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Short communication

# Achieving solar-to-hydrogen evolution promotion using $TiO_2$ nanoparticles and an unanchored Cu co-catalyst

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ABSTRACT

Spherical Cu particles were successfully synthesized by a facile strategy at room temperature. The crystal phase and structure were characterized by XRD, SEM, and TEM measurements. The physical mixing of the as-synthesized copper spheres with $TiO_2$ nanoparticles could initial and promote solar-to-hydrogen evolution in methanol aqueous solution. TEM result showed that the partial of Cu co-catalyst attached on the surface of the host $TiO_2$ nanoparticles, although the interface of $TiO_2$-Cu non-existed in the synthetic process. On the basis of photo/electro-chemical measurements, it was proposed that charge transfer was accomplished via collisions between the $TiO_2$ and Cu nanoparticles, which promoted charge separation and subsequently photocatalytic hydrogen evolution in the suspension.

## 1. Introduction

The shortage of energy and the pollution of fossil fuels make us urgently seek cleaner source of energy. The emergence of photocatalysis has attracted considerable attention for the use of sunlight and its conversion into hydrogen energy [1–4]. In the past decade, the preparation of photocatalysts has focused on the construction of various binary or ternary composite materials [5–10]. Such hybrid could effectively separate photogenerated electron-hole pairs and improve the activity of hydrogen production [8,11–15]. However, most of the synthesis strategies suffered from some drawbacks such as a high temperature, long reaction time, addition of surfactants, and complicated shape-control processes. On the other hand, it is reasoned that the physical mixing of unanchored co-catalysts and host-catalysts would lead to improved photocatalytic efficiency towards solar-to-hydrogen evolution.

Recently, Liu et al. [16] proposed a collision-contact mechanism for photocatalytic hydrogen evolution by mixing $Cd_{0.5}Zn_{0.5}S$ photocatalyst with a NiSx co-catalyst, which confirms the possibility of photocatalytic hydrogen evolution upon mechanically catalysts mixture. Inspired by the previous work and the present challenge, we herein tried to produce hydrogen by combining titanium oxide photocatalyst with an unanchored metallic copper co-catalyst in methanol aqueous solution. The physical mixing approach is different from a traditional heterojunction that depends on close interconnection between photocatalyst and co-catalyst. The spherical Cu particles was prepared and used as a co-catalyst to promote the solar-to-hydrogen evolution of $TiO_2$ nanoparticles. The possible collisions between $TiO_2$ nanoparticles and Cu particles for the photocatalysis enhancement was also discussed.

## 2. Experimental section

$TiO_2$ nanoparticle aggregate was fabricated by a hydrothermal treatment of the titanium glycolate precursor according to previous study [17]. In a typical fabrication of spherical copper nanoparticles, 0.37 g $CuSO_4{\cdot}5H_2O$ was dissolved into 100 mL deionized water. Then, 0.15 g trisodium citrate and 1 g sodium hydroxide were added into the solution and sonicated to get a homogeneous solution. Subsequently, 50 mL deionized water containing 6.6 g ascorbic acid was poured into the above solution. The mixed solution was stirred for 2 h under room temperature. The obtained precipitation was collected and washed by centrifuge with water and ethanol for several times and finally dried at for 12 h.

X-ray powder diffraction (XRD) was carried out on a Bruker D8 Advance diffractometer at a scan rate of 10°/min in the 2$\theta$ range from 10° to 80°. Scanning electron microscopy (SEM) and EDX analysis was conducted on a JSM 5510 LV at the operating voltage of 5 kV. Transmission electron microscopy (TEM) images were visualized on a

