Boosting photocatalytic hydrogen production from water by photothermally induced biphase systems

Shaohui Guo1, Xuanhua Li1✉, Ju Li2 & Bingqing Wei3

Solar-driven hydrogen production from water using particulate photocatalysts is considered the most economical and effective approach to produce hydrogen fuel with little environmental concern. However, the efficiency of hydrogen production from water in particulate photocatalysis systems is still low. Here, we propose an efficient biphase photocatalytic system composed of integrated photothermal–photocatalytic materials that use charred wood substrates to convert liquid water to water steam, simultaneously splitting hydrogen under light illumination without additional energy. The photothermal–photocatalytic system exhibits biphase interfaces of photothermally-generated steam/photocatalyst/hydrogen, which significantly reduce the interface barrier and drastically lower the transport resistance of the hydrogen gas by nearly two orders of magnitude. In this work, an impressive hydrogen production rate up to 220.74 μmol h⁻¹ cm⁻² in the particulate photocatalytic systems has been achieved based on the wood/CoO system, demonstrating that the photothermal–photocatalytic biphase system is cost-effective and greatly advantageous for practical applications.
Solar-driven hydrogen production from water is a potentially efficient way to address the environmental problems and global energy crisis of fuel production. In particular, hydrogen gas has a high energy capacity (143 MJ kg\(^{-1}\)) and releases no toxic emissions\(^1\). Therefore, an efficient and rapid photocatalytic hydrogen-production method is urgently needed\(^2,3\). There are three main types of solar-driven hydrogen production systems: particulate photocatalysis, photovoltaic-assisted electrolysis (PV-E), and photoelectrochemical cells (PEC)\(^4\), where the particulate photocatalysis is predicted to be more cost-effective than the other two systems\(^5\). Unfortunately, the solar to hydrogen conversion efficiency in particulate photocatalysis remains low though many strategies, including structural and defect engineering, plasmonic effects, and elemental doping, have been discussed to improve photocatalysts’ optical absorption and photo-induced charge separation and transport\(^6,7\).

In this work, from the phase-interface perspective, we design an efficient and cost-effective photocatalytic system composed of integrated photothermal–photocatalytic materials that can easily convert liquid water to water steam via photothermal transpiration effect with charred wood substrates. And the steam is simultaneously split into hydrogen by the photocatalysts loaded on the wood under light illumination without additional energy. The design exhibits biphase interfaces of self-generated steam/photocatalyst loaded on the charred wood substrates/hydrogen gas. Our strategy of the photothermally induced biphase interfacial feature differs from previous studies of the room-temperature vapor in moisture environment to reduce the catalysts corrosion (the humidity was realized through a complex microfluidic micrometric\(^8,9\), convection effect\(^10\), and hydrophobic effect\(^11\) and plasmonic thermal effects\(^12\) and near-infrared photothermal effects\(^13,14\) in the triphase interfaces of liquid water/photocatalyst/hydrogen. This photothermal–photocatalytic biphase system kinetically lowers the hydrogen gas’s transport resistance by nearly two orders of magnitude to allow the easy escape of hydrogen gas from the system. It also thermodynamically reduces the interface barrier in the adsorption process of gas-phase water molecules to photocatalysts. In this work, such a biphase system significantly improves the photocatalytic hydrogen production rate up to 220.74 μmol h\(^{-1}\) cm\(^{-2}\) for the wood/CoO system and 3271.49 μmol h\(^{-1}\) cm\(^{-2}\) for the wood/CuS–MoS\(_2\) heterophotocatalyst.

### Results

**Constructing a photothermal–photocatalytic system on charred wood.** A photothermal–photocatalytic system was skillfully designed and implemented by applying natural wood to generate water steam via photothermal transpiration under the light illumination simulated by a solar simulator at AM 1.5 G illumination (100 mW cm\(^{-2}\))\(^6,16–18\). Also serving as the substrate for the photocatalytic reaction, a wood slice was cut from a tree perpendicular to its growth direction, and the surface of the wood slice was carbonized by a simple heating process for improving the steam resistance by nearly two orders of magnitude to allow the easy escape of hydrogen gas from the system. It also thermodynamically reduces the interface barrier in the adsorption process of gas-phase water molecules to photocatalysts. In this work, such a biphase system significantly improves the photocatalytic hydrogen production rate up to 220.74 μmol h\(^{-1}\) cm\(^{-2}\) for the wood/CoO system and 3271.49 μmol h\(^{-1}\) cm\(^{-2}\) for the wood/CuS–MoS\(_2\) heterophotocatalyst.

