficient and inexpensive photoelectrode materials has become an effective

way to improve the performance of PFC systems. As a typical photocathode material, Cu_2O has a relatively narrow band gap and can efficiently utilize visible light^[23]. The cuprous oxide Cu_2O and copper oxide CuO coupling material (Cu_xO) has excellent photoelectrochemical stability and photoelectrocatalytic performance^[24]. Wang et al.^[25] found that embedding CuO nanowires in Cu_2O film can improve the photoelectrochemical performance (PEC) of the electrode and significantly improve the stability of the electrode. Zhang et al. $\text{CuO-Cu}_2\text{O}$ heterojunction and used it as a photoelectrocatalytic electrode. The stability of the electrode was significantly improved, which further indicated that Cu_xO could significantly inhibit the photocorrosion of Cu_2O and facilitate the effective segregation of photogenerated electron-hole pairs. In addition, the highly ordered Cu_xO nanowire array morphology helps to promote mass transfer, thereby improving the photoelectrocatalytic performance of the PFC system, thereby increasing the rate of redox reactions at the cathode and anode^[27].

Given this, the Bi_2O_3 catalyst, which features a simple preparation process, was chosen as the photoanode, while the Cu_2O photocatalyst with uniform morphology was selected as the photocathode, replacing the high-cost Pt electrode. This approach improves the utilization rate of light energy and simultaneously enhances the pollutant removal capability of the PFC system.

2 Preparation and characterization of materials

2.1 Experimental materials

Materials: Bi_2O_3 and Cu_2O photoelectrodes were prepared from raw materials such as bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, Pure analysis, 99.0%) NaOH (Pure analysis, 96.0%) and $\text{Cu}(\text{CH}_3\text{COO})_2$ (Pure analysis, 99.0%). Methylene blue (MB, Pure analysis, 98.0%) was used as the degradation substrate of photocatalytic fuel cell, and Na_2SO_4 (Pure analysis, 99.0%) was used as electrolyte. Isopropanol (IPA, Pure analysis, 98.0%), p-benzoquinone (PBQ, Pure analysis, 98.0%), triethanolamine (TEOA, Pure analysis, 99.0%) and dimethyl sulfoxide (DMSO, Pure analysis, 99.0%) were used for free radical capture experiments.

2.2 Experimental instruments

Instruments: electronic balance, ultrasonic cleaning instrument, mechanical stirrer, high pressure reactor, X-ray diffractometer, X-ray photoelectron spectrometer, high resolution projection electron microscope, X-ray energy spectrometer, fluorescence spectrophotometer, ultraviolet-visible spectrophotometer, scanning electron microscope, specific surface analyzer.

2.3 Photoelectrode preparation

2.3.1 Preparation of photoanode

The preparation of Bi_2O_3 photoelectrode is divided into two stages: Bi_2O_3 photocatalytic material synthesis and FTO substrate loading molding. The methods used are hydrothermal synthesis and drop coating. Figure 1 presents a flowchart of the specific preparation process. Firstly, a proper amount of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ is dissolved in deionized water, and the solution A is obtained after continuous stirring for 30min. Additionally, a 4mol/L NaOH solution is prepared to serve as the pH regulator for Solution A. The pH of Solution A is adjusted to 9 using the NaOH solution, with continuous stirring for 1h to obtain solution B. The solution B was placed in a 100 mL autoclave and subjected to reaction at 120 °C for 12 hours. After the reaction, we cooled the mixture to room temperature and carried out centrifugation and washing. The photocatalytic material Bi_2O_3 was prepared by drying at 60°C for 6h. Subsequently, the loading and photoanode forming of Bi_2O_3 on FTO substrate were carried out. In a 5mL beaker, the binder Nafion solution and anhydrous ethanol were added in a specific proportion, and then a small amount of Bi_2O_3 powder photocatalytic material, prepared via the aforementioned hydrothermal method, was weighed and transferred into the beaker. The mixed solution underwent ultrasonic stirring for 30 minutes, resulting in a uniformly dispersed Bi_2O_3 solution. FTO served as the conductive substrate for the photoelectrode; it was pretreated by cleaning with deionized water and anhydrous ethanol, followed by drying. The conductivity of the FTO surface was verified using a specialized conductive pen, and Bi_2O_3 was uniformly deposited onto the FTO conductive substrate by drop coating. By adjusting the range of the pipette gun, the amount of Bi_2O_3 mixed solution is controlled to adjust the number and thickness of the photoelectrode coating. After repeated coating, the electrode was dried at 60°C for 5min, and finally a stable $\text{Bi}_2\text{O}_3/\text{FTO}$ photoanode was formed.

