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Significantly Enhanced Photocatalytic Hydrogen Evolution over Cu_2O Embedded on TiO_2 Aerogels under Simulated Solar Light Irradiation

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Authors' contributions

This work was carried out in collaboration among all authors. Author LJ designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Authors KW and ZZ managed the analyses of the study. Authors WW, JH managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

A high surface area mesoporous Cu_2O embedded on TiO_2 (Cu_2O-TiO_2) aerogel was prepared and used in photocatalytic splitting of water under simulated solar light irradiation. Highly efficient hydrogen production was achieved over 3 wt% Cu_2O-modified TiO_2 aerogel photocatalyst with a high rate of 1.40 mmol/(g·h) under simulated solar irradiation. The hydrogen production efficiency of 3 wt% Cu_2O-modified TiO_2 aerogel was about 33 and 9 times higher than those of pure TiO_2 aerogels (0.043 mmol/g·h) and Cu_2O-modified commercial TiO_2, Degussa P25 (0.15 mmol/g·h) with the same ratio, respectively. For comparison, no hydrogen was detected when Cu_2O was used alone as the catalyst, and the activity of Cu_2O mechanically mixed TiO_2 aerogel with the same ratio was 13 times lower than Cu_2O-TiO_2 aerogel. This result implied that the Cu_2O loading was benefit to promote the separation and migration of electron-hole pair. Furthermore, the Cu_2O loading enhanced the absorbance in 300-800 nm region as compared to pure TiO_2 aerogel. Cu_2O-

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TiO_2 aerogels have very high specific surface area (400-500 m^2/g) and good recyclability for at least 3 cycles, which suggests that the materials have promising prospects in photocatalytic hydrogen production.

Keywords: Cu_2O; TiO_2 aerogels; hydrogen evolution; solar-light-activated; photocatalysis.

1. INTRODUCTION

In view of increasingly serious energy and environmental problems, photocatalytic hydrogen production from water splitting has attracted great attention since hydrogen has been identified as a promising fuel for sustainable energy supply [1-3]. Most of the semiconductor materials reported in the literature as photocatalysts are based on TiO_2 [4-9]. Unfortunately, the photocatalytic hydrogen production efficiency involving TiO_2 alone was relatively low [10-13]. Many approaches have been investigated to improve the hydrogen production rate of TiO_2 [14-16]. For example, hybrid TiO_2 and Cu_xO systems have been used to photocatalyze hydrogen evolution [17-22]. In particular, Cu_2O/TiO_2 composite has been found to exhibit high hydrogen evolution yield under the solar light irradiations since Cu_2O is one of the few p-type direct band gap semiconductors [21, 23-28].

Recently, aerogels consisting of open and highly porous structure have attracted great attention in various applications [29,30]. However, the study of photocatalytic hydrogen production from water splitting on aerogels was still very limited [31-35]. Given the aforementioned photoactivities and porosity of titania aerogels and enhancement of Cu_2O cocatalyst performance, we may expect that integration of TiO_2 aerogels and Cu_2O cocatalyst would adopt their merits in photocatalysis. Herein Cu_2O embedded on TiO_2 aerogels (Cu_2O-TiO_2) were synthesized, and used in photocatalytic splitting of water under solar light irradiation. It is demonstrated in this research that the photocatalytic activity of Cu_2O-TiO_2 aerogels for hydrogen evolution under solar light is significantly enhanced in comparison with pure TiO_2. Furthermore, the photostability of composites and the effects of Cu_2O content on the specific surface area and the photocatalytic activity of Cu_2O-TiO_2 aerogels were also investigated.

2. EXPERIMENTAL DETAILS

All reagents were of analytical grade (purchased from Aladdin–Holdings Group, China) and were used without further purification. Distilled water was used in all experiments.

2.1 Synthesis of Catalysts

2.1.1 Preparation of TiO_2 aerogels

TiO_2 aerogel was synthesized with a process modified from ref. [36]. A mixture of 20.0 mL (0.2713mol) acetone (CH_3COCH_3, 99%) and 0.54 mL (5.3 mmol) acetylacetone ($CH_3COCH_2COCH_3$, 99%) was added into 6.0 grams (24.07 mmol) of tetrabutyl titanate ($Ti(OC_4H_{9-n})_4$, 99%) under stirring. Then a mixture of acetone (7.6 mL) and water (1.2 mL) was added dropwise to form a solution which gradually transformed into a wet-gel. After aging at room temperature for 24 h, the gel was placed in a 50 mL autoclave and acetone was added until 80% of the volume of the autoclave was filled. The autoclave was heated at 313 K to form a crystalline TiO_2 wet-gel, which was then dried at room temperature for 4 h, 323 K for 4 h, 373 K for 2 h and 393 K for 2 h at atmospheric pressure to obtain the crystalline aerogels.