The CoO NPs are distributed ~2 mm along the walls of the wood microchannels, as evidenced by the Raman spectra at different depths from the top surface (Fig. 1b), where only four Raman spectra taken with an interval of 500 μm from the surface show the CoO Raman characteristic peaks at 473.6 and 540.9 cm\(^{-1}\)\(^,20\). When the wood/CoO system floats in the water, the immersion depth of the wood in the water is about 2 mm (Fig. 1c), indicating that the photocatalysts are not directly soaked in the liquid-phase water.

After CoO NPs coating on the wood, the wood/CoO system shows high light absorbance from 300 to 1000 nm compared to that of the pure wood, as shown in Fig. 1d, implying that the wood/CoO system can effectively utilize solar energy. Under light illumination, the surface temperature of the wood/CoO system is about 325 K (Fig. 1e), and the adhered photocatalysts become covered with steam produced by the photothermal transpiration in the wood interior. Simultaneously, the photo-induced electrons participate in the hydrogen evolution reaction at the photocatalytic active sites, and photo-induced holes participate in the H\(_2\)O\(_2\) generation (Fig. 1a). It should be noted that the local temperature of the CoO NP is estimated to be 346 K based on the potential (Fig. 1f, g, and Supplementary Fig. 7)\(^21\), which is higher than the global temperature (325 K, in Fig. 1e) because of the nanoscale effect. It is speculated that a higher local temperature is beneficial to enhance the photocatalytic reaction efficiency.

We investigated the effect of CoO NPs mass loading on the photocatalytic hydrogen gas production rate in the wood/CoO system (Fig. 2a). An optimized mass loading of about 38 mg cm\(^{-2}\) CoO NPs has been identified based on the experimental results. The photocatalytic H\(_2\) evolution rate in the wood/CoO system with 38 mg cm\(^{-2}\) CoO NPs loading is about 5776 μmol h\(^{-1}\) g\(^{-1}\) (i.e., 220.74 μmol h\(^{-1}\) cm\(^{-2}\)), 17 times higher than that of the triphase CoO NPs (337 μmol h\(^{-1}\) g\(^{-1}\), agrees well with the values reported under similar conditions)\(^19\), as shown in Fig. 2b. For clarification, the photocatalytic activity of wood alone was measured under the same condition (Supplementary Fig. 8), and no trace of hydrogen gas and oxygen gas were detected after 2 h of reaction, indicating that the wood does not have photocatalytic activity. Moreover, we also studied the effect of solar intensity on the photocatalytic response of the wood/CoO system. As shown in Fig. 2c, the rate of hydrogen evolution grows with the increase of solar intensity but not a linear relation. This is mainly because of the temperature rising on the wood/CoO surface caused by the increase in solar intensity (Supplementary Fig. 9). A higher temperature can exponentially improve the rate of hydrogen evolution, as evidenced in the following section.

In addition, the biphase wood/CoO system exhibits superior stability in photocatalytic activity. The long-period photocatalytic hydrogen production measurement with the wood/CoO system was conducted for 5 days (Fig. 2d). On day 1, the initial hydrogen production rate in 1 h is 221.56 μmol h\(^{-1}\) cm\(^{-2}\), and the average hydrogen production rate during 8 h reaction is 194.14 μmol h\(^{-1}\) cm\(^{-2}\). On day 5, the average hydrogen production rate during 8 h reaction is 174.73 μmol h\(^{-1}\) cm\(^{-2}\). Thus, after 5 days (40 h) test, the photocatalytic hydrogen evolution performance maintains about 90%, exhibiting that photocatalytic stability can be significantly improved through the wood/catalysts system compared to that in the previous work, which only holds 1 h of reaction\(^22\). We also studied the morphological stability of the wood/CoO system. After the photocatalytic reaction, the CoO NPs remain well attached to the wood matrix structure, further confirming the stability of the wood/CoO system (Fig. 2e, f, Supplementary Figs. 10 and 11). There is little difference in the reflection spectra and X-ray photoelectron spectroscopy (XPS) spectra of the wood/CoO system before and after the photocatalysis process (Supplementary Figs. 12 and 13). Besides, the inductively coupled plasma emission (ICP) and ultraviolet–visible (UV–Vis) spectra of the bulk water in the wood/CoO system after the photocatalytic reaction have been measured (Supplementary
There are few amounts of element Co in the bulk water based on the ICP measurement results and the absorption spectrum, exhibiting the wood/CoO system’s excellent stability. It can be concluded that the photothermal–photocatalytic system displays a significant advantage in substantially enhancing the H2 evolution rate from water splitting. It is noticed that the ratio of photocatalytic H2 and O2 production is not equal to 2:1 (Supplementary Figs. 15 and 16), mainly due to the generation of H2O2 by-product in the photocatalytic process (Supplementary Fig. 17).

