Development of TiO_2@porphyrin nanocomposites as photoelectrochemical materials for water splitting in hydrogen production

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ABSTRACT

Photoelectrochemistry (PEC) is a technology that integrates light absorption on semiconductor materials with electrode-driven oxidation and water-splitting processes, producing oxygen and hydrogen. In this study, we report the synthesis of TiO_2@porphyrin hybrid materials by the self-assembly method and evaluate the photocatalytic water splitting ability of the hybrid materials. Analytical methods such as UV-vis, SEM, cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry (LSV) were used to determine the hybrid material formation and photoanode performance. The nanomaterials were synthesized by the self-assembly method with a fiber structure of 30-50 nanometers in diameter and several micrometers in length. The results showed that TiO_2@porphyrin nanomaterials have potential applications in H_2 production from water.

Keywords: Photoelectrochemical water splitting; TiO_2@porphyrin hybrid material; Green hydrogen; Self-assembly.

1. INTRODUCTION

Excessive reliance on traditional fossil fuels has confronted us with a series of serious crises: energy shortages, environmental pollution, and global warming [1, 2]. To address these concerns, it is essential to research and develop clean and renewable energy sources to meet the ever-growing energy demand. In this context, hydrogen energy, also known as hydrogen fuel, is considered a carbon-free fuel source and a versatile alternative to fossil fuels, particularly in transportation and energy storage applications [3, 4]. Among the methods for hydrogen production, photoelectrochemical (PEC) water splitting is recognized as a sustainable strategy for generating abundant, high-purity, and environmentally friendly hydrogen. In PEC, the most critical factor is the development of efficient, stable, safe, and low-cost photoelectrodes. Semiconductor photocatalyst materials have attracted the attention of researchers both domestically and internationally for water-splitting hydrogen production since Fujishima and Honda demonstrated the potential of TiO_2 semiconductor materials in splitting water into H_2 and O_2 [5, 6].

TiO_2 possesses outstanding advantages such as chemical stability, photocatalytic activity, non-toxicity, and low cost, making it a research focus for many scientists. However, its practical application still faces many challenges due to limitations in absorbing light across the full spectrum. The creation of heterostructures helps overcome these drawbacks and improve the efficiency of the water-splitting process. Recent studies have focused on developing new photocatalysts that can operate in the visible light region, relying on organic semiconductor nanostructures with low band-gap energy and high light absorption efficiency. Among these, nanostructured porphyrins, formed through the self-assembly of conjugated porphyrin monomers—have been considered promising catalysts [7]. The photocatalytic activity of nanostructured porphyrins has been demonstrated [8, 9]. The fabrication of TiO_2@porphyrin hybrid material increases the optical activity of the material under visible light, overcoming the disadvantage of TiO_2 (only absorbing UV light). Porphyrin acts as a photosensitizer with excellent charge transfer ability, which will further expand the application of hybrid materials.

Xin Wang's research group developed ultrathin porphyrin-based metal–organic frameworks (MOFs) to produce clean and renewable hydrogen via highly efficient photocatalysis, achieving a remarkably high hydrogen production rate of up to 8.52 mmol g^{-1} h^{-1} under broad visible-light irradiation [10]. In another report, a 2D copper tetrakis(4-carboxyphenyl)porphyrin MOF was synthesized and used as a photocatalyst for overall water splitting. Under visible-light irradiation (λ > 450 nm), it achieved a hydrogen production rate of 120 μmol H_2 g_catalyst^{-1} h^{-1}, which is among the highest rates ever reported [11].

To date, reports on combining inorganic–organic semiconductors for PEC applications remain limited. Herein, we report a simple synthesis of TiO_2@porphyrin hybrid materials via a self-assembly method and their potential application as photoelectrodes for water-splitting reactions.

2. EXPERIMENTAL SECTION

2.1. Materials

The chemicals used in this study include TiO_2, NaOH, and HCl, all purchased from Sigma-Aldrich. Tetrakis(4-carboxyphenyl)porphyrin (TCPP) was obtained from Xilong Chemical Co., Ltd., China. All chemical reagents used were of the highest analytical grade available and were used without further purification. Deionized water was used throughout the experimental process.