2.1.2 Preparation of Cu_2O-TiO_2 aerogels

The Cu_2O-TiO_2 aerogels were prepared by impregnation method [30, 31]. In a typical synthesis, TiO_2 aerogel (1.0 g) was dispersed in distilled water (80 mL), and then a certain volume of $Cu(NO_3)_2{\cdot}3H_2O$ aqueous solution (0.05 M) was added. The weight percentages of Cu_2O in the photocatalyst samples were 0, 1, 3, 5, 7 and 10; the resulting samples were labeled as CTx, where x =0, 1, 3, 5, 7 and 10, respectively. Also, pure Cu_2O sample was prepared without the TiO_2 aerogel. The mixed solutions were stirred for 2 h at room temperature. After that, the suspensions were heated at 373 K for 12 h to remove water. Finally, the solid samples were calcined at 523 K for 4 h in air. We also prepared two simples for comparison. Cu_2O-P25 was prepared with the same method as CT3 but replaced the TiO_2 aerogel by P25. According to weight percentages of Cu_2O in CT3, the 3 wt% Cu_2O mixed TiO_2 aerogel was prepared by mechanical mixing method using the pure Cu_2O and TiO_2 aerogel.

2.1.3 Characterization of photocatalysts

Scanning electron microscopy (SEM) images of the samples were taken on a FEI Quanta 200FEG microscope. Pore size distributions, BET surface areas, and pore volumes were measured by nitrogen adsorption/desorption using a NOVA2000e gas sorption analyzer (Quanta chrome Corp). Prior to theanalysis, the samples were degassed at 423 K for 1 h. X-ray powder diffraction (XRD) experiments were conducted on a D/max-3B spectrometer with Cu K_α radiation. Scans were made in the 2θ range: 283-363 K with a scan rate 283 K/min (wide angle diffraction). X-ray photoelectron was performed on a PHI5500ESCA analyzer. The main parameters were as follows: Mg K_α, 200 W, vacuum~10^{-7} Pa. High-resolution transmission electron microscopy (HRTEM) imagines were taken on a TEM (TECNAI G2S-TWIN F20). UV-Vis diffuse reflectance spectra (DRS) were measured on a Shimadzu UV-2401PC photometer. X-ray Photoelectron Spectroscopy (XPS) were in an ultrahigh vacuum chamber with a base pressure below 2.66×10^{7} Pa at room temperature. Photoemission spectra were recorded by a Thermo fisher Scientific spectrometer (K-Alpha^{+}) equipped with standard monochromatic Al K_a excitation source. All binding energies were referenced to C_{1s} at 284.8 eV.

2.1.4 Photocatalytic hydrogen production

The photocatalytic hydrogen evolution by water splitting was performed in a glass reaction cell with quartz cover connected to a closed gas circulation. 50 mg photocatalysts was dispersed in 100 mL of 10 vol % methanol aqueous solutions. And the suspension was exposed to a 300W Xe lamp equipped. Then the reaction solution was stirred continuously and cooled to room temperature by a flow of water. The amount of hydrogen evolved was determined at an interval of 1 h with online gas chromatography.

2.2 The Reproducibility of Photocatalysts

The recyclability study was carried out 3 times in order to determine the stability of the photocatalyst. Each test was carried out as described above for 5 hours under simulated solar light irradiation. After each test was completed, the gaseous products were evacuated from the reactor, and the material was centrifuged, then washed with deionized water and filtered. After dried at 343 K, the material was reused in reactor for hydrogen generation.

3. RESULTS AND DISCUSSION

3.1 Characterizations

Table 1 summarized the textural properties of all the materials. All the Cu_2O-TiO_2 aerogels have high surface areas(400-500 m^2/g). The surface areas, average pore size and pore volumes of the Cu_2O-TiO_2 aerogels are lower than those of CT0, which can be due to the pore blockage induced by Cu_2O loadings. The enhancement in H_2 production may be attributed to the high dispersion of catalyst in methanol aqueous solution and the high specific surface area of Cu_2O-TiO_2 aerogels. SEM and high-resolution TEM images of Cu_2O-TiO_2 aerogels are shown in Fig. 1(a), (b), (c) and (d), respectively. SEM reveals that this sample has no regular morphology and aggregated (Fig. 1 (a-b)). Fig. 1 (c-d) shows that the aggregated nanocrystal is composed of disordered primary nanoparticles (20-30 nm in size).

