Three-dimensional ordered macroporous g-C₃N₄-Cu₂O-TiO₂ heterojunction for enhanced hydrogen production

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ABSTRACT In this study, a g-C₃N₄-Cu₂O-TiO₂ photocatalyst with a novel three-dimensional ordered macroporous (3DOM) structure was successfully prepared using a sacrificial template strategy and a photodeposition method. The influence of the special porous structure with cross pore channels on the photocatalytic properties of the as-prepared sample was studied in detail. Compared with the original photocatalyst (TiO₂ with 3 wt% Pt), g-C₃N₄-Cu₂O-TiO₂ exhibited a higher specific surface area and more active sites, thus accelerating the separation efficiency of the photogenerated electron-hole pair. Consequently, the as-prepared photocatalyst showed good photocatalytic performance, reaching a maximum hydrogen production rate of 12,108 $\mu\text{mol g}^{-1} \text{h}^{-1}$ and approximately five times higher than that of the pristine comparison sample. The enhanced photoactivity of the g-C₃N₄-Cu₂O-TiO₂ heterojunction can be ascribed to its double p-n heterojunction and robust porous structure, where the photodeposited Cu₂O plays a synergistic catalytic role in the photocatalytic process and the outer clad g-C₃N₄ layer prevents Cu₂O oxidation. Additionally, the possible photocatalytic mechanism was briefly discussed based on the experimental results. This work identifies viable pathways for developing low-cost heterojunction photocatalysts with highly efficient photocatalytic activity toward improved solar energy conversion.

Keywords: noble metal-free cocatalyst, cross pore channels, 3DOM structure, photocatalytic hydrogen evolution

INTRODUCTION

Recently, photocatalysis has been recognized as a promising technology for environmental remediation and solar-to-chemical energy conversion [1–3]. Among these topics, hydrogen production from photocatalytic evolution has been widely studied [4,5]. TiO₂ is arguably the most popular among the reported semiconductor photocatalysts owing to its low cost, high activity, and good stability [6,7]. However, owing to the large optical band gap ($E_g = 3.16 \text{ eV}$) of pristine TiO₂ with deficient active sites, it shows poor solar energy utilization ability [7,8]. Therefore, TiO₂-based photocatalysts with a narrow band gap and exposed active sites are urgently needed to enrich visible light absorption and improve photocatalytic performance. A common strategy for improving the surface active sites and photocatalytic properties of TiO₂ is using three-dimensional

(3D) porous structures [9–11]. Recently, pore creation using polymethylmethacrylate (PMMA) nanospheres has become an emerging technique for preparing porous structures and offers simple operation, complete responsiveness, and cost-effectiveness [12]. However, increasing the light absorption area alone does not eliminate the potential defects of the photocatalytic application of TiO₂. Thus, fabricating TiO₂-based heterojunction photocatalysts with well-matched band gaps is another effective way for achieving improved photocatalytic properties of TiO₂.

As an emerging photocatalyst, graphitic carbon nitride (g-C₃N₄) is favored by many researchers owing to its narrow band gap ($E_g = 2.7 \text{ eV}$) and suitable negative conduction band (CB) edge for hydrogen evolution [10,13]. In addition, compounding TiO₂ and g-C₃N₄ can effectively increase the flat plate potential, reduce the band gap energy, and vary the position of the energy band, which is beneficial for boosting the charge mobility at the heterogeneous interface [14,15]. Moreover, some metallic substances have been found to possess excellent cocatalytic properties in the photocatalytic hydrogen production process [16,17]. However, the high cost of precious metals has limited their applications. Therefore, various substances have been proposed to replace such precious metals in the actual operation, such as metal oxides (NiO, In₂O₃, CoO, etc.) [18–20], metal phosphides (NiP, CoP, FeP, etc.) [14,21–23], and metal sulfides (CdS, MoS₂, NiS₂, etc.) [24–27]. Among the listed three kinds of complexes, metal oxides have received considerable attention owing to their simple preparation process and low toxicity of raw materials. In this context, as a cheap metal oxide, Cu inherently offers the advantages of low production cost and convenience; additionally, its ability to conduct electricity facilitates improved catalytic performance. Nowadays, researchers have conducted studies on Cu-loaded catalysts [28,29]. Compared with Cu, as a p-type semiconductor with a narrow band gap ($E_g = 2.17 \text{ eV}$), Cu₂O has shown excellent photocatalytic properties recently [30,31]. However, Cu₂O is well known to be extremely reactive in air and can be easily oxidized to CuO. Thus, the inhibition of the Cu₂O oxidation reaction in the photocatalytic process has become a key research topic.