Understanding the phase-interface effect on catalytic performance. From the phase-interface perspective, the photothermal–photocatalytic system exhibits biphasic interfaces of photothermally-generated steam/photocatalyst/hydrogen gas. To understand the phase-interface effect on the photocatalytic performance, we conducted experiments with a biphasic photocatalytic system containing injected water steam/solid photocatalysts (Fig. 3a and c). Water steam was injected and controlled by a steam flowmeter into a transparent reactor, where CoO NPs powder catalysts were placed on the surface of a filter paper, and no sacrificial agent was added to the photocatalytic system. Under light illumination, the steam in the reactor was photocatalytically converted to H2, which was detected by the gas chromatography (GC) (Fig. 3c). For comparison, the liquid/solid/gas triphase system of water/photocatalyst/hydrogen in common photocatalytic hydrogen evolution reaction has also been included. As shown in Fig. 3b, hydrogen bubbles are generated when the solid photocatalysts are interacting with liquid water under light illumination. The produced hydrogen gas is then collected by passive transport against the liquid water phase.

Hydrogen production in the biphasic photocatalytic reaction system was evaluated with different flow rates of water steam (from 5 to 88 ml h⁻¹) injected into the reactor chamber (Fig. 3c, d, Supplementary Figs. 18 and 19). The rate of hydrogen production from steam increases along with the increase of steam flow rate from 5 to 62 ml h⁻¹. When the steam flow rate further grows, the hydrogen production rate is stabilized because the quantity of...
water molecules reaches saturation during the photocatalytic reaction. At the optimal flow rate (i.e., 62 ml h⁻¹), the maximum hydrogen evolution rate is ~6200 μmol h⁻¹ g⁻¹, 18 times higher than that in the triphase reaction system (337 μmol h⁻¹ g⁻¹). The biphasic photocatalytic system also shows excellent stability of the photocatalyst, as shown in Fig. 3e. After three cyclic measurements, the amount of H₂ evolution concurs with that in the first measurement. And the morphology and absorption spectra of CoO NPs after the photocatalytic reaction also keep unchanged, confirming the excellent stability of the photocatalyst (Supplementary Figs. 5, 20, and Fig. 3f).

The main factors governing the photocatalytic hydrogen evolution in the biphasic reaction system are the temperature and the state of water in comparison to the triphase reaction system. Figure 4a shows the temperature-dependent of the photocatalytic hydrogen evolution rate with the CoO NPs photocatalyst in the triphase reaction system. As the reaction temperature increases from 298 K to close to 373 K, the hydrogen evolution rate monotonically increases from 336.73 μmol h⁻¹ g⁻¹ (note that 373 K is the steam-conversion temperature of liquid water). It should be noted, however, no trace hydrogen is detected after 2 h of reaction at near 373 K if light illumination is not applied, implying that the catalytic reaction cannot be thermally triggered (Supplementary Fig. 21). Furthermore, the relationship between the rate of H₂ evolution reaction V and the reaction temperature T can be well-fitted with the Arrhenius equation:

\[
V = 3748519.38e^{\left(\frac{-3748519.38}{RT}\right)}
\]

According to Eq. (1), the activation energy for the hydrogen production over CoO was deduced to be 23.023 kJ mol⁻¹. The activation energy is a key indicator to reflect whether photocatalytic hydrogen evolution reaction occurs easily. The smaller the activation energy is, the easier the hydrogen production process will become. Therefore, a low activation energy here indicates that the hydrogen production process is easily conducted on the CoO NPs. Furthermore, the H₂ evolution rate at 373 K is estimated to be 2236.76 μmol h⁻¹ g⁻¹. However, it is much lower than the H₂ evolution rate (6200.42 μmol h⁻¹ g⁻¹, see Fig. 3d) in the biphasic reaction system at the same temperature of 373 K, indicating that the temperature effect on improving the H₂ evolution rate is limited although a higher reaction temperature does promote the photocatalytic hydrogen evolution reaction. Thus, in addition to the reaction temperature, the state of water plays a crucial role in enhancing the hydrogen evolution of the biphasic reaction system.