2.2. Synthesis of TiO_2@porphyrin

The TiO_2@porphyrin composite material was synthesized via a self-assembly method through reprecipitation. In this process, 8 mg of monomeric TCPP porphyrin molecules were dissolved in 2 mL of 0.1 M NaOH. TiO_2 was then dispersed into the porphyrin solution at a ratio of 15 TiO_2: 1 porphyrin using ultrasonic treatment for 20 minutes. Subsequently, 0.1 M HCl solution was slowly added dropwise to the mixture until the pH reached approximately 6 - 7, at which point the characteristic green color of nano-porphyrin appeared. The solution was stored in the dark prior to use.

2.3. Preparation of the electrode

The three-electrode system used consisted of: a working electrode made from FTO (fluorine-doped tin oxide) glass plates with an area of 1 cm² coated with the composite material, a platinum counter electrode, and an Ag/AgCl reference electrode. The image of the electrode and measurement setup is shown in figure 1.

(a) (b)

Figure 1. *(a) Working electrode conditioned in Na_2SO_4 solution and (b) the three-electrode system used.*

Preparation of the binder: A 5% Nafion solution was diluted and used as the electrode binder at a concentration not exceeding 10% of the total solution volume. The Nafion solution was thoroughly mixed with the synthesized nanomaterial, followed by continuous magnetic stirring and ultrasonic treatment for 2 hours to obtain a homogeneous mixture.

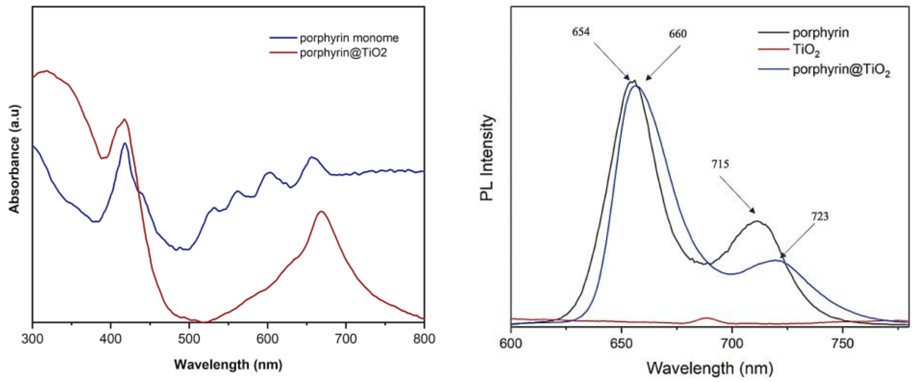
The FTO substrates were cleaned in four sequential ultrasonic steps using distilled water - ethanol - acetone - distilled water. The working area on each FTO substrate was fixed at 1 cm × 1 cm. Using a micropipette, 10μL hybrid materials were evenly coated on the FTO surface and allowed to dry naturally for 24 hours, followed by 2 similar coatings. The concentrations of materials on the electrodes were investigated: 30mg/mL, 50mg/mL, 80 mg/mL. The experiments were repeated 3 times. Before electrochemical measurements, the working electrode was immersed in Na_2SO_4 electrolyte solution for approximately 30 minutes.

2.4. Characterizations

The UV–vis absorption spectra were recorded using an Ocean Optics system equipped with a DH-2000-BAL light source, a USB4000 spectrometer, and a cuvette holder. The morphology and structure of the materials were characterized by field-emission scanning electron microscopy (FESEM, Hitachi S-4200). Electrochemical measurements, including cyclic voltammetry (CV), linear sweep voltammetry (LSV), and electrochemical impedance spectroscopy (EIS), were carried out using an Autolab PGSTAT302N multifunctional electrochemical workstation. The electrolyte solution used was 0.5 M Na_2SO_4, and a xenon lamp (LAX-C100) served as the light source. The light source's intensity was around 100 $mWcm^{-2}$.

3. RESULTS AND DISCUSSION

The optical properties of the samples were investigated using UV - vis spectroscopy, as shown in figure 2a. The UV–vis spectrum of porphyrin molecules exhibits a strong Soret absorption peak at 420 nm, which results from the transition from $a_1u(\pi)$ to e_g^* (π), and four weaker peaks in the range of 500–700 nm, attributed to Q bands corresponding to the $a_{2u}(\pi) \rightarrow e_g^*$ (π) transition [12]. After the self-assembly process, the UV–vis spectrum displays the characteristic absorption peaks of both porphyrin nanofibers and TiO_2 nanoparticles. A shoulder around 325 nm is attributed to TiO_2 nanoparticles. Upon self-assembly of porphyrin monomers, the Soret band at 420 nm significantly decreases in intensity and shifts to 418 nm, confirming aggregate formation and indicating that J-type supramolecular assemblies are responsible for the synthesis of the porphyrin nanostructures. Furthermore, the four peaks in the Q-band region of the monomer merge into a relatively strong single peak at 670 nm, further demonstrating the successful self-assembly of porphyrin molecules.