Based on the aforementioned discussion, a 3D ordered mesoporous (3DOM) g-C₃N₄-Cu₂O-TiO₂ heterostructure is designed in the current research. In this structure, both g-C₃N₄ and TiO₂ are n-type semiconductors, while Cu₂O is a p-type semiconductor; thus, this special structure simultaneously contains double p-n heterostructures. A unique feature of the as-

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prepared photocatalyst is the construction of the double p–n heterostructures with a 3DOM structure, which enhances the photocatalytic performance and enables high hydrogen production efficiency without the participation of noble metals. The formation of p–n heterostructures considerably enhances the electron–hole pair separation efficiency in photocatalytic hydrogen production [32,33]. The 3DOM structure facilitates the photocatalytic light absorption. The loaded g-C₃N₄ can not only broaden the light absorption range of TiO₂ but also prevent Cu₂O oxidation in the inner layer [34]. Benefiting from the synergy between the abovementioned structural features, the resulting optimal photocatalyst shows excellent photocatalytic hydrogen production performance, superior to the pristine TiO₂ with a Pt content of 3% prepared using the same method. The photocatalytic mechanism and the corresponding relationship between the special porous structure and photocatalytic efficiency are also briefly discussed based on the experimental results. Hence, this work provides an original opinion for the design of hybrid high-efficiency photocatalysts with multiple synergistic hydrogen production reactions.

EXPERIMENTAL SECTION

Materials

Titanium butoxide and dicyandiamide (DCDA) (analytically pure) were purchased from Aladin Corporation. Ethylene glycol, anhydrous methanol, methyl methacrylate (MMA), sodium hydroxide, and copper nitrate were procured from Sinopharm. All the reagents were used as raw materials without subject to any additional purification process.

Synthesis of 3D porous TiO₂ matrix

First, 3 mL of ethylene glycol, 2 mL of anhydrous methanol, and 1 mL of hydrochloric acid were mixed in a 25-mL beaker. Then, the PMMA nanospheres were slowly added to the mixed solution. Finally, 3 mL of titanium butoxide was mixed with the above-mixed solution by stirring for 30 min to form a homogeneous solution. This mixture was set still for 24 h. Thereafter, the white TiO₂ precursor was obtained by filtering the top-layer clear liquid and drying for 12 h at 70°C. Subsequently, the sample was calcined at 700°C in air for 2 h to obtain a white powder, which was simply called 3D T. Moreover, a TiO₂ sample without the addition of PMMA microspheres was prepared

using the same approach, which was named T.

Preparation of 3D porous Cu₂O–TiO₂ using the photodeposition method

The suspension was prepared by mixing 50 mL of deionized water, 10 mL of ethanol, x mmol L^{−1} Cu(NO₃)₂·3H₂O (x = 0.01, 0.03, 0.05, and 0.07), and 80 mg of 3D T. The pH was adjusted to 9–10 using 1 mol L^{−1} NaOH. For dissolved oxygen removal, nitrogen gas was continuously aerated into the sealed container for approximately 20 min. The slurry was illuminated under a 300-W Xe lamp in a nitrogen environment and stirred continuously for 6 h. The top layer of the blue suspension was removed by filtration and dried at 70°C for 12 h to obtain the blue powder. The deep blue powder was obtained by calcining the blue powder for 2 h at 550°C in an Ar/H₂ atmosphere. The as-obtained samples with the addition of different amounts of copper (0.01, 0.03, 0.05, and 0.07 mmol L^{−1}) were named 1C-T, 3C-T, 5C-T, and 7C-T, respectively.