The temperature effect can be systematically analyzed from two aspects: thermodynamics and kinetics. Three reaction steps, including the adsorption of water molecules, the adsorption of hydrogen atoms, and the hydrogen gas production in photocatalytic reaction, have been involved. First, the Gibbs energy in the triphase system has been calculated at 298 and 373 K, where the pure CoO structure without any group is used to simulate the CoO status in the neutral environment because the pH value of the reactant water is approximately equal to 7. As shown in Fig. 4b, the change of reaction temperature from 298 K to 373 K influences the first and second steps. The Gibbs energy of the water molecule adsorption process at 298 K is about 0.426 eV, and it is about 0.145 eV for the hydrogen adsorption process.
Comparatively, they are reduced to 0.331 and $-0.054$ eV, respectively, at 373 K. As expected, the high reaction temperature in the triphase photocatalytic system would thermodynamically favor the water molecule adsorption process.

In addition to kinetically promote the transport of water molecules, high temperatures will reduce hydrogen transport resistance as well so that the photocatalytic reaction rate can be accelerated. This can be evidenced by the hydrogen gas diffusion coefficient $D_L$ in a liquid-phase environment, calculated by the Stokes–Einstein equation:

$$D_L = \frac{7.4 \times 10^{-8} T (\psi_{H_2O} M_{H_2O})^{0.5}}{\mu V_{H_2}}$$

where $T$ is the temperature, $\psi_{H_2O}$ (=2.26) is the “association” parameter of the solvent water, $M_{H_2O}$ and $\mu$ denote the molecular weight and viscosity of water, respectively, and $V_{H_2}$ is the molar volume of hydrogen. When the temperature is increased from 298 to 373 K, the hydrogen gas diffusion coefficient $D_L$ is increased. Thus, hydrogen transport resistance is slightly decreased.

A more significant effect on promoting the photocatalytic hydrogen-evolution reaction comes from the state change of the water phase. When the water phase changes from liquid to steam at the same temperature (373 K), interestingly, the first and second step of the photocatalytic reaction (i.e., the water molecule adsorption process and the hydrogen adsorption process) has been significantly influenced. The Gibbs energy of the water molecule adsorption process substantially decreases from 0.331 eV in the triphase system to $-0.212$ eV in the biphase system, and it also reduces ($-0.054$ vs. $-0.007$ eV) for the hydrogen adsorption process (Fig. 4c), indicating that the water molecule adsorption process and hydrogen adsorption process in the biphase system become much more comfortable than that in the triphase system. Kinetically, the hydrogen gas diffusion coefficient $D_G$ in the gaseous environment can be calculated by the Chapman–Enskog theory:

$$D_G = \frac{A \ast T^{3/2}}{P \ast \sigma^2 \ast \Omega}$$

where $A (=1.858 \times 10^{-3})$ is an empirical coefficient$^{23,24}$, $M$ is the
collision diameter, and $\Omega$ is a temperature-dependent collision integral. The produced hydrogen bubbles experience frictional resistance in adjacent interlayers from relative motion with the environmental particles. Owing to the interfacial frictional resistance in adjacent interlayers from relative motion with the pure CoO surface. The photocatalyst is CoO NPs. In addition to the exemplary wood/CoO system, the photothermal photocatalytic system reaches up to 85,604 $\mu$mol h$^{-1}$ g$^{-1}$ (Supplementary Fig. 27), 16 times that of the triphase CuS–MoS$_2$ photocatalyst (5350 $\mu$mol h$^{-1}$ g$^{-1}$) (Supplementary Fig. 28). It is noted that no photocatalytic oxygen gas was produced because of the energy band positions of the CuS–MoS$_2$ photocatalyst (Supplementary Fig. 29). It is speculated that the photo-induced holes react with some S ions from CuS/MoS$_2$ catalyst as shown based on the XPS results (Supplementary Fig. 30). Figure 5g summarizes the H$_2$ evolution rates of typical particulate photocatalysts reported to date. The H$_2$ evolution rates were 70,000, 64,426, and 11,090 $\mu$mol h$^{-1}$ g$^{-1}$ in InP/ZnS, PTB7-Th/ET-ODTBR NPs, and 2D/2D NiS/VS-ZnIn$_2$S$_3$/WO$_3$, respectively. They were 23,410 and 16,300 $\mu$mol h$^{-1}$ g$^{-1}$ based on the