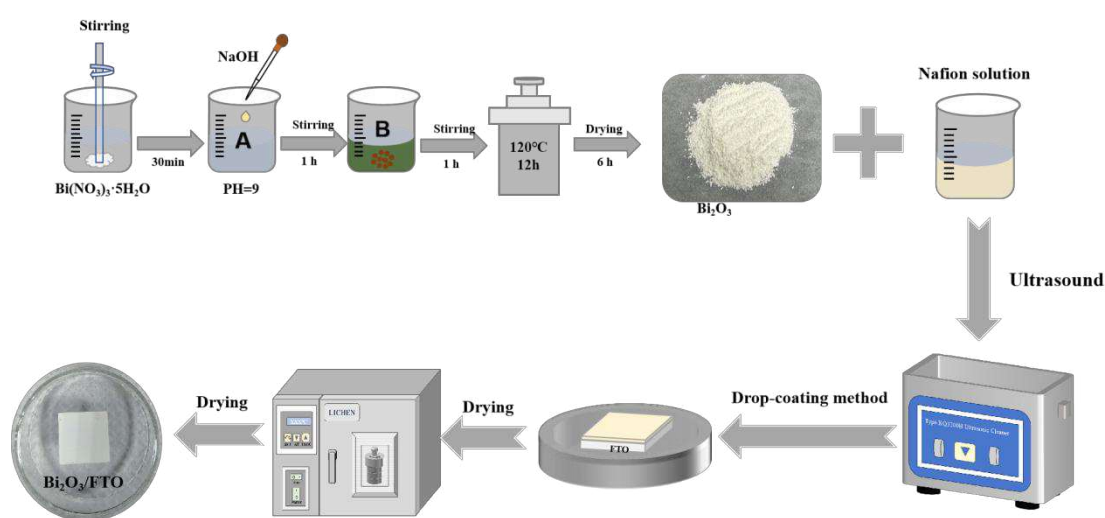


Fig. 1 Flow chart of Bi_2O_3 photoanode preparation

2.3.2 Photocathode preparation

The preparation of Cu_2O photocathode is mainly completed by hydrothermal reduction method and drop coating method. Firstly, $\text{Cu}(\text{CH}_3\text{COO})_2$ was dissolved in deionized water and heated in a water bath using a water bath pan. The solution A was obtained after stirring for 1h. An appropriate amount of glucose solution was added to solution A, and a 4 mol/L NaOH solution was prepared and used to adjust the pH of solution A to 13, followed by continued stirring for 1h to obtain solution B. The solution B was transferred to a 100 ml autoclave for reaction at 100°C over 12h. After cooling to ambient temperature, the resulting material was collected by centrifugation and subjected to multiple washing cycles. The brick red Cu_2O photocatalytic material was prepared after drying at 60°C for 6 hours. A specific amount of Cu_2O semiconductor catalyst was uniformly mixed with the binder Nafion solution and an appropriate volume of anhydrous ethanol. After 30 min of ultrasonication, the mixture was stirred with a pipette tip for several minutes until the solid particles were uniformly dispersed in the Nafion solution. Using FTO as the conductive substrate, it was immersed in deionized water and anhydrous ethanol for several minutes, then washed and dried for later use. The mixed liquid was uniformly coated on the surface of the pretreated FTO conductive substrate by drop coating method, and each layer was dried for 5min to form a uniform and dense Cu_2O photocathode. As shown in Figure 2.

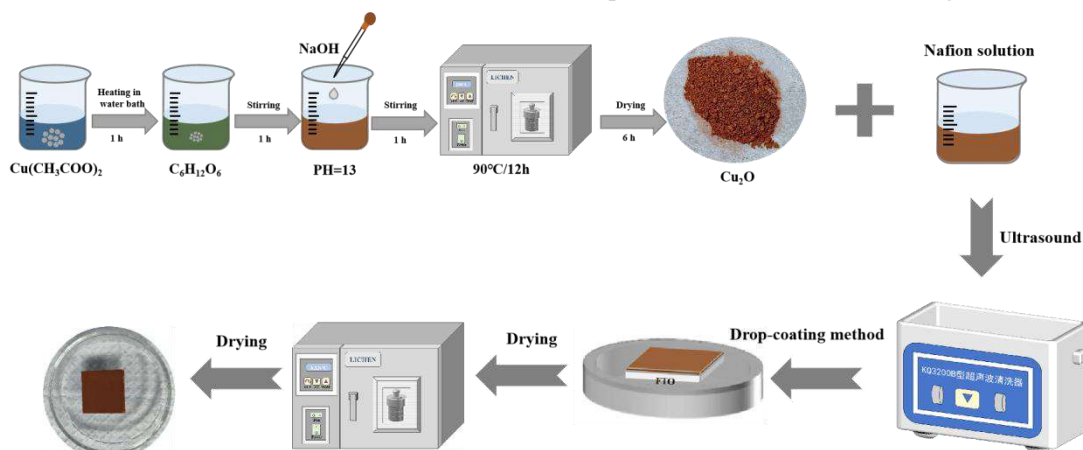


Fig. 2 Flow chart of Cu_2O photocathode preparation

2.4 PFC reactor structure design

The structure of the $\text{Bi}_2\text{O}_3\text{-Cu}_2\text{O}$ dual-photoelectrode photocatalytic fuel cell (Bi-Cu PFC) reactor is depicted in Fig. 3. The reactor is constructed from quartz, with a single chamber measuring $\phi 5 \times 8$ cm. The visible light-responsive Bi_2O_3 is used as the photoanode, and the high-performance Cu_2O is used as the photocathode. The maximum photoelectric area measures 2×2 cm. The two electrodes are positioned side by side. The cathode and anode are connected by a wire and connected in series with a 10Ω external resistance to form a closed loop. The electrolyte solution was composed of 0.1mol/L Na_2SO_4 solution and 10mg/L MB solution. Without special

instructions, the PFC system uses 10mg/L MB solution. Before evaluating the photocatalytic performance of the two-electrode PFC, dark adsorption was performed for 30min under dark conditions, so that the photoelectrode and the solution reached an adsorption-desorption equilibrium state. In the later stage of the photoreaction, 3ml of the reaction solution was taken every 20min. The absorbance value of this sample solution was determined with a ultraviolet-visible spectrophotometer, and the photocatalytic activity of the Bi-Cu PFC system was evaluated according to Formula 1^[28].

$$\text{Degradation rate} = (C_0 - C) / C_0 \quad (\text{Formula 1})$$

In this experiment, a three-electrode system was constructed with Bi₂O₃ photoanode as the working electrode, Cu₂O as the counter electrode and Ag/AgCl as the reference electrode. To guarantee data reproducibility, each set of experiments was replicated three times. The whole experimental process was carried out at room temperature. The xenon lamp system was employed to provide the light source. By adjusting the current of the xenon lamp system, the light intensity was adjusted, and the light intensity was measured by the illuminometer. The light intensity was 100mW/cm², and the mass transfer rate was improved by magnetic stirring. With the help of an electrochemical workstation, the i-t curve, electrochemical impedance spectroscopy and LSV polarization curve of the photoelectrode were obtained, so as to evaluate the power generation capacity of the photoelectrode.