(a) *(b)*

Figure 2. *(a) UV–vis spectra of porphyrin monomer (blue line) and TiO_2@porphyrin hybrid material (red line), (b) Fluorescence spectra of molecular porphyrin, TiO_2 and TiO_2@porphyrin.*

The fluorescence properties of porphyrin monomer molecules and TiO_2@porphyrin were studied by photoluminescence spectroscopy (figure 2b). The fluorescence spectra of porphyrin molecules in the samples showed two characteristic emission peaks at 654 and 715 nm. However, in the fluorescence spectrum of TiO_2@porphyrin, we observed two emission peaks at 660 and 723 nm. The change in the position of these emission peaks may be due to a combination of the spatial arrangement of porphyrins, the hybridization between materials, leading to a change in the energy level of the hybrid material.

Figure 3a shows the XRD pattern of the porphyrin@TiO_2 hybrid material. The peaks at 25.4°, 38°, 48°, 54°, and 55.1° are assigned to the (101), (004), (200), (105), and (211) planes of anatase-phase TiO_2 nanoparticles [13], respectively, with sharp and intense diffraction peaks. This indicates that the formation of the hybrid material does not alter the crystallinity of the TiO_2 nanoparticles. The peaks observed at around 16° and 17.5° are attributed to the crystalline nature of the self-assembled porphyrin nanofibers, likely resulting from aromatic π–π stacking between porphyrin molecules. For pure porphyrins that have not been self-assembled, the XRD spectrum does not show peaks due to the organic nature of the material. This has been demonstrated in several previous studies, demonstrating the formation of porphyrin nanomaterials.

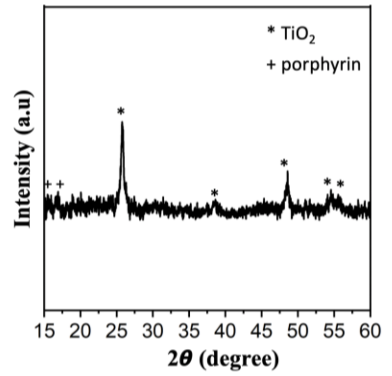
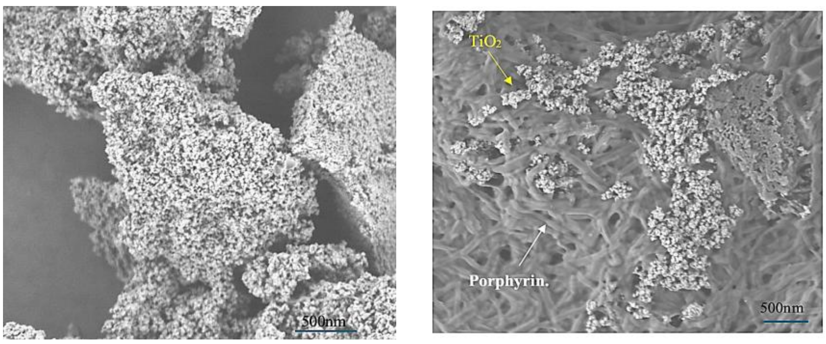


Figure 3. *XRD pattern of the TiO_2@porphyrin hybrid material.*

The morphology of the nanostructured porphyrin material was characterized by scanning electron microscopy (SEM), as shown in figure 4.



(a) *(b)*

Figure 4. *(a) XRD pattern of the TiO_2@porphyrin hybrid material, (b) SEM image of the TiO_2 and TiO_2@porphyrin hybrid material.*

It can be observed that, after the self-assembly process, TiO_2 nanoparticles with sizes of about 20–30 nm are well integrated into the network of porphyrin nanofibers, which have relatively uniform diameters of 30–50 nm and lengths of several micrometers. Based on these results, the successful formation of porphyrin@TiO_2 hybrid material with defined nanoscale dimensions and morphology can be confirmed. Next, we examined the electrochemical properties of the

TiO_2@porphyrin nanohybrid material. Figure 5 shows the effect of sample concentration on the resulting photocurrent density. It was observed that the sample with a concentration of 50 mg/mL produced the highest signal and the smoothest coating layer. At a concentration of 80 mg/mL, the surface of the material, after being coated onto the FTO substrate and dried, exhibited "surface cracking" (a phenomenon not observed in the 30 mg/mL and 50 mg/mL samples), indicating that excessively high concentrations negatively affect the coating film. Therefore, the optimal coating concentration for the TiO_2@porphyrin hybrid material was determined to be 50 mg/mL.