Preparation of 3D porous g-C₃N₄–Cu₂O–TiO₂ by impregnation

Approximately 2 g of dicyandiamide was dissolved in 25 mL of deionized water. Thereafter, the 5C-T sample was placed inside the dicyandiamide aqueous solution and stirred for 12 h in the dark to precipitate the white flocs on the surface of the samples. After removing the top-layer liquid *via* filtration, the brown flocs were placed inside an oven at 70°C to remove the water and then calcined at 550°C in the air for 2 h to form g-C₃N₄ on the surface of the sample. This sample was labeled as CN-C-T. The detailed synthesis process is shown in Scheme 1. A control sample of 3DOM TiO₂ coated with g-C₃N₄, labeled as CN-T, was also prepared to further verify the experiment.

Characterization

The crystal structures of the samples were identified using X-ray diffraction (XRD, D8-FOCUS, BrukerAXS, Panalytical). A PerkinElmer ultraviolet–visible (UV–vis) spectrometer and an FLS980 spectrophotometer were used to measure the optical absorbance and photoluminescence (PL) spectral patterns, respectively. X-ray photoelectron spectroscopy (XPS) was performed to analyze the chemical bonds of substances using a VG Scientific ESCALAB Mark II spectrometer equipped with two ultrahigh vacuum (UHV) chambers (Escalab 250XI, Thermo-Fisher). Scanning electron microscopy (SEM, SU3500) was

Scheme 1 Illustration of the synthesis of 3D porous TiO₂ loaded Cu₂O with g-C₃N₄ as a protective layer.

employed to observe the sample morphologies. The textures of the as-prepared samples were analyzed using transmission electron microscopy (TEM FEI Talos F200S). N_2 adsorption/desorption isotherms and the corresponding pore size distribution were studied using a Micromeritics ASAP2460 surface area analyzer.

Photocatalytic hydrogen production measurement

In a typical photocatalytic process, 0.05 g of photocatalyst was added to a 0.3-L airtight quartz container containing 90 mL of deionized water and 10 mL of triethanolamine (TEOA). After performing the ultrasonic treatment and thorough stirring, the mixed solution was charged with nitrogen for 20 min to completely expel air. The gaseous product was measured using gas chromatography (GC-2014, SHIMADZU) with a thermal conductivity detector under a 300 W Xenon lamp as the light source.

Photoelectrochemical performance measurements

The photoelectrochemical performance was tested on a CHI 660E workstation using a three-electrode system with an aqueous solution of $0.5 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ as the electrolyte. The as-prepared photocatalyst functioned as the working electrode. A Pt plate was used as the counter electrode, and a Ag/AgCl electrode was used as the reference electrode. The working electrode was prepared by mixing 5 mg of sample, 10 μL of Nafion, and 150 μL of ethanol on fluorine-doped tin oxide (FTO) glass, which was dried at 25°C for 12 h after being dispersed on the plate.

RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of the as-prepared samples. In the case of 3D T, the (101), (004), (200), (105), (211), (116), (220), and (215) planes of TiO_2 correspond to anatase TiO_2 (PDF No. 02-0387). However, in the case of CN-C-T, the characteristic peaks of (110), (101), (111), (211), (220), and (301) planes correspond to rutile TiO_2 (PDF No. 03-1122). On the one hand, this phenomenon is attributed to the reaction process in the experiment that promotes the transformation of TiO_2 from the anatase phase to the rutile phase. On the other hand, no obvious Cu diffraction peak is observed in the C-T and CN-C-T patterns, attributed to the addition of low contents of Cu (5 wt%), which cannot be detected using the testing instrument. To support the presence of Cu in the C-T and CN-C-T samples, their XPS spectra are shown below.