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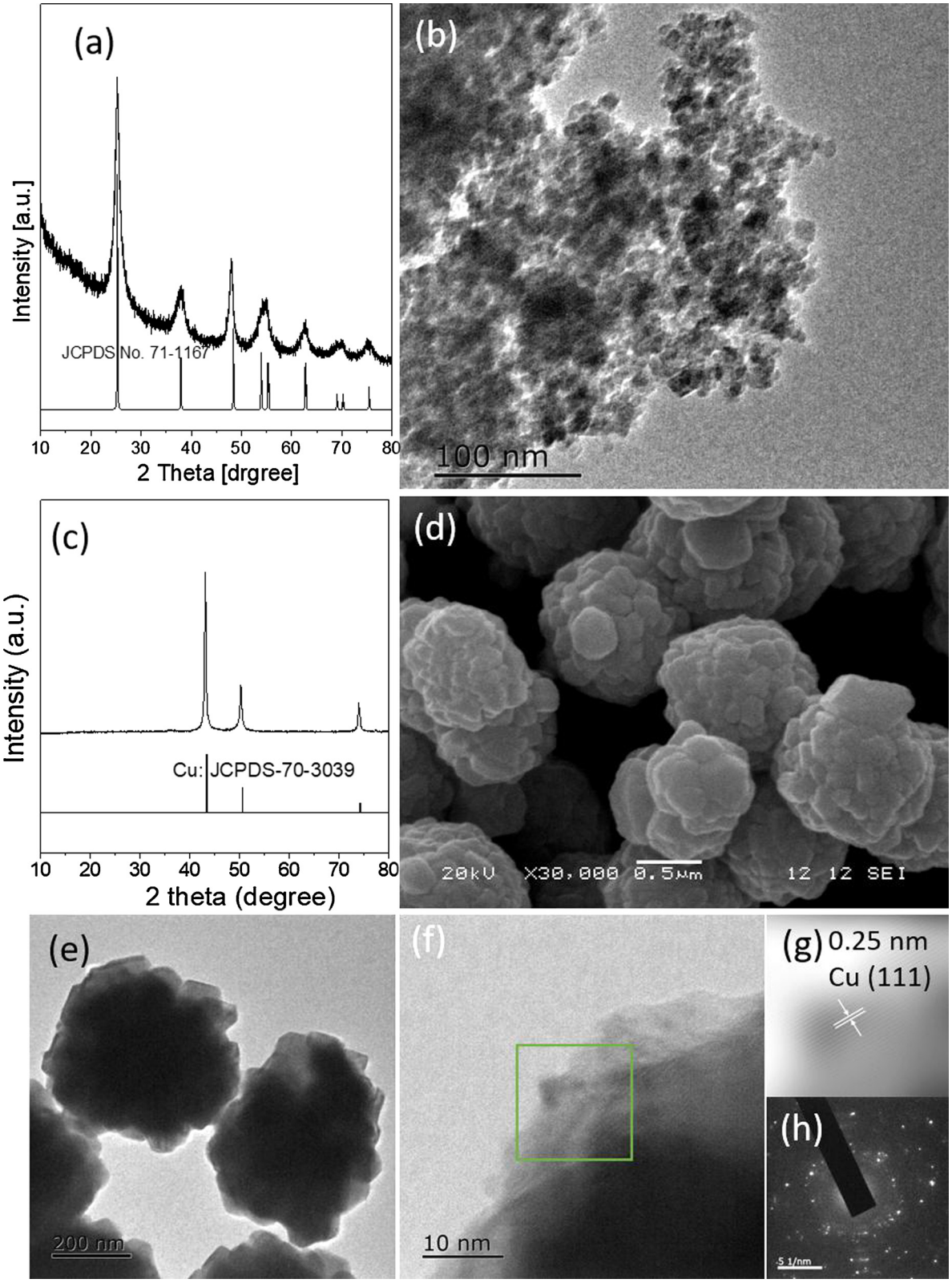


**Fig. 1.** (a) XRD-pattern and TEM-image of $TiO_2$, (c) XRD-pattern, (d) SEM, (e) TEM, (f and g) HRTEM, and (h) SAED-pattern of Cu.