Fig. 2 shows the XRD patterns of the CTx samples with x varying from 0 to 10 in comparison to the pattern of Cu_2O. It is seen only anatase phase of TiO_2 were observed CT0 and Cu_2O-TiO_2 aerogel photocatalysts. No characteristic diffraction peaks of Cu_2O were observed due to the low content of Cu_2O and weak crystallization.

Table 1. Summary of textural properties of all the Cu_2O-TiO_2 aerogel samples

Sample	Brunner-Emmet-Teller (BET) measurements (m^2/g)	Pore volume (cm^2/g)	Pore diameter (nm)
CT0	507.8	1.25	9.9
CT1	483.4	1.09	8.9
CT3	471.3	1.16	9.5
CT5	406.6	0.96	8.2
CT7	451.7	0.91	9.0
CT10	438.3	0.92	8.3

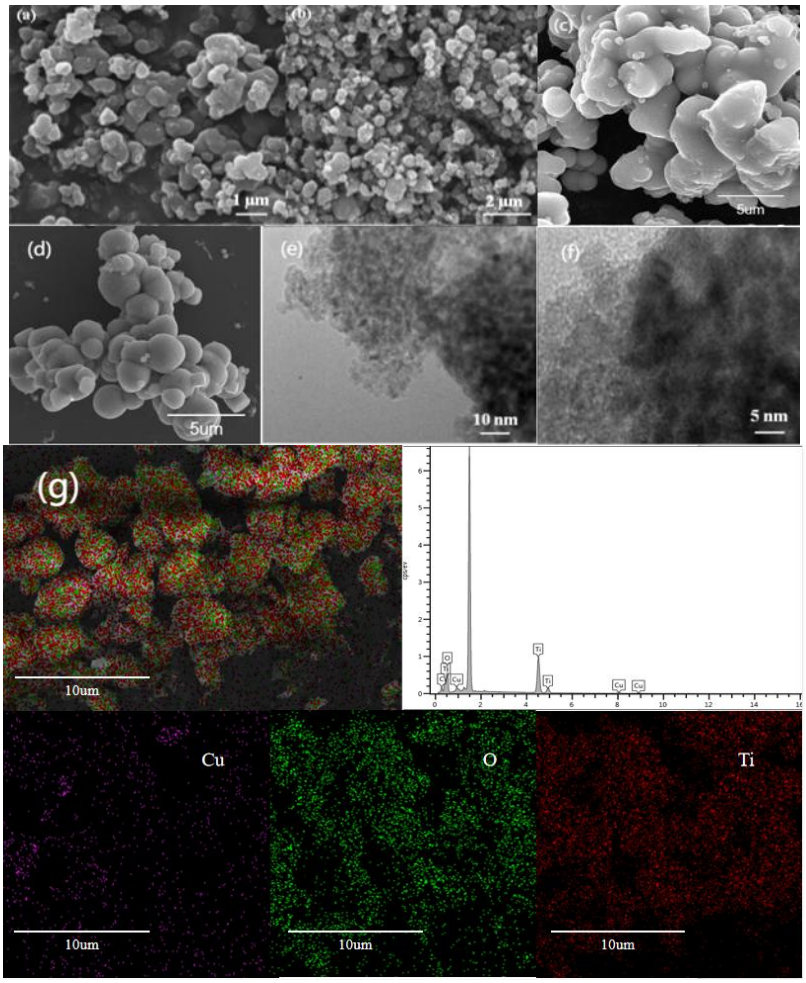
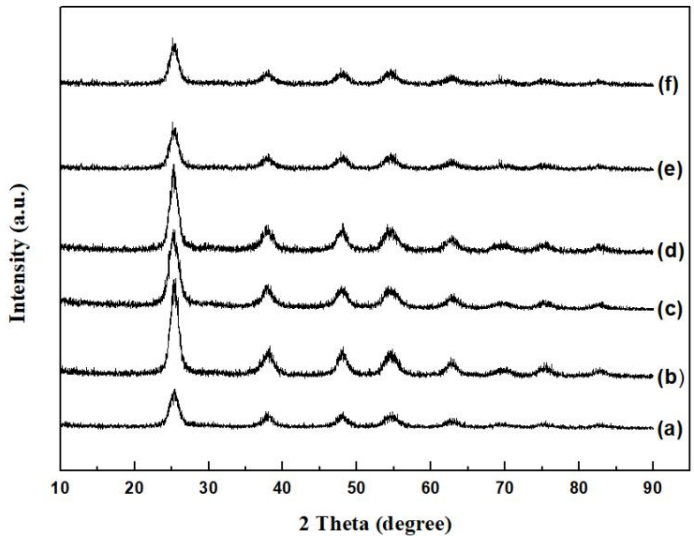