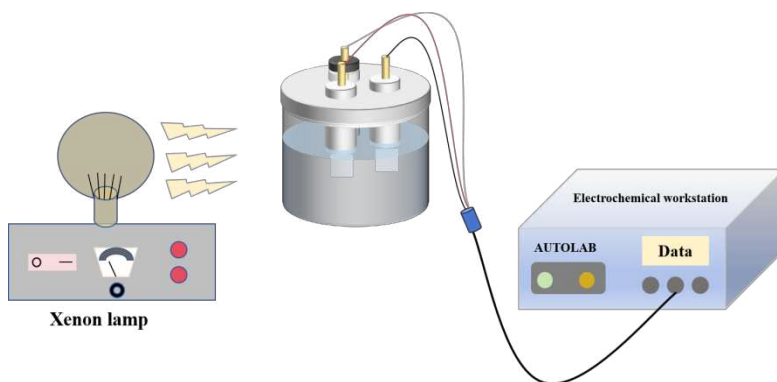


Fig. 3 Photoelectric performance test device of Bi₂O₃ photoanode

3 Results and discussion

3.1 Photoelectrode characterization test analysis

3.1.1 XRD analysis

X-ray diffraction (XRD) was employed to characterize the Bi₂O₃ photoanode material, aiming to identify its crystal structure. Figure 4(a) further reveals the crystallinity of Bi₂O₃ through the XRD spectrum of the sample. Bi₂O₃ exhibits strong diffraction peaks at diffraction angles of 25.69°, 28.27°, 31.53°, 33.31°, 41.32°, 42.25°, 46.36°, 54.82°, 59.12°, 76.78°, and Bi₂O₃

standard card (PDF # 27-0050) (210), (201), (002), (220), (212), (320), (222), (421). The (412) and (611) crystal planes have good matching degree. The results show that the diffraction peaks are basically consistent with the diffraction peaks of the standard card, and no impurity phase was detected, demonstrating the excellent crystallinity of the Bi_2O_3 .

The X-ray diffraction pattern of the Cu_2O photocathode material (Fig.4 (b)) shows that the prepared Cu_2O photocathode material is almost consistent with the standard card (PDF # 05-0667). The characteristic peaks of Cu_2O at 29.6° , 36.5° , 42.3° , 52.5° , 61.3° , 73.5° , 77.3° are attributed to the (110), (111), (200), (211), (220), (311), (222) crystal planes of PDF # 05-0667.

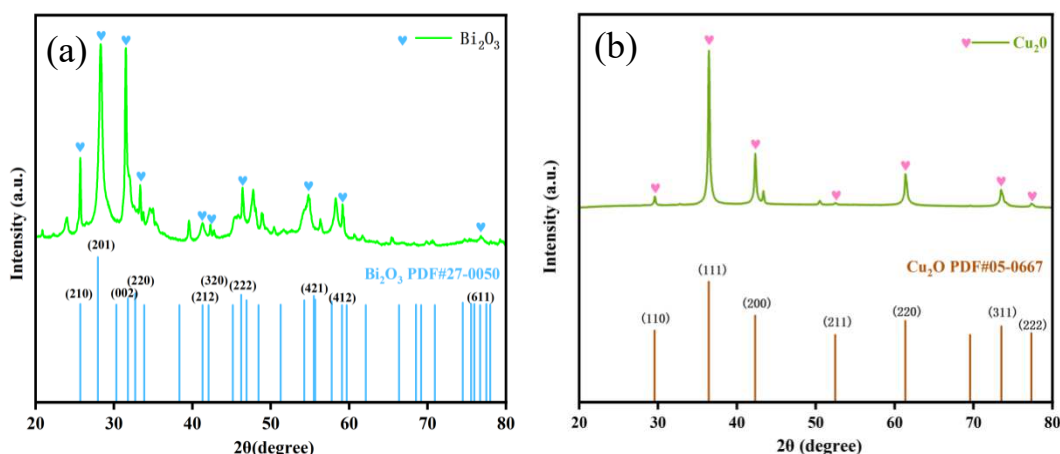


Fig. 4(a): X-ray diffraction pattern of Bi_2O_3 ; Fig. 4(b): XRD spectra of Cu_2O

3.1.2 SEM analysis

Scanning electron microscopy (SEM) was employed to examine the morphologic features of the photoelectrode material. As displayed in Figure 5 (a), Bi_2O_3 exhibits an irregular nanosheet structure with a thickness of about 50-80nm, a rough surface and some spherical particles. The irregular electrode material can effectively enhance the contact area between the electrolyte and the Bi_2O_3 photoanode, and further improve the photoelectrochemical performance of Bi-Cu PFC. According to the ImageJ software, the average size of Bi_2O_3 nanosheets is about $1.2 \pm 0.3 \mu\text{m}$. Fig.5 (b) reveals that the morphology and structure of the photocathode Cu_2O are uniformly distributed spherical particles with an average particle size of about $450 \pm 50 \text{ nm}$, and its morphology is uniform. It can be seen that the photocathode can maintain a relatively stable state and show good catalytic activity in the subsequent photoelectrocatalytic performance study. Energy Dispersive X-ray Spectroscopy (EDS) was utilized to analyze the elemental makeup of the sample. Figure 5 (c) - (d) confirms that there are two elements of O and Bi in the Bi_2O_3 photoanode, and the mass fraction and atomic ratio of the two elements can be seen from Figure 5 (e). The spherical Cu_2O photocathode material possesses a large specific surface area, which facilitates the generation of abundant photogenerated electron-hole pairs, suggesting its superior

photocatalytic performance. The EDS spectrum and the element distribution spectrum (f) - (g) displayed in Fig. 5 (h) indicate the presence of Cu and O elements, demonstrating that the Cu_2O photocathode material has been successfully synthesized through the hydrothermal method.