JEM-2000, using an accelerating voltage of 200 kV. The oxidation state of the catalyst was examined by X-ray photoelectron spectroscopy (XPS, VG Multilab2000) using Al Kα (1486.6 eV) radiation, while the binding energies were calibrated from the C1 s photoelectron peak (284.7 eV). The ultraviolet-visible (UV–vis) spectra of the products were collected on a spectrophotometer (UV2550, Shimadzu, Japan). Photoluminescence spectra were detected with a HITCHI F4600 fluorescence spectrophotometer. Transient photocurrent density and electrochemical impedance spectra were analyzed according to previous work [18].

Photocatalytic hydrogen generation was performed according to previous study [19]. Typically, 25 mg $TiO_2$ nanoparticles with different

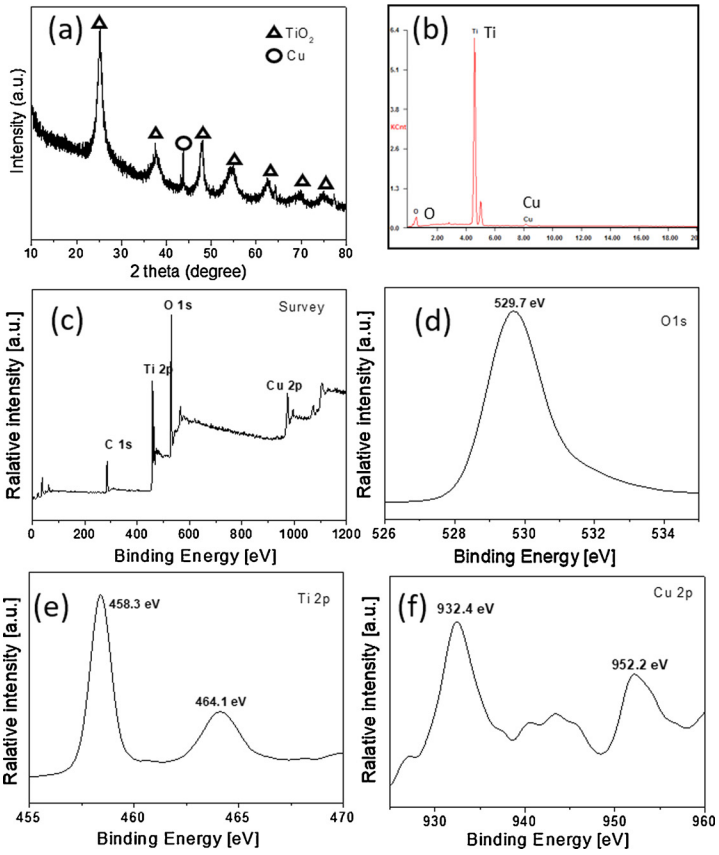


**Fig. 2.** (a) XRD-pattern, (b) EDX spectra, (c) XPS survey spectrum, and (d) O 1s, and (e) Ti 2p XPS, (f) Cu 2p spectra of the mixture containing$TiO_2$ and Cu (5 wt%).