Fig. 1. SEM of (a-b) Cu_2O-TiO_2 aerogel with different crystal sizes, (c) TiO_2 aerogel, (d) Cu_2O, HRTEM images (e-f) of CT3, (g) SEM-EDS mapping of CT3



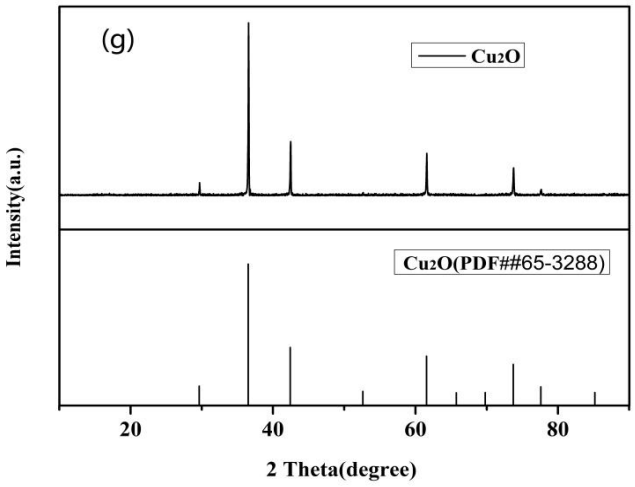


Fig. 2. X-ray diffraction pattern of (a) CT0, (b) CT1, (c) CT3, (d) CT5, (e) CT7, (f) CT10，(g)Cu2O

To further confirmed the existence of Cu_2O, X-ray photoelectron spectroscopy (XPS) measurements analysis of CT3 aerogel sample was performed, and the survey spectrum and high-resolution scans are shown in Fig. 3. In Fig. 3(a), Cu, Ti and O photoelectron lines from the sample were detected along with C peaks. In Fig. 3(b), Cu $2p_{3/2}$ spin orbital splitting photoelectrons were located at binding energies of 932.03 eV, and were assigned to the compound of Cu_2O [37-39]. By comparing the peak change of Ti in the Fig. 3(c), we can see that the binding energy of Ti in the doped composite material is 0.1 electron volts higher than that of the pure titanium dioxide aerogel.

Fig. 4 displays the UV-vis diffuse reflection spectra of the samples. A significant increase in the absorption at wavelengths shorter than 400 nm can be assigned to the intrinsic band gap absorption of TiO_2 [36]. The UV-vis spectra of CT3 with Cu_2O loading exhibit obviously enhanced absorption in the 300-800 nm region compared with that of pure TiO_2 aerogel (CT0). The absorption edge of CT3 obviously shifts to the visible-light region in comparison to CT0, implying that the prepared samples may have photocatalytic activity under simulated solar irradiation.

3.2 Photocatalytic H_2 Production Activity

Fig. 5 and Fig. 6 show the comparison of the photocatalytic H_2 production activity of the samples. As observed from Fig. 5, the content of Cu_2O has significant influence on the photocatalytic activity of TiO_2 aerogels. With the increasing Cu_2O content loaded on TiO_2 aerogel, the photocatalytic activities increased initially while it decreased later. (Fig. 5a). It is probably due to the pore blockage and the reduction of active sites induced by the increasing Cu_2O content. As shown in Fig. 5b, CT3 shows the highest photocatalytic H_2 production efficiency (1.40 mmol/(g·h)), which exceeds that of CT10 (0.54 mmol/(g·h)) about 2.6 times.