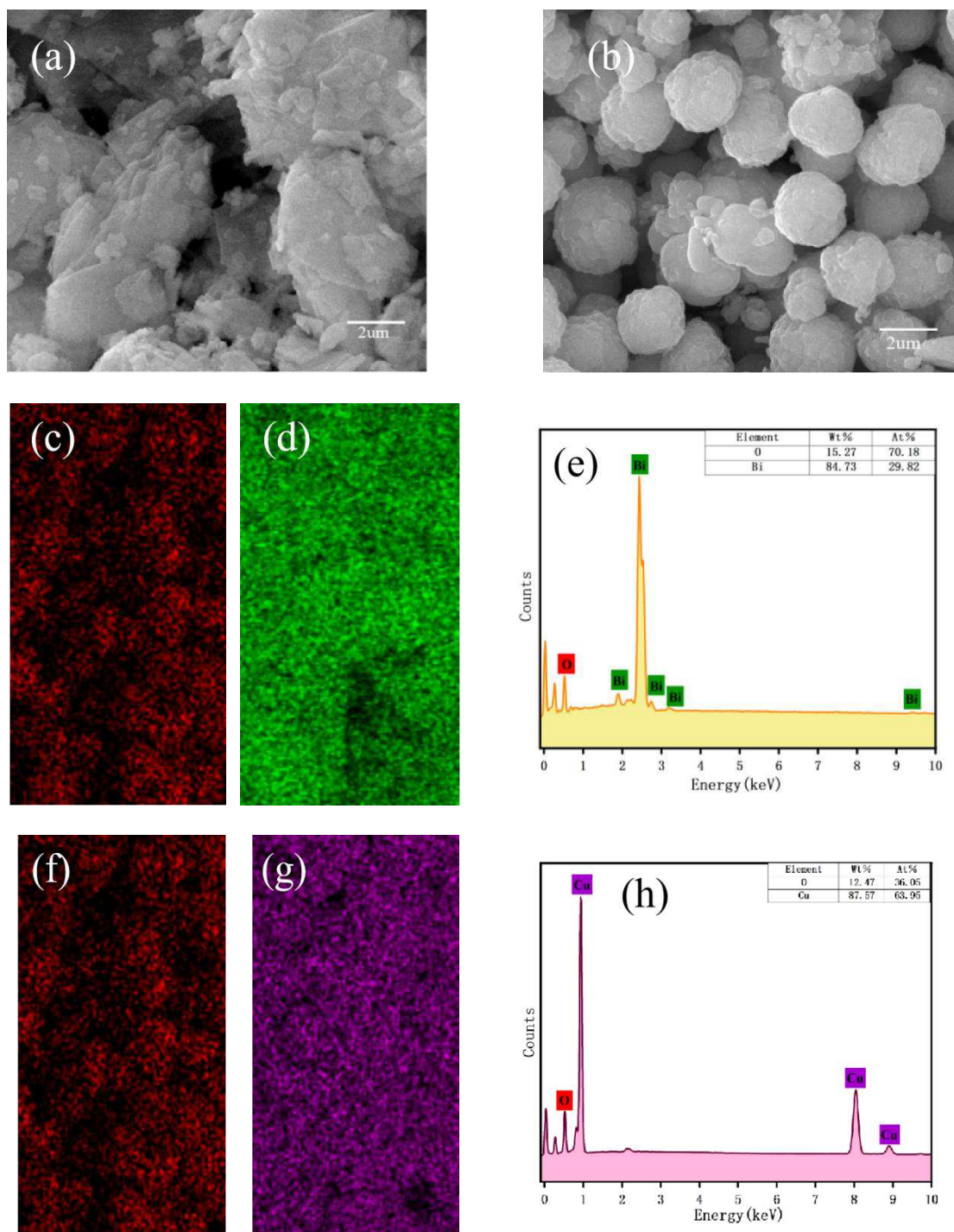


Fig. 5 (a) displays the SEM spectra of Bi_2O_3 ; (b) shows the morphology structure diagram of Cu_2O ; (c) - (d) and (e) present the Bi_2O_3 element distribution spectra and EDS; (f) - (g) and (h) illustrate the Cu_2O EDS spectra of the samples.

3.1.3XPS analysis

High-resolution XPS was employed to determine the elemental composition and valence states of the photoelectrode materials. Figure 6 (a) - (c) reveals that the Bi_2O_3 photoelectrode material contains two elements of O and Bi, which is consistent with the EDS analysis results. Figure 6 (d) illustrates the full spectrum of Cu_2O photocathode material, confirming the presence of Cu and O elements as evidenced by the bandgap and absorbance coefficient detailed in scientific literature. Figure 6(e) shows the Cu 2p high-resolution spectrum with two characteristic peaks centered at 952.2 and 932.4 eV, corresponding to Cu 2p_{1/2} and Cu 2p_{3/2}, respectively. The O 1s high-resolution spectrum (Figure 6 (f)) exhibits a characteristic peak at 530.6 eV.

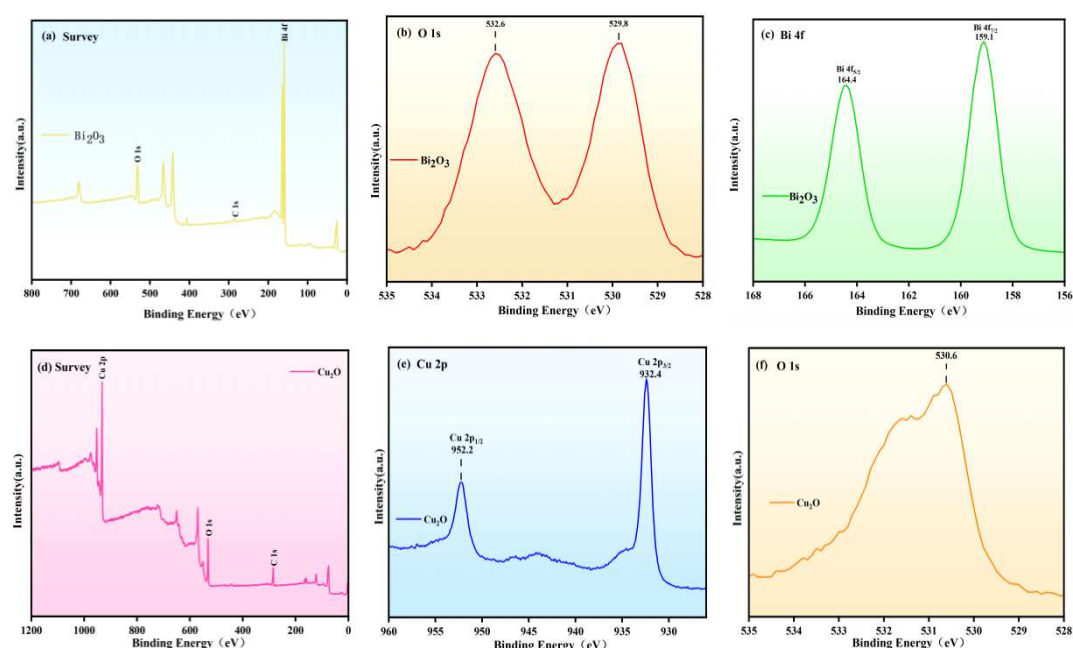


Fig.6 XPS spectra of samples; (a) Full spectrum of Bi_2O_3 ; (b) (c) High-resolution spectra of Bi_2O_3 photoanode O and Bi elements; (d) Cu_2O full spectrum; (e) (f) High resolution spectra of Cu and O elements in Cu_2O photoanode