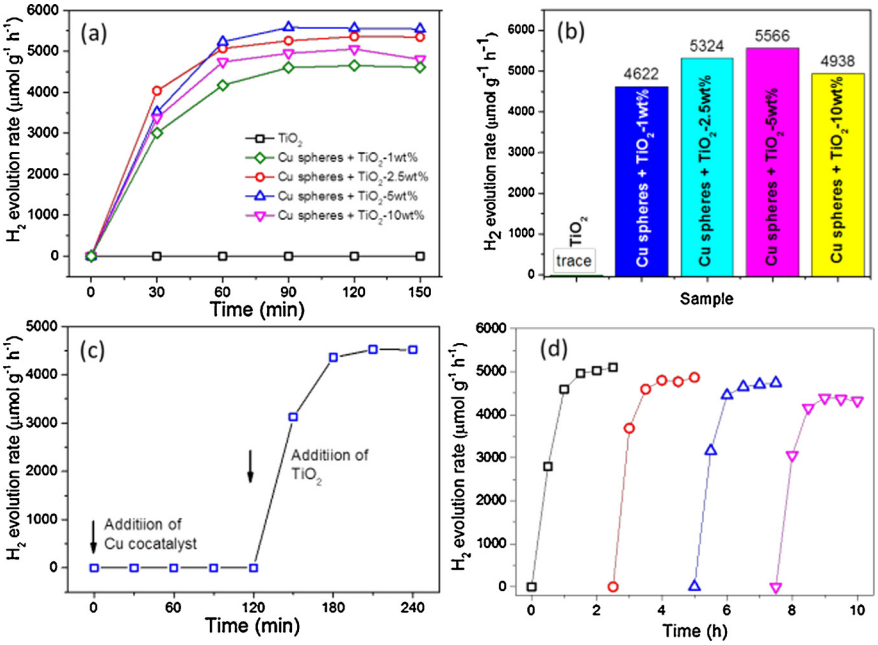


**Fig. 3.** (a and b) photocatalytic hydrogen evolution upon $TiO_2$ nanoparticles with different amounts of Cu particle; (c) photocatalytic hydrogen evolution under different conditions; (d) cyclic hydrogen evolution behavior of the photocatalysis system.

amounts of copper particles were dispersed into 50 mL of 20 vol.% methanol aqueous solution. The hydrogen generated was detected by on-line gas chromatography (GC-7900, TCD, $N_2$ as a carrier gas), and the reaction lasted for 4 h with 300 W Xe lamp. The $H_2$ production was measured every hour by gas chromatography (GC).

## 3. Results and discussion

Fig. 1a and b shows the XRD-pattern and TEM-image of the as-prepared $TiO_2$ product, respectively. It can be clearly seen that $TiO_2$ nanoparticle attached each other was successfully synthesized. Fig. 1c indicates the high impurity of the as-obtained copper material, because

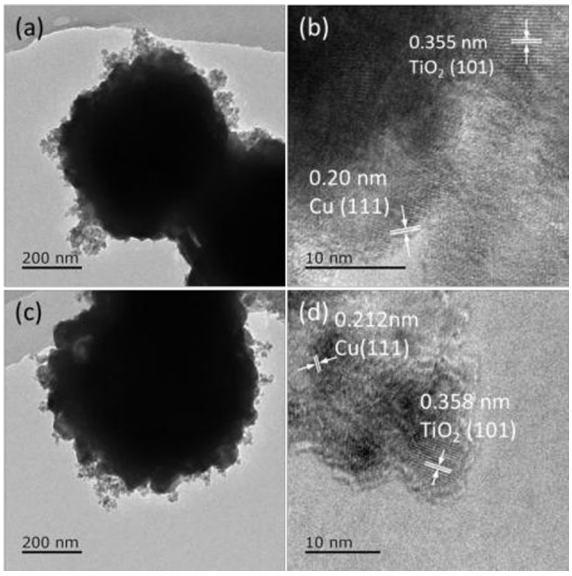


**Fig. 4.** TEM and HRTEM-image of the mixture of $TiO_2$ and Cu particles (5 wt%) before (a and b) and after (c and d) photocatalytic hydrogen evolution.

no other diffraction peak was detected. As depicted in Fig. 1d and e, the copper product showed the spherical morphology with rough surface. The Fig. 1g and f displays the lattice d-spacing of 0.25 nm, which corresponds to the (111) crystal plane of Cu. The SAED-pattern displayed in Fig. 1h further confirms the good crystalline of copper particle.

When mixed the obtained $TiO_2$ nanoparticle with Cu particles (5 wt %), as shown in Fig. 2a, diffraction peaks of both $TiO_2$ and Cu were observed. Furthermore, as displayed in Fig. 2b, the EDX analysis of the mixture suggested that it was composed of Ti, O, and Cu elements. XPS analysis was further determine the chemical states of the component elements of the $TiO_2$ and Cu mixture. As can be seen in Fig. 2c, it displays the presence of Cu, Ti, O, and C element. Fig. 2d displays the O 1s peak of the mixture, and the binding energy peak at 529.7 eV is attributed to the $O^{2-}$ ions in the $TiO_2$. The peaks in the Ti 2p spectrum (Fig. 2e) located at 458.3 and 464.1 eV, which corresponds to Ti $2p_{3/2}$ and Ti $2p_{1/2}$, respectively [20–22]. As presented in the high-resolution XPS spectrum of Cu 2p (Fig. 2f),the binding energies of 932.4 and 952.2 eV are attributed to Cu $2p_{3/2}$ and Cu $2p_{1/2}$, respectively, suggesting the existing of Cu [23–25].