As part of efforts to further investigate the presence of trace elements in the CN-C-T sample, Fig. 2 shows the XPS spectra of the samples. As shown in Fig. 2a, the presence of five elements (Cu, Ti, C, N, and O) can be clearly distinguished in the total spectrum of the CN-C-T composite. The two strong peaks clearly observed in the XPS spectrum of Cu are mainly ascribed to the Cu^+ phase. However, in Fig. 2b, satellite peaks of Cu^{2+} are observed [35,36]. The main reason for the appearance of Cu^{2+} is the introduction of air calcination during the cladding of $\text{g-C}_3\text{N}_4$, which induces the transformation of a small portion of Cu^+ into Cu^{2+} . However, the peak area indicates that the content of Cu^{2+} is considerably smaller than the content of Cu^+ ; hence, the main valence state of copper is assessed to be Cu^+ [37]. To verify the formation of $\text{g-C}_3\text{N}_4$ in the samples, C and N were subjected to XPS tests as shown in Fig. 2c, d. The XPS spectral profile of C reveals peaks at 284.7, 286.3, and 288.4 eV. The first two peaks belong to the contaminated C, while the latter corresponds to the $\text{N}=\text{C}-\text{N}$ binding mode. The presence of N is also

Figure 1 XRD patterns of the as-prepared 3D T, C-T, and CN-C-T.

demonstrated in the XPS patterns, where the three peaks at 399.6, 400.0, and 402.2 eV in Fig. 2d are attributed to $\text{N}=\text{C}-\text{N}$, $\text{N}-(\text{C})_3$, and $\text{N}-\text{H}$, respectively [38]. Thus, the formation of $\text{g-C}_3\text{N}_4$ can also be demonstrated in the experiment. In Fig. 2e, f, compared with pure TiO_2 , a significant peak shift of Ti 2p and O 1s can be observed in the CN-C-T sample. The occurrence of this phenomenon is inextricably linked to the reduction step in the experiment, which results in more oxygen vacancies in the CN-C-T sample [39]. To detect the stability of Cu_2O in CN-C-T, the sample after the hydrogen production test was collected for XPS characterization as shown in Fig. 2g, h. Compared with Fig. 2b, Fig. h shows a significant increase in the content of Cu^{2+} in the CN-C-T sample. However, the overall content of Cu^+ is still dominant in the sample, further illustrating the stability of Cu_2O in the as-prepared photocatalyst.

To fully investigate the morphology and distribution of the elements in the sample, SEM and TEM tests were conducted; the results are shown in Fig. 3. As shown in Fig. 3a, the morphology of the CN-C-T sample exhibits a 3DOM structure, which is confirmed by the TEM result shown in Fig. 3b. Fig. 3c presents the high-resolution TEM image of the CN-C-T sample. The present spacing distance of $d = 3.25 \text{ \AA}$ corresponds to the (110) plane of TiO_2 (PDF: 03-1122). Considering that Cu_2O is selectively deposited, there is a direct contact between $\text{g-C}_3\text{N}_4$ and the 3D porous structure of TiO_2 . Therefore, the direct contact of C_3N_4 with TiO_2 does not affect the experimental results. To further verify the experimental results, CN-T was also prepared as a comparison sample. Moreover, the presence of Cu agglomerates in Fig. 3g can indicate the selective deposition of Cu. Hence, to explore the elemental distribution in the CN-C-T sample, the elemental mapping was examined as shown in Fig. 3d–i. Except for the appearance of agglomeration in parts of Cu, the distribution of C and N is generally uniform, indicating an excellent cladding effect. In addition, the distribution of Ti and O is uniform.