3.1.4 Uv-vis DRS analysis

Figures 7(a) and 7(c) present the $U_{V\text{-vis}}$ DRS spectra of Bi_2O_3 and Cu_2O photoelectrodes, which allow for the determination of the band gap energy (E_g). In Fig. 7(a) and (c), the band gap energy of the samples is determined by the intercept of the tangent line with the x-axis. The E_g of Bi_2O_3 and Cu_2O photoelectrode materials obtained by formula 2 is 2.84 eV and 1.82 eV, respectively. The valence band position (VB) of the sample material was obtained by X-ray photoelectron spectroscopy (VB-XPS) characterization, and the valence band value (EVB) was obtained.

According to the band structure position of the photoelectrode material and the Uv-vis DRS analysis results, the conduction band position (CB) is obtained from formula 3, which is an important part of the mechanism analysis. As shown in Fig.7 (b) (d), extending the straight line

near 0 eV, the intersection of the tangent line and the extension line is the energy value corresponding to the valence band position. The results show that the EVB of Bi₂O₃ and Cu₂O are 1.964 eV and 1.85 eV, respectively.

$$(ah\nu)^{1/n}=A(h\nu-E_g) \quad (\text{Formula 2})$$

$$ECB = EVB-E_g \quad (\text{Formula 3})$$

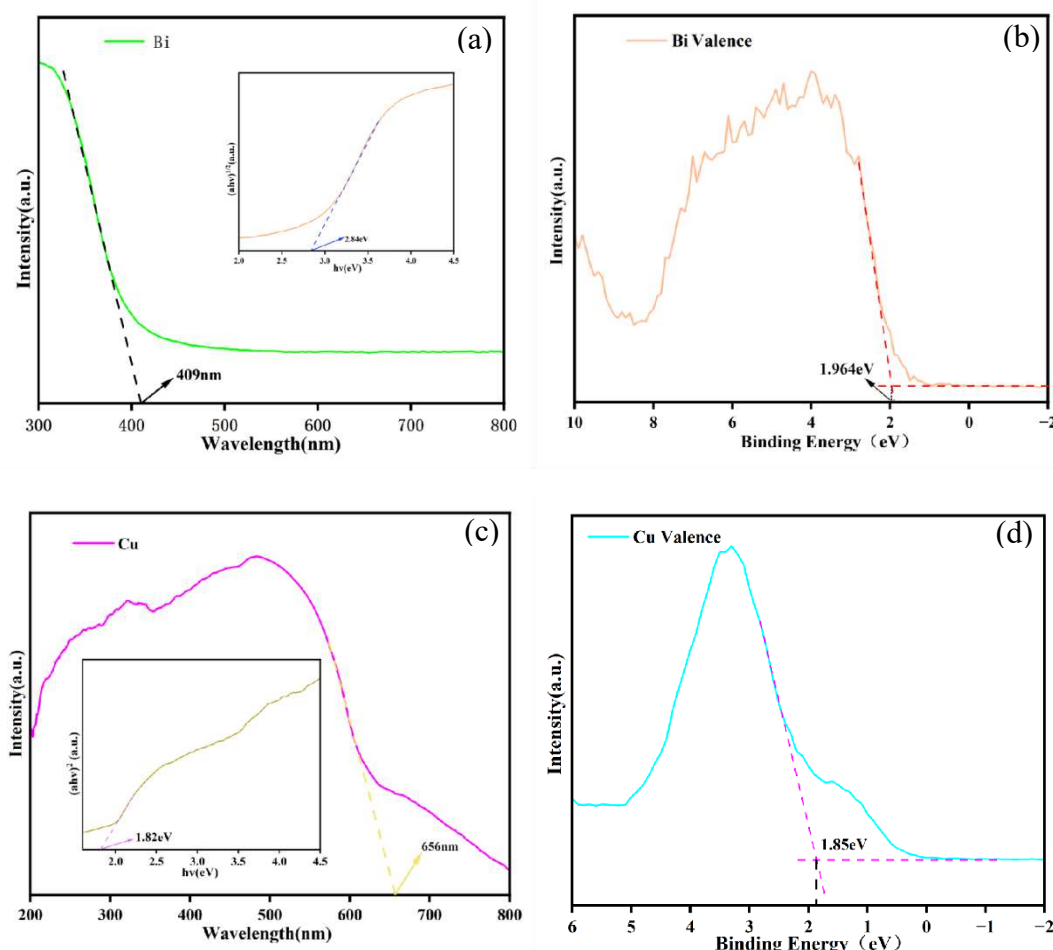


Fig.7 (a) UV-vis DRS spectra of Bi₂O₃ ; (b) VB-XPS diagram of Bi₂O₃ ; (c) UV-Vis diffuse reflectance spectra of Cu₂O photocathode material (illustrated as $(ah\nu)^{1/2}$ - $h\nu$ curve) ; (d) Cu₂O VB-XPS diagram

3.2 PFC Performance Study

3.2.1 Photocatalytic performance test of Bi₂O₃-Cu₂O PFC system

The Bi-Cu PFC system was constructed by using Bi₂O₃ as photoanode and Cu₂O as photocathode. In order to further evaluate the removal ability of Bi-Cu PFC system to organic pollutants, methylene blue was adopted as the target dye to explore the degradation capability of Bi-Cu double photoelectrode PFC system to methylene blue. As presented in Fig.8, the experimental results demonstrate that the Bi-Cu PFC system exhibits excellent degradation performance during MB degradation, with high degradation rates observed are 96.46%,

respectively. The Cu₂O photocathode replaces the Pt electrode to construct a dual photoelectrode PFC system, which can effectively improve the degradation ability of the photocatalytic fuel cell.