We also studied the photocatalytic efficiency of CT0, Cu_2O-P25, 3 wt% Cu_2O mixed TiO_2 aerogel and Cu_2O for comparison (Fig. 6). The photocatalytic efficiency for CT3 is about 33, 9, and 13 times higher than those of CT0, Cu_2O-P25 and 3 wt% Cu_2O mixed TiO_2 aerogel, respectively (Fig. 6b). No hydrogen was detected when Cu_2O alone was used as the catalyst, suggesting that pure Cu_2O was not active for photocatalytic hydrogen production under the experimental conditions studied (Fig. 6a). The sample CT0 exhibited a very low photocatalytic activity owing to the rapid recombination between CB electrons and VB holes in TiO_2 aerogels [36]. The sample prepared by mechanical mixing method (3 wt% Cu_2O mixed TiO_2 aerogel) exhibited higher photocatalytic hydrogen production activity than CT0 and pure Cu_2O. However, its activity is still 13 times lower than CT3. This suggests that the loading of Cu_2O was benefit to promote the electron transfer and reduce the recombination of electron-hole pair [37]. Due to the matching of the band gap structure between Cu_2O and TiO_2, photogenerated electrons could transfer from the conduction band of copper oxides to TiO_2, while the holes at the valence band of TiO_2 might move to that of copper oxides [21,22].

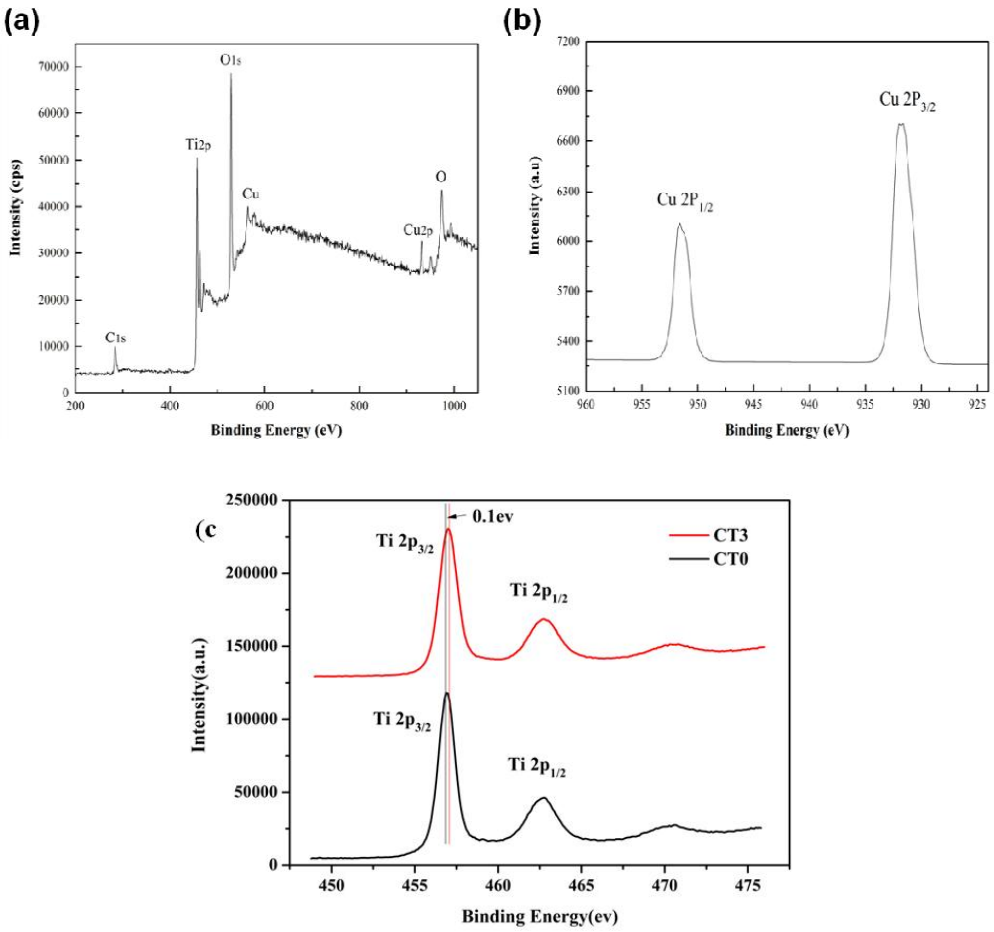


Fig. 3. (a) XPS survey spectrum of 3 wt% Cu_2O-TiO_2 aeroge photocatalyst, (b) High resolution Cu 2p spectrum, (c)Comparison of high-resolution spectra of Ti before and after doping