![Fig. 4 The factors governing the biphase photocatalytic hydrogen evolution: temperature and liquid-to-gas-phase changes of water.](image-url)

The universality of the photothermal–photocatalytic system. In addition to the exemplary wood/CoO system, the photothermal–photocatalytic system can also extend to other photocatalysts. To demonstrate the universal feature of the photothermal–photocatalytic biphase system, different photocatalysts, i.e., MoS$_2$, C$_3$N$_4$, and TiO$_2$ were, respectively, spin-coated on the carbonized wood slices to construct wood/photocatalyst architectures (Fig. 5a–c and Supplementary Figs. 22–24). The MoS$_2$, C$_3$N$_4$, and TiO$_2$ photocatalysts are all uniformly distributed and attached to the microchannel walls of the wood. The particulate photocatalytic hydrogen-evolution reactions were carried out in all the wood/photocatalyst reaction systems (Fig. 5d and Supplementary Fig. 25). All of the photocatalysts realize photothermal–photocatalytic hydrogen production, but no oxygen is detected at the same time because of the difficulty in downshifting the valence band positions (e.g., MoS$_2$, C$_3$N$_4$) and complex surface deformation reaction (e.g., TiO$_2$). The H$_2$ average production rates of the wood/MoS$_2$, wood/C$_3$N$_4$, and wood/TiO$_2$ photothermal–photocatalytic systems are 155.77, 95.54, and 59.87 $\mu$mol h$^{-1}$ cm$^{-2}$, respectively. For each photocatalyst, the apparent quantum yield (AQY) of the photothermal–photocatalytic biphase system dominates compared with the previously reported photocatalyst systems (Fig. 5e), and the measured data are listed in Supplementary Table 2.

In addition to the monothetic particulate photocatalysts, a heterojunction photocatalyst, i.e., CuS–MoS$_2$, has also been introduced to the photothermal–photocatalytic systems to verify the universality (Supplementary Fig. 26). Similar to the monothetic particulate photocatalysts, the CuS–MoS$_2$ photocatalyst has adhered to the microchannel walls of the wood matrix, as shown in Fig. 5f. The photocalytic H$_2$ average production rate of the biphase wood/CuS–MoS$_2$ photothermal–photocatalytic system reaches up to 85,604 $\mu$mol h$^{-1}$ g$^{-1}$ (Supplementary Fig. 27), 16 times that of the triphase CuS–MoS$_2$ photocatalyst (5350 $\mu$mol h$^{-1}$ g$^{-1}$) (Supplementary Fig. 28). It is noted that no photocalytic oxygen gas was produced because of the energy band positions of the CuS–MoS$_2$ photocatalyst (Supplementary Fig. 29). It is speculated that the photo-induced holes react with some S ions from CuS/MoS$_2$ catalyst as shown based on the XPS results (Supplementary Fig. 30). Figure 5g summarizes the H$_2$ evolution rates of typical particulate photocatalysts reported to date. The H$_2$ evolution rates were 70,000, 64,426, and 11,090 $\mu$mol h$^{-1}$ g$^{-1}$ in InP/ZnS, PTB7-Th/ET-ODTBR NPs, and 2D/2D NiS/VS-ZnIn$_2$S$_3$/WO$_3$, respectively. They were 23,410 and 16,300 $\mu$mol h$^{-1}$ g$^{-1}$ based on the
COF materials. The CdS-based photocatalysts including 2D NMF/CdS, Cd0.5Zn0.5S-NiSx-Pt, MnOx@CdS/CoP, and CdS/m-TiO2/G achieved a H2 evolution rate of 45,201, 42,600, 23,840, and 950 μmol h⁻¹ g⁻¹, respectively. An H2 evolution rate of 16,600 μmol h⁻¹ g⁻¹ was reported on the Cu SAC-TiO2-Pt photocatalyst. The optimized C3N4-based heterojunction photocatalysts, including GD-CN, Pt-CNPS-NH2, V-CN55, and Pt@Au NRs/C3N4 achieved an H2 evolution rate of 23,060, 37,219, 13,600, and 10,350 μmol h⁻¹ g⁻¹, respectively. In the reports involving vapor phase water, the photocatalytic hydrogen production rates were relatively low, and the leader was 11,090 μmol h⁻¹ g⁻¹ based on the MoS2-TiO2 hybrid. The photothermal–photocatalytic system, i.e., the wood/CuS–MoS2 device, outperforms all of these photocatalysts with an H2 evolution rate of 85,604 μmol h⁻¹ g⁻¹ (i.e., 3271.49 μmol h⁻¹ cm⁻²) without any external assistance, e.g., sacrificial agents, photovoltaic or photoelectrochemical assistance, demonstrating that the photothermal–photocatalytic biphasic system can substantially enhance the photocatalytic hydrogen evolution from water.