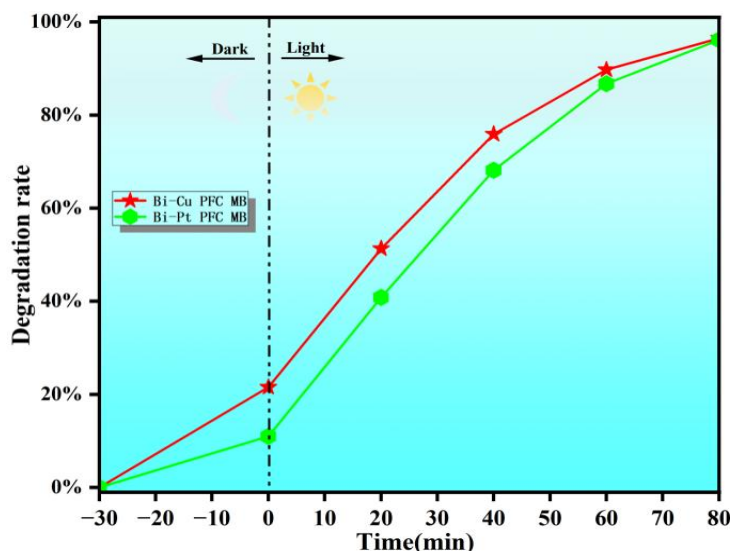


Fig.8 Removal rate of MB dye by Bi-Cu PFC

The main active substances of the Bi-Cu PFC system in the MB degradation process were investigated by free radical capture experiments. TEOA, IPA, and PBQ capture agents were selected to inhibit h^+ , $\cdot OH$, and $\cdot O_2^-$ free radicals, respectively. As shown in Figure 9, the pollutant removal ability of the Bi-Cu PFC system decreased after the addition of IPA and PBQ capture agents, indicating that $\cdot OH$ and $\cdot O_2^-$ free radicals play a role in the dye degradation process. After the incorporation of TEOA, the degradation rate of MB by Bi-Cu PFC system was significantly inhibited, and the removal efficiency of MB was 49%, indicating that h^+ free radicals are primarily responsible for the degradation of the MB solution.

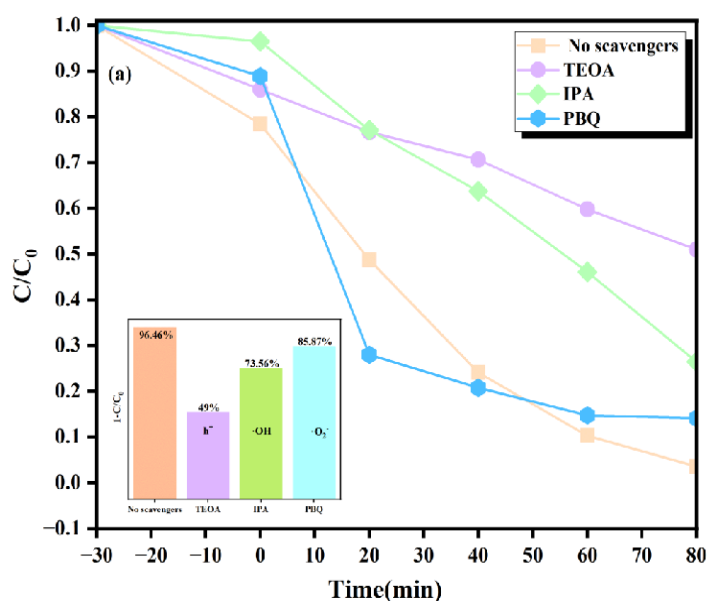


Fig.9 Free radical trapping experiment of Bi-Cu PFC system

3.2.2 Characterization of photoelectric properties of Bi₂O₃-Cu₂O PFC system

The Bi-Cu PFC system has good photocatalytic activity and can effectively remove organic pollutants. In order to explore the effect of Bi-Cu PFC system in converting the chemical energy of organic pollutants into electrical energy, the power generation performance of Bi-Cu two-electrode PFC system was tested by electrochemical workstation. A three-electrode system was constructed, with the working electrode was connected to the Bi₂O₃ photoanode, the counter electrode was connected to the Cu₂O photocathode, and Ag/AgCl was used as the reference electrode. In order to obtain reliable and effective experimental data, the test experiments were repeated many times. The experiment utilized a 100W xenon lamp system as the light source, which was operated at an intensity of 100mW/cm² to ensure accurate simulation of the desired lighting conditions. The i-t curve, EIS curve and LSV polarization curve of Bi-Cu PFC system were obtained by testing, and the effects of different organic pollutants and electrolyte concentrations on the power generation capacity of Bi-Cu PFC system were investigated.

The photocurrent response curve of the Bi-Cu PFC system is shown in Fig.10, which is obtained alternately under 30s illumination and 30s dark. As shown in the figure, the Bi-Cu PFC system exhibits excellent photocurrent performance. The n-type semiconductor Bi₂O₃ and the p-type semiconductor Cu₂O generate photogenerated electron pairs under illumination, and the electron transfer process generates electrical energy. Consequently, the photocurrent increases rapidly under illumination and the photocurrent density is 0.01mA/cm².

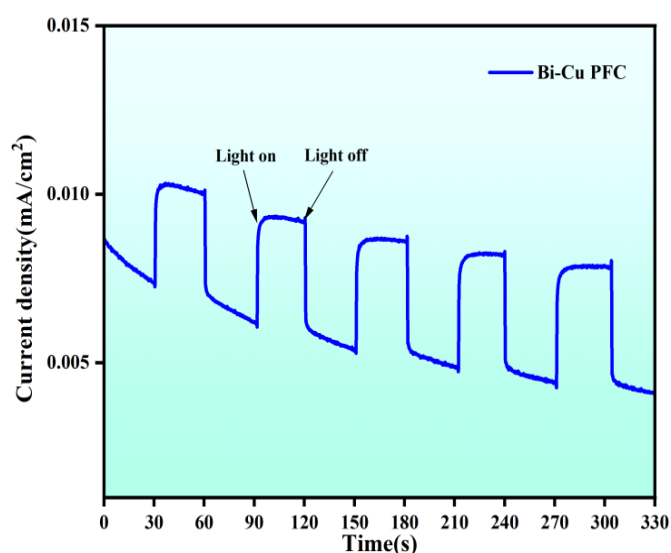


Fig.10 Jsc-t curve of Bi-Cu PFC system

Through a three-electrode system, the linear sweep voltammetry was utilized to record the change of the working electrode potential with the current size, and the power generation capacity