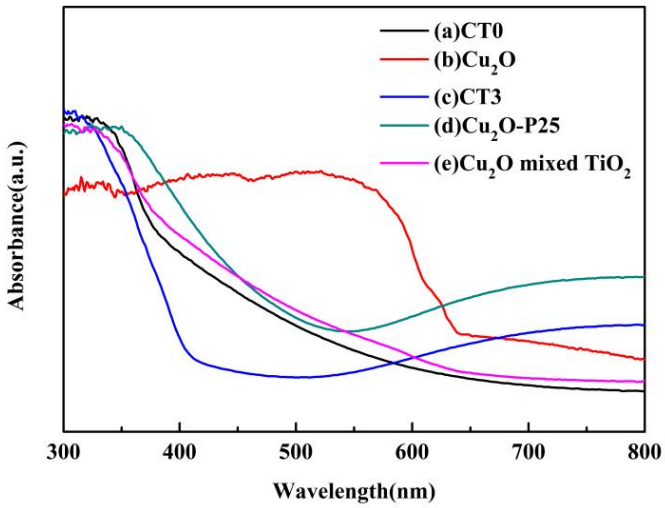


Fig. 4. UV-Vis spectra of , (a) CT0, (b) Cu_2O, (c) CT3, (d) Cu_2O-P25, (e)Cu_2O mixed TiO_2

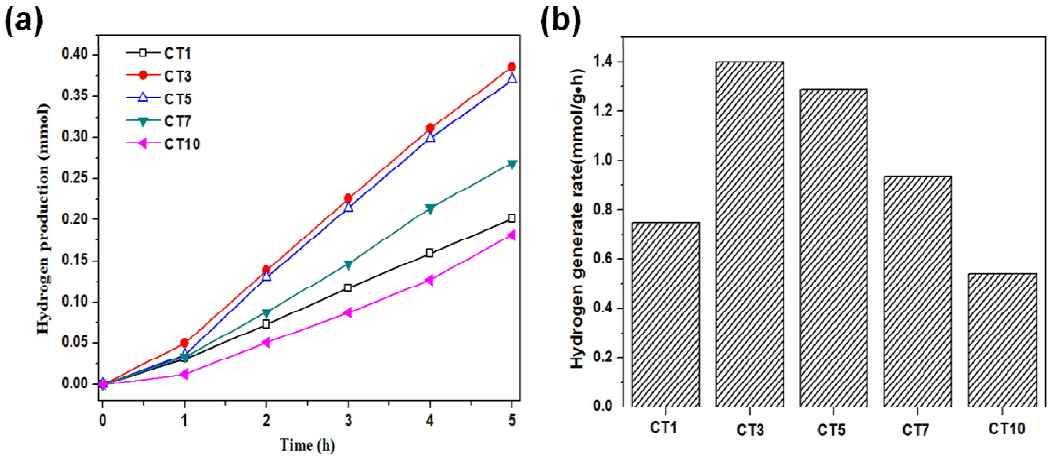


Fig. 5. Comparison of H_2 production and H_2 production efficiency over CT1, CT3, CT5, CT7 and CT10

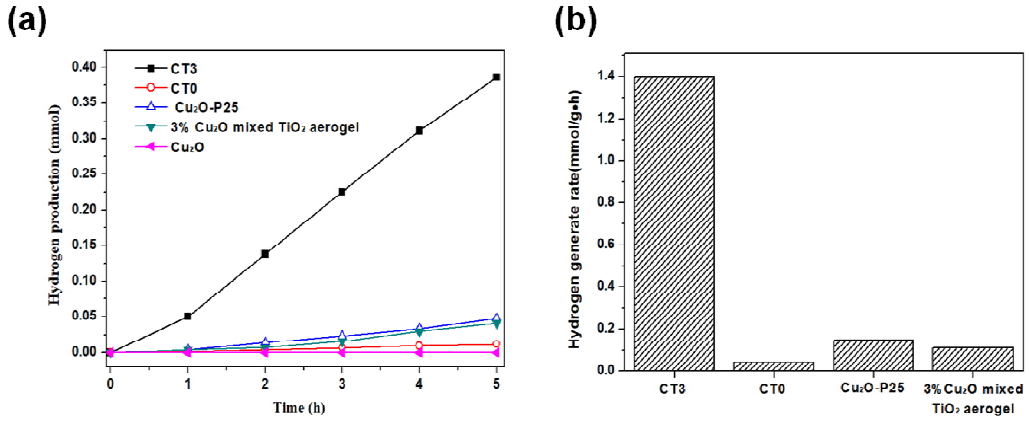


Fig. 6. Comparison of H_2 production and H_2 production efficiency over CT3, CT0, Cu_2O-P25, 3 wt% Cu_2O mixed TiO_2 aerogel, and Cu_2O