Moreover, the photothermal–photocatalytic biphasic system is promising for practical applications because it can easily be realized through the transpiration process of wood loaded with particulate photocatalysts. This natural process converts liquid water to steam under the same light illumination without additional energy input. As an example of a demonstration, the wood/CuS–MoS2 was put in a reaction cell filled with simulated seawater (Supplementary Fig. 31), and the hydrogen collector was connected to the gas outlet. When exposed to natural sunlight, the hydrogen collector exhibits a visible bulge after 2 h of reaction. Although the salts (e.g., NaCl) in the seawater are possible to adhere to wood tunnels to clog the matrix structures, which lead to a decrease in steam production during evaporation, the H2 production rate in this exemplary test is about 37,219 μmol h⁻¹ g⁻¹ (i.e., 1422.38 μmol h⁻¹ cm⁻²) (measured by GC), confirming the strong photocatalytic ability in a seawater environment. And after 6 h of reaction, the H2 production rate remains consistent with that from the first test, exhibiting excellent photocatalytic stability.

Discussion

We have designed and demonstrated an integrated photothermal–photocatalytic system that helps achieve the dominant photocatalytic hydrogen evolution rate of 85,604 μmol h⁻¹ g⁻¹ (i.e., 3271.49 μmol h⁻¹ cm⁻²) among the particulate photocatalysts.
Such excellent performance was achieved by replacing the traditional triphase photocatalytic interfaces (liquid water/photocatalyst solid/hydrogen gas) with the biphasic photocatalytic interfaces (photothermally-generated water steam/photocatalysts loaded on charred wood substrates/hydrogen gas). The wood carrier functions simultaneously as the photocatalyst substrate as well as the steam generator under solar light, which is significantly advantageous for practical applications. This photocatalytic–photocatalytic system reduced the barrier of the water molecule adsorption process and minimized the delivery resistance of the produced hydrogen gas, enabling efficient and environmentally safe fuel for next-generation applications on an industrial scale.

Methods

Synthesis of CoO, MoS2, C3N4, TiO2 and CuS–MoS2 photocatalysts. CoO NPs were fabricated by a heating process with the hydrothermal method and a tube furnace. In all, 2 g of CoCl2·6H2O powder was added to a mixed solution with 8 ml n-octanol and 32 ml ethanol by stirring for 3 h. After that, the mixture was transferred to a 50 ml Teflon-lined stainless steel autoclave, and then heated at 200 °C for 6 h. When the autoclave was cooled down to room temperature, the powders were placed in a quartz tube furnace. The tube was filled to ambient pressure with Ar gas flowing at 240 s.c.c.m. The Ar flow rate and 1 atm. pressure were maintained throughout the preparation process. The tube was continuously heated from 25 °C to 600 °C in 3 h. After maintaining the tube furnace at 600 °C for 200 °C for 6 h. When the autoclave was cooled down to room temperature, the powders were then dispersed in pure water, and the CoO NPs were then centrifuged at 1670 × g for 10 min (Amiotech TGL-15B Centrifuget). After that, the prepared photocatalysts (0.3 g) were added to the surface of the wood substrate loaded on charred wood substrates/hydrogen gas). The wood carrier functions simultaneously as the photocatalyst substrate as well as the steam generator under solar light, which is significantly advantageous for practical applications. The wood/photocatalyst systems were carried out similarly to the triphase reaction measurement. The light-driven reaction was carried out in the quartz cell, and the steam flow rate was used to monitor the solar to steam conversion efficiency.