of Bi-Cu PFC under different Na_2SO_4 electrolyte concentrations was explored. The current-electrode potential curve of Bi-Cu PFC was obtained at a scanning rate of 5mV/s. The power density, short-circuit photocurrent density, open-circuit voltage and fill factor of Bi-Cu PFC were calculated according to the formula. The J_{sc} -V and JV_{max} -V characteristic curves were drawn after processing the LSV test data. Figure 11 shows that when the electrolyte concentration is 0.1mol/L, the maximum power density and short-circuit photocurrent density of Bi-Cu PFC are the largest, JV_{max} and J_{sc} are $10.08\mu\text{W}/\text{cm}^2$ and $0.075\text{mA}/\text{cm}^2$, respectively.

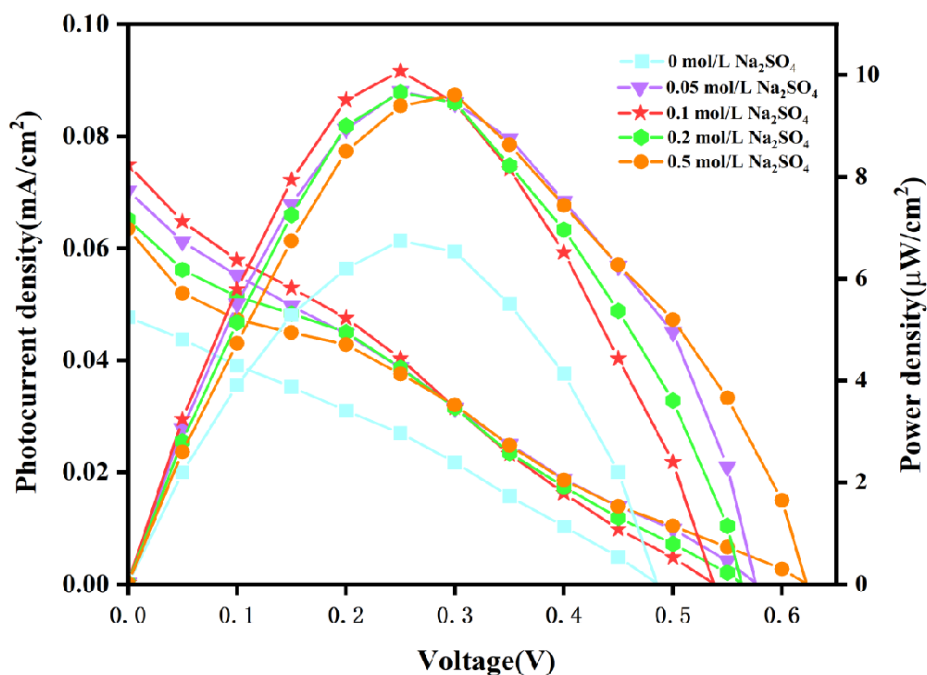


Fig.11 Effect of electrolyte concentration on power generation of Bi-Cu PFC

As shown in Figure 12, different concentration gradients of methylene blue were used as degradation substrates to further evaluate the power generation capacity of Bi-Cu PFC system during the degradation of MB with different concentrations. The LSC polarization curve of Bi-Cu PFC was measured at a scanning rate of 5mV/s, and the intuitive J_{sc} -V and JV_{max} -V curves were drawn. When the target pollutant is 10mg/L methylene blue, the maximum power density, short-circuit photocurrent density and open-circuit voltage are $15.18\mu\text{W}/\text{cm}^2$, $0.122\text{ mA}/\text{cm}^2$ and 0.55V, respectively. The Bi-Cu PFC system effectively degrades the pollutant MB while generating a notable amount of electrical energy, demonstrating its excellent photoelectrocatalytic capability.