3.3 Possible Mechanism for the Enhanced Photocatalytic H_2 Production Activity

The result of UV−vis diffuse reflectance spectra implied that the Cu_2O loading enhanced the absorbance in 300-800 nm region as compared to pure TiO_2 aerogel. On the other hand, the conduction band edge of TiO_2 is higher than that of Cu_2O. The conduction band edge of Cu_2O has a less negative potential than H^+/H_2 potential [38]. This facilitates the interfacial electron transfer from Cu_2O to H^+ in the solution. Under simulated solar irradiation irradiation, TiO_2 and Cu_2O were activated at the same time. Photogenerated electrons transfer from the conduction band of TiO_2 into Cu_2O, and accumulate at their lower conduction bands, while holes accumulate at the valence band of TiO_2 and Cu_2O [39]. Consequently, the photogenerated electron in Cu_2O can effectively reduce the protons to form H_2. Obviously, the quantum size effects increase the band gap in Cu_2O and also shift the conduction band to facilitate the transfer of photogenerated electrons. Although Cu_2O was activated by the light, photogenerated electrons could still be transferred from the conduction band of TiO_2 into that of Cu_2O, which resulted in a low activity of the sample CT1. In fact, the conduction band of bulk Cu_2O is less negative and may not allow for direct transfer of electrons from Cu_2O to H^+ in the solution [40]. Therefore, with increasing Cu_2O content up to 3 wt%, the number of the Cu_2O

formed on the titania surface increases, resulting in the increase of its photocatalytic activity. However, when Cu_2O is higher than 3 wt%, a further increase in the Cu_2O content results in the reduction or disappearnce of the quantum confinement effect, causing a decrease of the photocatalytic activity.

According to the absorption spectrum, use the Tauc-plot formula to convert the absorption spectrum：

$$\alpha Ahv^{1/n} = A(hv-Eg) \quad (1)$$

In formula (1):α is the absorption coefficient, h is Planck's constant; v is the optical frequency, n is a constant,direct band gap semiconductor n=1/2,indirect band gap semiconductor n=2.Use formula (1) to calculate the band gap and draw a tangent to the absorption cut-off edge,the results are shown in Table 1. CT3 has the narrowest band gap, which is 1.52 ev.

In the analysis of transient photocurrent response, the stronger the photocurrent, the higher the photogenerated carrier separation efficiency. It can be clearly seen from Fig 8(a) that Cu_2O-TiO_2 has a fast photocurrent response under light conditions. It is worth noting that the photocurrent density of CT3 is significantly stronger than that of other composite materials. This is because the doping of Cu_2O enhances the generation and separation of photogenerated carriers, and the doping of 3wt% shows the strongest transient state Photocurrent.

Electrochemical impedance (EIS) is another effective electrochemical method to reveal the transfer and separation efficiency of electrons on the electrode. The study believes that a small EIS arc radius indicates that the charge transfer resistance between the working electrode and the electrolyte solution is small.The electrode has a more effective photo-generated charge transfer capability. As shown in Figure 8(b), compared with other materials, the EIS arc radius of CTx decreases with the increase of Cu_2O content, and the arc radius is minimized in CT3.

As the weight percentage of Cu_2O increases, the arc radius becomes larger, which further shows that Cu_2O doping enhances the separation and transfer of photogenerated electron-hole pairs.

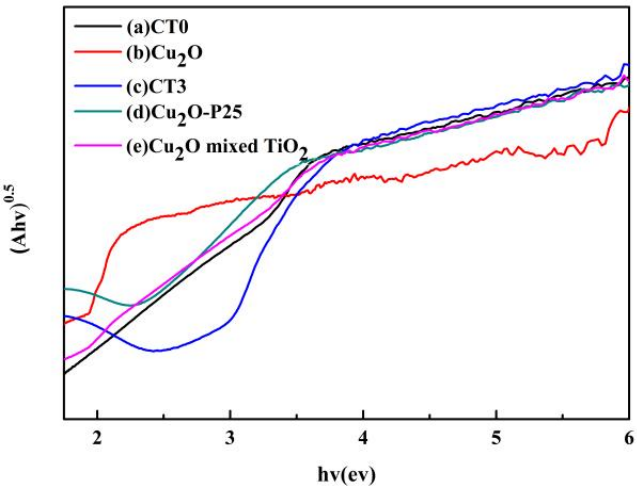


Fig. 7. $(Ahv)^{0.5}$ and hv relationship diagram of (a) CT0, (b) Cu_2O, (c) CT3, (d) Cu_2O-P25, (e) Cu_2O mixed TiO_2