The photocatalytic hydrogen production activity by mixing $TiO_2$ nanoparticles with Cu particle in the 20 vol.% methanol aqueous solution was evaluated. Fig. 3a and b display the photocatalytic activity towards solar-to-hydrogen upon $TiO_2$ nanoparticle with different amounts of Cu particles. It was observed that pure $TiO_2$ has no activity for hydrogen evolution. However, when the 1, 2.5, 5, and 10 wt% of Cu particle was used, the photocatalytic hydrogen evolution rate was 4622, 5324, 5566, and 4938 μmol/g/h. Interestingly, as shown in Fig. 1c, when pure Cu particle (5 wt%) was added into the methanol aqueous solution with light irradiation, there was no hydrogen production. Once the $TiO_2$ nanoparticle was further added into the above reaction system, it can be seen that an efficient hydrogen evolution was achieved. Furthermore, this photocatalysis system composed of $TiO_2$ nanoparticles with unanchored Cu particles exhibited good cyclic hydrogen evolution behavior. As shown in Fig. 3d, the hydrogen evolution reached about 4500 μmol/g/h after the photocatalysis experiment was performed four times.

Fig. 4 shows the TEM and HRTEM-image of the mixture of $TiO_2$ and Cu particles before and after photocatalytic hydrogen evolution. It was found, although the interface of $TiO_2$-Cu non-existed in the synthetic process, partial of the $TiO_2$ nanoparticles coupled with the spherical Cu