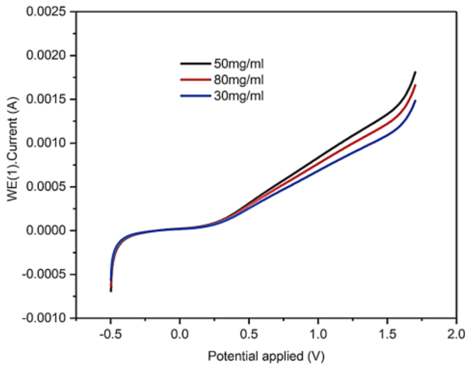
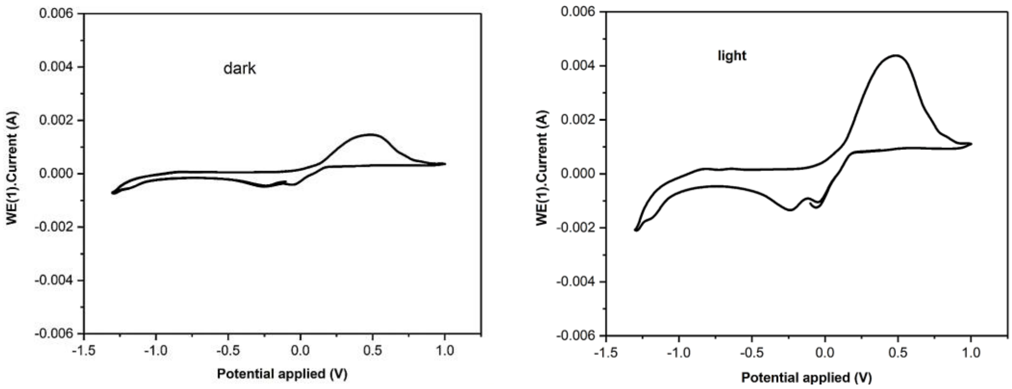


Figure 5. *LSV curves of TiO_2@porphyrin nanomaterials with different coating concentrations in a pH = 7 environment.*

Figure 6 shows the cyclic voltammetry (CV) measurement of the working electrode, recorded over a potential range from –1.3 V to 1 V vs. Ag/AgCl at a scan rate of 0.1 $V \cdot s^{-1}$. The results indicate that the CV of the FTO electrode coated with TiO_2@porphyrin hybrid material in 0.5 M Na_2SO_4 solution exhibits a characteristic redox couple, with a reduction peak at E = –0.25 V and an oxidation peak at E = 0.51 V vs. Ag/AgCl, attributed to the redox states of TiO_2. Figures 6a and 6b show that, under illumination, the recorded current density nearly doubles compared to the dark condition. This confirms that the TiO_2@porphyrin hybrid material can absorb energy from sunlight and act as a photocatalyst for the water-splitting reaction to produce hydrogen.



(a) *(b)*

Figure 6. *CV curves describing the electrochemical properties of the working electrode in 0.5 M Na_2SO_4 solution under (a) dark conditions and (b) illumination.*

The semiconducting nature and photoresponse capability of the hybrid material were evaluated using linear sweep voltammetry (LSV). The I–V characteristics of the TiO_2@porphyrin hybrid material are shown in figure 7. As seen in figure 7, the hybrid sample exhibits relatively stable performance across different light–dark cycles (~ 0.1 V), indicating good material stability and light responsiveness. The highest recorded photocurrent density was 1.78 mA/cm^2, compared to conventional TiO_2, which typically yields a photocurrent density of about 0.8 - 1.2 mA/cm^2 [14].

This demonstrates that hybridization with porphyrin enhances the photoelectrochemical performance of TiO_2. Meanwhile, porphyrin acts as a photosensitizer, absorbing light and generating electron-hole pairs. Upon light excitation, they can transfer electrons to the conduction band of TiO_2, thereby promoting charge separation. While the holes participate in oxidation reactions, the electrons are involved in reduction reactions (such as the reduction of O_2 to $•O_2^-$). In addition to extending the light absorption region into the visible spectrum, porphyrins also facilitate charge transfer by acting as a bridge that delivers electrons from water or organic substrates to TiO_2. Compared with the undoped sample, the enhanced CV properties demonstrate a marked improvement in charge transfer.