Table 2. Absorption band edge and band width of composite materials

Sample	Absorption band edge λ(nm)	Band gap Eg (eV)
CT0	659.6	1.78
Cu_2O	715.9	1.64
CT3	772.4	1.52
Cu_2O-P25	465.9	2.52
Cu_2O maxed TiO_2	978.4	1.20

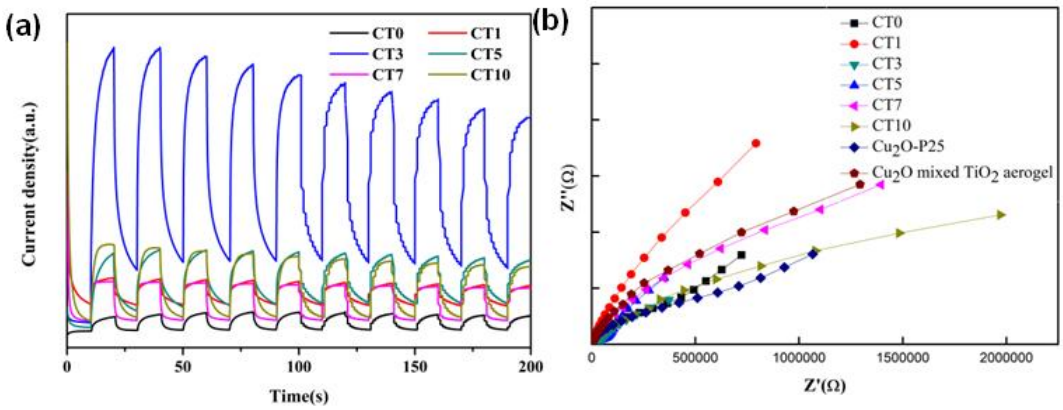


Fig. 8. Electrochemical test of the samples:(a) Nyquist polt, (b) Transient photocurrent density response of samples

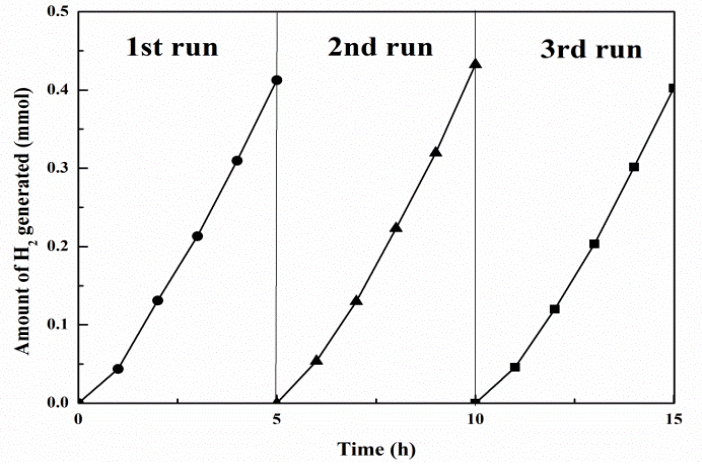


Fig. 9. Hydrogen production activity of the recycled photocatalyst (50 mg of the catalyst, 278 K) Cu_2O itself usually suffers from relatively poor photostability when used as a photocatalyst [18-22]

3.4 Reusability of the Recycled Photocatalysts

In order to confirm the reproducibility of H_2 production using Cu_2O-modified TiO_2 aerogel photocatalysts, three experiments were carried out at the same condition.The results were averaged and the average value of H_2 production is about 1.41 mmol/(g·h). The results are displayed in Fig. 7. However, when Cu_2O was combined with TiO_2 aerogel, its photostability was significantly enhanced.

4. CONCLUSION

In summary, high-surface-area (400-500 m^2/g) mesoporous of Cu_2O-TiO_2 aerogels with relatively high concentration of Cu_2O were prepared and used in photocatalytic splitting of water under simulated solar light irradiation. Cu_2O-TiO_2 aerogel containing 3 wt% Cu_2O exhibited the highest hydrogen evolution rate of 1.40 mmol/(g·h) which was about 33 and 9 times higher than those of pure TiO_2 aerogels (0.043 mmol/g·h) and Cu_2O-modified Degussa P25 titania (0.15 mmol/g·h). Moreover, the materials displayed good photocatalytic stability and long-term durability.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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