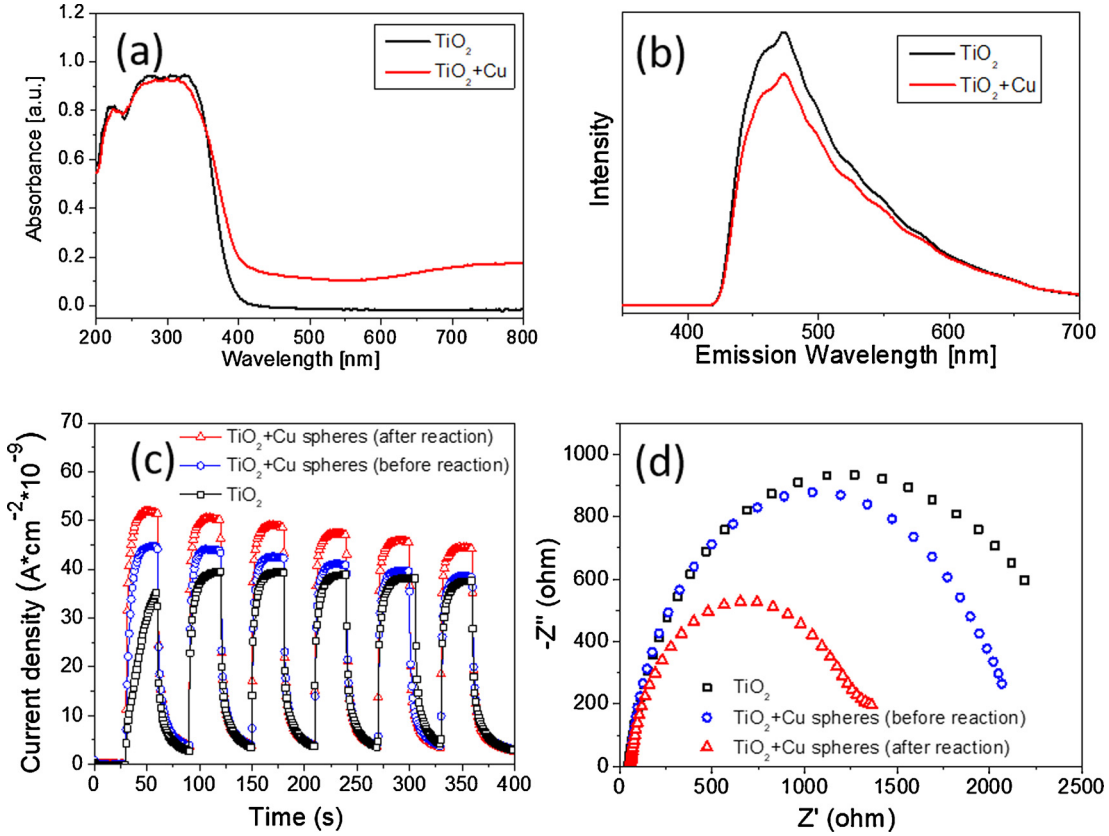


**Fig. 5.** (a) UV-DRS and (b) Photoluminescence (PL) spectra of the $TiO_2$ and the mixture containing$TiO_2$ and Cu (5 wt%); (c) Photocurrent response and (d) electrochemical impedance spectra (EIS) of $TiO_2$, and the mixture of $TiO_2$ and Cu particles (5 wt%) before and after photocatalytic $H_2$ evolution.

particles before and after solar-to-hydrogen evolution test. In a general, pure $TiO_2$ was hard to split water to hydrogen with light irradiation because of its rapid recombination of photoinduced electron-holes. While the loading of suitable non-noble metal co-catalysts could effectively utilize photogenerated charges and subsequently improve the solar-to-hydrogen activity [6,26–30].

Fig. 5a shows the UV-DRS of the pure $TiO_2$ and mixture of $TiO_2$ and Cu particles (5 wt%). It was found that the involving of Cu particles could enhance the visible light absorption of $TiO_2$ particles, and accordingly could effectively use solar energy. As shown in Fig. 5b, the mixture of $TiO_2$ and Cu particles (5 wt%) exhibited lower intensity than that of pure $TiO_2$ nanoparticles, it suggested that this mixture could have rapid electron-hole separation efficiency when $TiO_2$ nanoparticle was excited by the light irradiation [31–33]. Fig. 5c and d displays photocurrent response and electrochemical impedance spectra of $TiO_2$ and the mixture of $TiO_2$ and Cu particles before and after photocatalytic hydrogen evolution. It was observed that the $TiO_2$-Cu mixture after photocatalysis reaction had higher photocurrent intensity than the one before photocatalysis reaction and of pure $TiO_2$, which indicated it had better electron-hole separation efficiency. Furthermore, the $TiO_2$-Cu mixture after photocatalysis reaction exhibited the smallest arc radius, suggested that the involving of Cu particle was helpful to inhibit photogenerated electron-hole recombination [8,34–39]. On the basis of the above results, it was suggested frequent collisions between $TiO_2$ nanoparticles and Cu particles could improve the transfer of photogenerated electrons from $TiO_2$ to the Cu particles [16,40]. In this case, the photogenerated charges could be effectively utilized in the suspension and finally promote the solar-to-hydrogen evolution efficiency.

## 4. Conclusion

In summary, $TiO_2$ nanoparticles and spherical Cu particles were prepared used as the host photocatalyst and co-catalyst for solar-to-hydrogen evolution. The involving of Cu particle could initial and promote the photocatalytic hydrogen production because it can accelerate the electron-hole separation and charge transfer. It was proposed frequent collisions between $TiO_2$ nanoparticles and Cu particles could effectively utilize photogenerated charges in the suspension and accordingly enhance the photocatalysis efficiency.

## 5. Author contribution

Gang Cheng conducted the project, summarized the manuscript, and contributed the idea ; Mengmeng Zhang did some parts of the experiment; Chao Han read and polished the manuscript; Ying Liang and Kai Zhao contributed part to the idea and funding support for the project.

## Declaration of Competing Interest

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.

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