During the photocatalytic reaction, the gases were transferred into the sample loop by a peristaltic pump and were further quantified by gas chromatography (Shimadzu GC-2014c; Ar carrier gas and molecular sieve-5A column), equipped with a thermal conductivity detector. The hydrogen gas yield of the reactor was measured every 15 min.

The hydrogen evolution in the injected water steam/photocatalyst biphasic system was carried out similarly to the triphase reaction measurement. The reaction was carried out in the quartz cell, and the steam flow rate was used to monitor the solar to steam conversion efficiency. The AQY is calculated based on the formula below:

\[
AQY = \frac{2 \times n \times N_A}{(E + A + T + λ)/(h/λ)} \times 100\%
\]

where \(n\) is the H2 yield, \(N_A\) is the Avogadro number, \(E\) is light intensity, \(A\) is the irradiation area, \(T\) is the time, \(λ\) is the wavelength, \(h\) is the Planks constant, and \(C\) is the speed of light.

The H2O2 concentration was determined through UV–Vis absorption spectra.

\[
\text{H}_2\text{O}_2 = \frac{A_270 - A_235}{A_270 - A_235} \times \frac{0.1}{0.4} \times 0.1 \times 0.01 \text{ mol L}^{-1}
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The coexistence of the liquid water/photocatalysts/hydrogen gas triphase system, 50 ml of deionized water was added to the transparent reactor chamber, and then the filter paper with photocatalysts was taken into the middle of the quartz cell. The steam was injected into the quartz cell, and then the sample loop by a peristaltic pump and were further quantified by gas chromatography (Shimadzu GC-2014c; Ar carrier gas and molecular sieve-5A column), equipped with a thermal conductivity detector. The hydrogen gas yield of the reactor was measured every 15 min.

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The H2O2 concentration was determined through UV–Vis absorption spectra.
The hydrogen and water adsorption energy on various surfaces is defined as:

$$\Delta E_{\text{ads}} = E_{\text{ads}} - E_{\text{gas}}$$

and 

$$\Delta G_{\text{ads}} = \Delta E_{\text{ads}} + \Delta S_{\text{ads}}$$

where $E_{\text{ads}}$ and $E_{\text{gas}}$ are the total energies of the slab model with H and H$_2$O adsorption, $E_{\text{gas}}$ is the energy of a clean slab surface, and $\Delta S_{\text{ads}}$ and $\Delta E_{\text{ads}}$ are that for hydrogen and water molecules.

The Hess equation can be calculated by taking zero-point energy and entropy corrections into account:

$$\Delta H = \Delta H_{\text{gas}} + \Delta H_{\text{ads}}$$

and

$$\Delta G = \Delta G_{\text{gas}} + \Delta G_{\text{ads}}$$

where $\Delta H_{\text{gas}}$ and $\Delta H_{\text{ads}}$ change due to the difference in H and H$_2$O adsorption. The dielectric constant of liquid water and gas water are indexed to be 81 and 1, respectively. At different pH values, $\Delta G_{\text{ads}} = 0.059 \times \rho \cdot H$. The solvent effect is considered through the implicit solvent model based on the VASPsol**. The dielectric constant of liquid water and gas water are indexed to be 81 and 1, respectively. The differences of Gibbs free energy for H and H$_2$O adsorptions, $\Delta G_{\text{ads}}$, are 0.367 kJ kg$^{-1}$ at 298 K and 0.4 kJ kg$^{-1}$ at 373 K, respectively, and the entropy change $\Delta S_{\text{ads}}$ is 0.367 kJ kg$^{-1}$ at 298 K and 0.4 kJ kg$^{-1}$ at 373 K.

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Author contributions
B.W. and X.L. conceived the concept and directed the research. S.G. and X.L. designed the project. S.G. carried out material synthesis and related characterization tests. J.L. gave the results and commented on the paper.

Competing interests
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