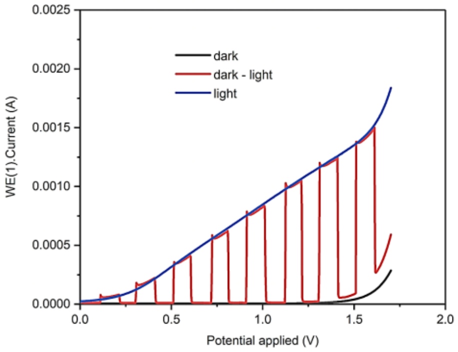


Figure 7. *I–V characteristics of the TiO_2@porphyrin electrode under light–dark cycles versus Ag/AgCl.*

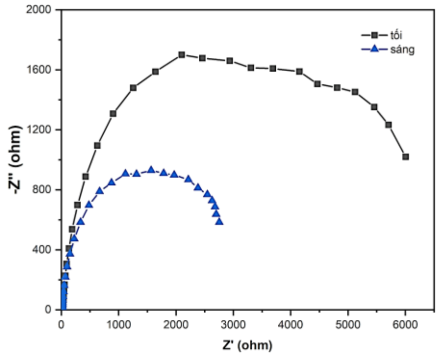


Figure 8. *EIS Nyquist plots of the porphyrin nanomaterial under light and dark conditions.*

In this study, a qualitative approach was employed by comparing the relative changes in the semicircle diameter across different cycles to evaluate the charge-transfer mechanism of the material [15] (figure 8). It can be observed that the semicircle diameter of this photoanode under illumination is approximately half of its resistance in the dark. As is well known, a semiconductor material with a smaller semicircle diameter possesses higher electrical conductivity, enabling more efficient charge carrier transport with lower resistance, and prolonging the recombination time of electron–hole pairs upon photon absorption. The presence of electrons thus reduces the resistance of the photoanode. This further confirms that the TiO_2@porphyrin hybrid material can effectively absorb and convert solar energy, contributing to the water-splitting process.

4. CONCLUSIONS

In this study, we successfully fabricated TiO_2@porphyrin nanofiber hybrid materials via a self-assembly process. The hybrid material exhibited good integration of TiO_2 nanoparticles with diameters of 20–30 nm into porphyrin nanofibers with diameters of 30–50 nm and lengths of several micrometers. In addition, the TiO_2@porphyrin photoanode demonstrated significant potential for water-splitting applications. The combination of porphyrin nanostructures and TiO_2 enhanced charge separation, leading to a substantial increase in the photocurrent density of the TiO_2@porphyrin photoanode under illumination compared to dark conditions. The successful integration of these two nanomaterials contributes to the advancement of innovative material design in the field of photoelectrochemical water splitting, paving the way for the development of environmentally friendly energy production technologies.

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TÓM TẮT

Nghiên cứu chế tạo nanocomposite TiO_2@porphyrin ứng dụng làm vật liệu quang điện hoá tách nước sản xuất hydro

Quang điện hóa (PEC) là công nghệ tích hợp khả năng hấp thụ ánh sáng của vật liệu bán dẫn với quá trình oxy hóa và tách nước trên các điện cực nhằm phân tách nước thành oxy và hydro. Trong nghiên cứu này, chúng tôi báo cáo quá trình tổng hợp vật liệu lai TiO_2@porphyrin bằng phương pháp tự lắp ráp và đánh giá khả năng quang xúc tác tách nước của vật liệu lai này. Các phương pháp phân tích như phổ UV–vis, hiển vi điện tử quét (SEM), quét thế tuần hoàn (CV), phổ trở kháng điện hóa (EIS) và quét thế tuyến tính (LSV) đã được sử dụng để xác định sự hình thành vật liệu lai và đánh giá hiệu suất của quang anốt. Vật liệu nano được tổng hợp bằng phương pháp tự lắp ráp với cấu trúc dạng sợi có đường kính 30–50 nanomet và chiều dài vài micromet. Kết quả cho thấy vật liệu nano TiO_2@porphyrin có tiềm năng ứng dụng trong sản xuất H_2 từ nước.

Từ khóa: Tách nước quang điện hóa; Vật liệu lai TiO_2@porphyrin; Hydro xanh; Tự lắp ráp.