To examine the variation in CN-C-T pore characteristics (pore volume, pore diameter, porosity, and surface area) for the as-prepared samples, N_2 adsorption/desorption isotherms were obtained (Fig. 4). Compared with data from previous studies [10], larger specific surface areas of the sample can induce the generation of more active sites and promote photochemical activity. In Fig. 4b, 3D T shows a larger specific surface area ($39.9 \text{ m}^2 \text{ g}^{-1}$) than CN-C-T ($37.9 \text{ m}^2 \text{ g}^{-1}$). This is attributed to the deposition of Cu_2O and a slight decrease in the specific surface

Figure 2 XPS spectra of CN-C-T composite photocatalyst: (a) survey XPS spectrum, (b) Cu 2p, (c) C 1s, (d) N 1s, (e) Ti 2p, (f) O 1s, and (g, h) survey XPS spectrum and Cu 2p spectrum for CN-C-T after the hydrogen production test.

area of CN-C-T for encapsulating g-C₃N₄.

Fig. 5 shows the UV-vis diffuse reflectance spectra of the 3D T, C-T, and CN-C-T samples, reflecting the optical absorption properties of the as-prepared samples. This figure clearly shows a significant increase in the absorption curve at approximately 610 nm. Given that this phenomenon only occurs in C-T and CN-C-T, it can be assumed that the salient absorption peak observed in these samples is attributed to the surface plasmon resonance (SPR) of trace amount of Cu present in the product [40,41]. The same absorption peak is significantly stronger in Fig. 5a, likely owing to the outer layer of g-C₃N₄ coating in CN-C-T, which improves the reflection absorption of external photons. Consequently, the absorptive capacity and SPR absorption of CN-C-T are stronger than those of C-T. In Fig. 5b, the light absorption range of 3D T (3.42 eV), C-T (3.37 eV), and CN-C-T (3.34 eV) shows a gradual expansion, thereby gradually increasing the light absorption capacity of all three samples.

Fig. 6a shows the PL spectra of the 3D T, C-T, and CN-C-T samples, wherein the separation efficiency of photogenerated electron-hole pair is explored. The PL intensity of CN-C-T is significantly lower than that of 3D T and C-T, thus indicating a

lower tendency of electron-hole recombination in CN-C-T. This result further confirms that the CN-C-T heterojunction is successfully constructed. Moreover, the transient photocurrent spectrum (Fig. 6b) and electrochemical impedance spectroscopy (EIS) Nyquist curve spectra (Fig. 6c) show that the heterogeneous structure is formed by the deposition of Cu₂O. In Fig. 6b, the photocurrent signals generated by CN-C-T are higher than those generated by C-T and 3D T under visible light; in comparison, in the EIS curves of Fig. 6c, the arc radii of CN-C-T and C-T are smaller than that of 3D T. Further, the radius of CN-C-T is slightly smaller than that of C-T. Both phenomena reveal that CN-C-T exhibits better charge transfer efficiency and more effective carrier separation efficiency than 3D T and C-T [11].

Fig. 7a shows the photocatalytic properties of the T, 3D T, and 5C-T samples prepared using similar methods. The only difference is that 3 wt% Pt is added in the T sample, while no Pt is added in the 3D T and 5C-T samples. The hydrogen production rate increases from 660 to 1674 $\mu\text{mol g}^{-1} \text{h}^{-1}$ by changing the TiO₂ morphology. The photocatalytic hydrogen production rate is further increased by loading Cu₂O on 3D T by photodeposi-

Figure 3 (a) SEM image of CN-C-T, (b, c) TEM images of CN-C-T, and elemental mapping of (e) Ti, (f) O, (g) Cu, (h) C, and (i) N for CN-C-T.

Figure 4 (a) N_2 adsorption/desorption isotherms and (b) the corresponding Barrett-Joyner-Halenda (BJH) pore size distribution of the 3D T and CN-C-T samples.