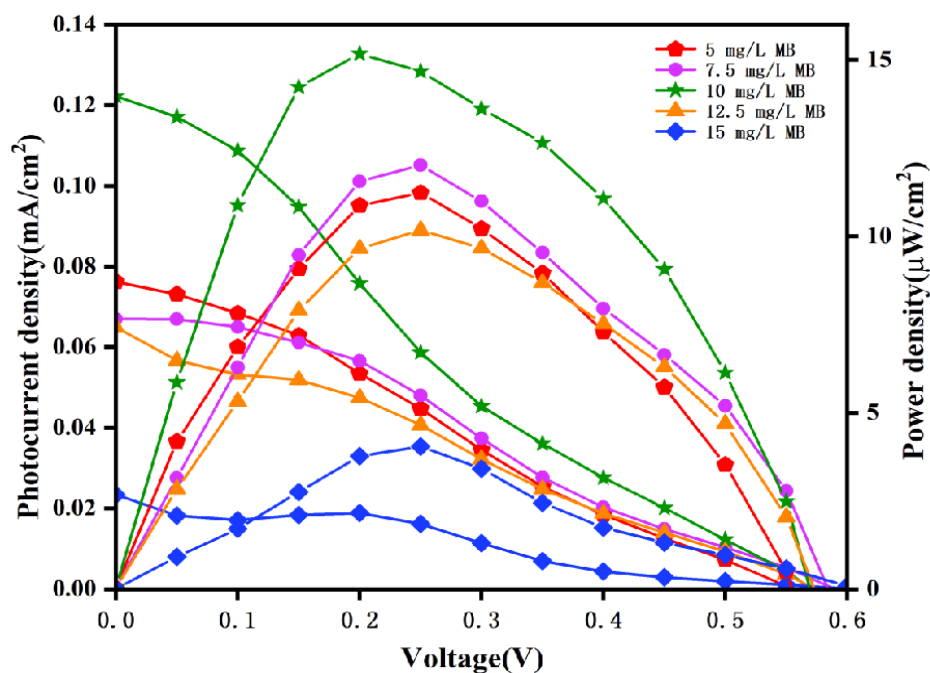


Fig.12 Effect of substrate concentration on Bi-Cu PFC power generation

3.2.3 Study on the mechanism of MB degradation in Bi₂O₃-Cu₂O PFC system

The removal mechanism of MB by Bi-Cu PFC system is shown in Figure 13. In Bi-Cu PFC system, the surface of Bi₂O₃ photoanode and Cu₂O photocathode is excited by light, resulting in a large number of electron-hole pairs. The photogenerated electrons from the Bi₂O₃ photoanode surface travel through the external circuit to the Cu₂O photocathode, generating a photocurrent which in turn significantly improves the charge separation efficiency in the photoelectrodes. As the primary active substance in the degradation process of pollutants, most h⁺ radicals are directly involved in the degradation process of MB, degrading MB dyes into small molecules such as carbon dioxide and water to achieve green degradation. A small amount of h⁺ reacts with H₂O to produce •OH, which achieves the purpose of MB pollutant removal. The e⁻ on the face of the Cu₂O photocathode reacts with dissolved O₂ to produce •O₂⁻ radicals, achieving MB degradation while generating electrical energy.

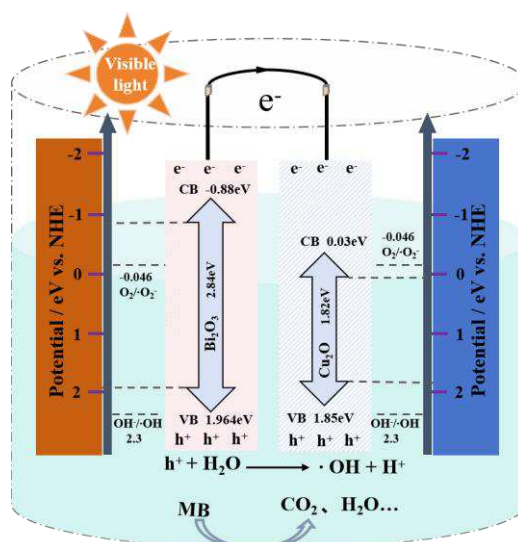


Fig.13 Mechanism diagram of MB degradation in Bi-Cu PFC system

3.2.4 Study on the reusability of Bi₂O₃-Cu₂O double electrode

Through the cycle stability experiment, the stability of the photoelectrode in the use process was investigated. The photoelectrode with good stability can play an important role in the current industrial application, ensure the removal ability of the PFC system to pollutants and the efficiency of power generation, and reduce the production cost. As shown in Fig.14, the long-term operational stability of the Bi-Cu PFC system was assessed under the conditions of 0.1mol/L Na₂SO₄ and 10mg/L MB. After the Bi-Cu PFC system completed a photocatalytic degradation experiment, the electrode sheet was repeatedly cleaned and dried for a certain length of time, and the electrolyte under the same conditions was replaced to facilitate the next photocatalytic experiment. After several stability experiments, the removal rate of pollutant MB by Bi-Cu PFC system remained above 83.72%. The reason for the slight decrease in the degradation rate is that after multiple cycles, a small amount of MB degradation intermediates are adsorbed on the surface of the photoelectrode, resulting in some active sites being blocked, and the photocatalytic activity is slightly reduced. In the process of stirring and washing, a very small amount of photocatalyst falls off from the FTO substrate, and the electrode load decreases slightly. The results of XRD, XPS characterization and ICP-OES detection of the photoelectrode after cycling showed that there was no obvious phase structure change, element valence change and metal dissolution, which proved that the Cu₂O photocathode had good photocorrosion resistance, indicating that the photoelectrode had excellent stability and could be reused.

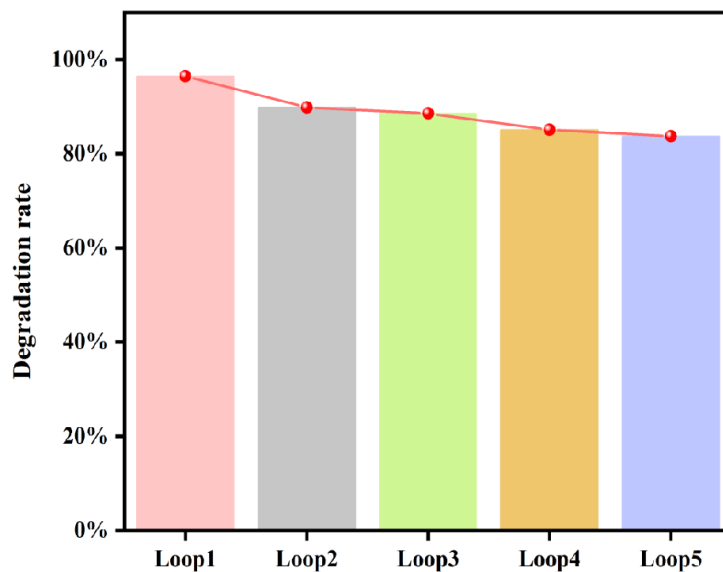


Figure 14 Stability test of Bi-Cu PFC

4 Conclusion

The Bi_2O_3 photoanode and Cu_2O photocathode were fabricated using the drop-coating method. The resulting photoelectrode surfaces were uniform and dense. The characteristics of Bi_2O_3 photoanode materials and Cu_2O photocathode materials were studied by XRD, SEM, XPS, Uv-vis DRS and other characterization methods. The irregular nano-flake structure of the Bi_2O_3 photoanode offers more photocatalytic active sites. The Cu_2O photocathode material exhibits a uniform spherical particle morphology. The morphology of the sample is uniform. This indicates that the photocathode can maintain a relatively stable state, demonstrating good catalytic activity in subsequent photoelectrocatalytic performance studies. The degradation rate of MB in Bi_2O_3 - Cu_2O PFC system is as high as 96.46% within 80min. Replacing the Pt electrode with a Cu_2O semiconductor as the photocathode enhances light source utilization and reduces costs. The experimental results of five cycles show that the Bi-Cu PFC two-electrode system has good reusability and stability. The substrate concentration and electrolyte concentration have an effect on the degradation effect and power generation capacity of PFC. The Bi_2O_3 - Cu_2O photocatalytic fuel cell (PFC) demonstrates superior photocatalytic efficiency and electricity generation capabilities during the degradation of methylene blue (MB).

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Notes

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