Figure 5 (a) UV-vis diffuse reflectance spectra and (b) transformed Kubelka-Munk functions of 3D T, C-T, and CN-C-T.

tion, achieving a value of $9482 \mu\text{mol g}^{-1} \text{h}^{-1}$. To investigate the most suitable loading amount of Cu_2O , C-T was prepared with different loading amounts, which were labeled as 1C-T (1 wt% Cu_2O), 3C-T (3 wt% Cu_2O), 5C-T (5 wt% Cu_2O), and 7C-T (7 wt% Cu_2O), respectively. The results of the photocatalytic hydrogen production tests conducted on these samples are shown in Fig. 7b, indicating that the highest photocatalytic hydrogen production rate is achieved at 5 wt% Cu_2O loading. When the Cu_2O content is higher than 5 wt%, the performance decreases significantly owing to the impeding beneficial light

absorption of TiO_2 by the superfluous Cu_2O . Cu_2O is well known to be highly susceptible to oxidation in the air. Therefore, to inhibit the oxidation of Cu_2O , the g- C_3N_4 layer prepared by impregnation was used to cover the C-T sample in this experiment. Results show that the photocatalytic performance of the samples is enhanced by constructing this heterogeneous structure. Fig. 7c further shows a comparison of the photocatalytic hydrogen production rate of the samples before and after the g- C_3N_4 coating. The performance is improved from 9482 (5C-T) to $12,108 \mu\text{mol g}^{-1} \text{h}^{-1}$ (CN-C-T) after the g- C_3N_4 coating.

Figure 6 (a) PL spectra, (b) transient photocurrent spectra, and (c) EIS Nyquist plots of the 3D T, C-T, and CN-C-T.

Figure 7 (a–c) Photocatalytic hydrogen production rate, (d) time courses of visible-light photocatalytic hydrogen evolution on the T, 3D T, C-T, CN-T, and CN-C-T samples, (e) photocatalytic hydrogen production rates of C-T and CN-C-T at different days, and (f) cycling stability test for CN-C-T.

Compared with the T (bulk TiO_2) sample with added 3 wt% Pt, the CN-C-T sample without Pt exhibits higher photocatalytic performance, indicating that the composite modification surpassed the cocatalytic effect of noble metal Pt. Comparing the performance of CN-C-T with that of CN-T (TiO_2 coated with $\text{g-C}_3\text{N}_4$), results indicate that on the one hand, Cu_2O is instrumental in the enhanced photocatalytic performance of photocatalysts. On the other hand, when Cu_2O and 3wt% Pt are present simultaneously (CN-C-T-Pt), although the photocatalytic performance is enhanced compared with that of CN-C-T, only slight improvements are observed. In addition, Pt is expensive, implying that its application may not be cost-effective.

Next, the cycling stability test was conducted to test the consistency of the as-prepared samples. Fig. 7d indicates that the hydrogen production rate of C-T shows a significant bias fold after 1 h, which may be attributed to the oxidation of Cu_2O . This finding can also be verified with Fig. 7e. After being exposed to air for seven days, a significant decrease in the performance of C-T can be observed. In comparison, only a slight decrease in the photocatalytic performance of CN-C-T is observed because of the presence of the $\text{g-C}_3\text{N}_4$ protective layer. Therefore, these

results further illustrate the protective effect of $\text{g-C}_3\text{N}_4$ on the oxidation of Cu_2O .

Scheme 2 presents an illustration of the photocatalytic hydrogen mechanism of the CN-C-T sample. The porous structure attributed to the PMMA nanospheres enhances the light absorption area of the material. It also allows more H_2O to penetrate the photocatalyst. The double p–n heterostructure is constructed to ensure higher electron mobility within the sample, which leads to faster hydrogen production and the suppression of the recombination of the photogenerated electron–hole pair. The enhanced light irradiation on the sample surface is first absorbed by the $\text{g-C}_3\text{N}_4$ surface layer, after which the light penetrating the $\text{g-C}_3\text{N}_4$ layer excites the $\text{g-C}_3\text{N}_4$ electrons to jump from the valence band (VB) to the CB. Owing to the presence of the protective layer, the incident light will be refracted between the $\text{g-C}_3\text{N}_4$ and TiO_2 layers when it becomes scattered light. Then, the Cu_2O nanoparticles, acting as cocatalysts, produce resonant collective oscillations of electrons under the light stimulation, which subsequently decays into electron–hole pairs by Landau damping [30,42]. Additionally, the band gaps of $\text{g-C}_3\text{N}_4$ and TiO_2 are 2.66 and 3.42 eV, respectively. Thus, their VB values can be calculated to be 1.35 and 3.02 eV,

Scheme 2 Illustration of the photocatalytic hydrogen production mechanism of CN-C-T.

respectively, according to the following formula: $E_{\text{NHE}}/V = \Phi - 4.44 + E_f$ ($\Phi = 4.37$ eV), where NHE stands for the normal hydrogen electrode. Given the equation $E_{\text{CB}} = E_{\text{VB}} - E_g$, the CB values of g-C₃N₄ and TiO₂ are -1.31 and -0.42 eV, respectively. Moreover, the Fermi level (E_f) of Cu₂O lies exactly between the CBs of g-C₃N₄ and TiO₂, implying that the electrons will be transferred from g-C₃N₄ to Cu₂O first and then to TiO₂. Here, Cu₂O acts as a cocatalyst and plays a bridging role. In this process, Cu₂O not only acts as a structural defect to trap electrons but also functions as an electron mediator to facilitate discrete electron-hole pairs. This fraction of electrons will be concentrated in the VB of TiO₂ and combine with photo-generated holes. This promotes the separation of the primary electron-hole pairs on TiO₂, thereby enhancing the hydrogen production rate of the material. In summary, an all-solid-state Z-type heterojunction of g-C₃N₄-Cu₂O-TiO₂ was constructed in this condition. The material could exhibit an excellent photocatalytic hydrogen production rate owing to the presence of the sacrificial agent (TEOA), which allows the elimination of excess holes in the experiment.

CONCLUSIONS

In summary, novel 3DOM g-C₃N₄-Cu₂O-TiO₂ photocatalysts were successfully prepared using a sacrificial template strategy after the photodeposition and impregnation methods. Benefiting from the synergistic characteristics of 3D porous structures and the double p-n heterostructures of g-C₃N₄-Cu₂O and Cu₂O-TiO₂, the as-prepared samples exhibited promising photocatalytic hydrogen production rates, achieving a maximum value of $12,108 \mu\text{mol g}^{-1} \text{h}^{-1}$. Importantly, the stability of Cu₂O was significantly improved owing to the protection of the g-C₃N₄ layer, thus ensuring the high stability of the special 3DOM of the g-C₃N₄-Cu₂O-TiO₂ photocatalysts. The facile method presented in this study provides a pathway for the further development of the design and synthesis of noble metal-free and low-cost photocatalysts with efficient photocatalytic performance for improved harvesting of renewable solar energy.

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Conflict of interest The authors declare that they have no conflict of interest.

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三维有序多孔 $g-C_3N_4-Cu_2O-TiO_2$ 异质结的光催化性能

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摘要 本文通过模板法与光沉积法成功制备了具有三维有序多孔结构的 $g-C_3N_4-Cu_2O-TiO_2$ 光催化剂, 并详细研究了特殊多孔结构对原制备样品光催化性能的影响. 与原有的光催化剂相比, 多孔结构的 $g-C_3N_4-Cu_2O-TiO_2$ 具有更高的比表面积和更多的活性位点, 从而加速了光生电子-空穴的分离效率. 因而, 该光催化剂表现出良好的光催化性能, 最大产氢率可达 $12,108 \mu\text{mol g}^{-1} \text{h}^{-1}$, 是原始对比样品产氢率的5倍左右. $g-C_3N_4-Cu_2O-TiO_2$ 对于光催化性能的增强可归因于其双p-n异质结和稳健的多孔结构. 光沉积 Cu_2O 在光催化过程中起协同催化作用, 外层包覆的 $g-C_3N_4$ 层保护 Cu_2O 以防止催化剂氧化. 此外, 本文探究了该催化剂的光催化机理. 本工作为开发具有高效光催化活性的低成本异质结光催化剂开辟了新途径.