Synergistic Modulation between Non-thermal and Thermal Effects in Photothermal Catalysis based on Modified In₂O₃

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doping greatly broadens the radiation response range and enhances the absorption intensity of semiconductors' intrinsic portion, and Cu doping facilitates the absorption of visible-infrared light. The concurrent incorporation of Fe and Cu offers synergistic benefits, resulting in improved radiation response range, carrier separation and migration, as well as higher photothermal temperature upon photoexcitation. Collectively, these advantages comprehensively enhance the photothermal synergistic water-splitting reactivity. The



characterizations under variable temperature conditions have demonstrated that the reaction temperature exerts a significant influence on the process of radiation absorption and conversion, ultimately impacting the non-thermal effect. The results of DFT calculations have revealed that the increasing temperature directly impacts the chemical reaction by reducing the energy barrier associated with the rate-determining step. These findings shine new light on the fundamental mechanisms underlying non-thermal and thermal effect, while also imparting significant insights for photo-thermal-coupled catalyst designing.

KEYWORDS: hydrogen production, photothermal catalysis, synergistic modulation, solar utilization, doped In_2O_3

1. INTRODUCTION

The utilization of solar energy for water splitting and hydrogen production presents a promising approach for harnessing intermittently dispersed solar energy and converting it into solar fuels, which aligns well with the demands of modern energy structures and supports sustainable development efforts, thereby mitigating the energy and environmental crises simultaneously.¹⁻³ Currently, the methods to realize solar hydrogen production can be basically divided into three types: I. Photocatalysis⁴⁻⁶ and photoelectric conversion technology^{7,8} based non-thermal effect of high-energy carriers in the solar radiation; II. Photo-to-thermal catalysis with high temperature generated by radiative thermal effect;⁹ III. A method of photothermal synergistic utilization coupling the non-thermal and thermal effect in the solar radiation.^{1,10,11} The type I mostly uses carriers generated by the excitation of high-frequency photons (ultraviolet-visible light) in semiconductors to directly drive photocatalytic reactions, in which the conditions are mild. The type II uses low-frequency photons to heat the reaction system, and high temperature could be created to overcome the

energy barrier in some reactions such as water splitting. It is much easier to achieve the full-spectrum utilization of solar radiation, but it is often faced with harsh conditions like high temperature and pressure. These conditions impose stringent demands on materials and equipment, leading to inefficient utilization of high-energy photons within the ultraviolet-visible light range. To improve the utilization efficiency of solar energy, more and more attention has been focused on type IIIphotothermal synergistic method.^{12,13}

The non-thermal effect of solar radiation, as elucidated in this study, primarily involves the generation and utilization of highenergy carriers. Meanwhile, the thermal effect is manifested through an increase in system temperature, which may be

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attributed to non-radiative relaxation of semiconductors,^{14,15} localized heating induced by plasma,^{16–18} thermal vibration of molecules,¹⁹ as summarized in our previous work.²⁰ It is noteworthy to distinguish the subtle differences from the definitions of "photochemistry" and "thermochemistry," "photochemical" and "photophysical" effects, and "photochemical" and "photothermal" effects in other studies.^{13,21–24} Obviously, there is currently growing evidence that synergistic mechanisms in non-thermal and thermal effect are of particular interest. Some people started from photocatalytic reactions and tried to elevate the reaction temperature, which has beneficial effects such as enhancing reaction kinetics, improving mass transfer, and promoting the desorption of products or harmful species.²⁵ Some other researchers introduced irradiation into the thermal catalysis process, especially for reactions that require high temperature. It is concluded that light excitation generates highenergy carriers to participate in the reaction, thereby promoting the activation of reactants, reducing the reaction energy barrier, adjusting the reaction paths, and maintaining catalytic activity.²⁰ Nevertheless, thermal and non-thermal effects do not always synergistically promote the reaction. In the photoexcitation process of semiconductors, without effective carrier transfer path, the temperature increased by the thermal effect will accelerate the carrier recombination, which is not conducive to the photothermal synergistic reaction.²⁶ Actually, it is still difficult to directly understand and elucidate the synergistic effect on photothermal problems, especially in the photothermal synergistic reaction system with solar radiation as the only energy source. In this case, there are more sophisticated competitive relationships and synergistic mechanisms between thermal and non-thermal effects, and the relevant research is still insufficient. It is a necessity to make continuous efforts and attempts to clarify the respective characteristics and interplay of thermal and non-thermal effects, design photo-thermal-coupling catalysts to promote the realization of real photothermal synergistic reactions and higher utilization of solar energy.

In this paper, we present our findings on the successful enhancement of the absorption and utilization of various solar radiation effects achieved through the implementation of transition metal double doping. Indium oxide, as one of the most influential catalysts,^{21,27,28} has been previously studied as a potential photocatalyst for water splitting to produce hydrogen.²⁹ Nevertheless, In_2O_3 is a relatively wide bandgap n-type semiconductor that leads to the rapid recombination of photogenerated charge carriers. It is been reported that strategies such as doping transition metals can effectively tune the bandgap of semiconductors to facilitate light absorption.³⁰ While composite or multifunctional catalysts have been widely explored to achieve prominent photothermal catalysis, there remains a gap in the development of pure and simple catalysts with comparable performance. In any case, a simple preparation method with high overall catalytic performance is the goal. Here, we designed a straightforward materials synthesis method and specifically explored the modification of transition metals Fe and Cu, which resulted in significant enhancements of both nonthermal and thermal effects of irradiation on the surface of In_2O_3 -based catalysts. It was found that both Fe doping and Cu doping promoted the absorption of solar radiation, albeit with varying effects on different wavelength ranges of light. Fe doping extended the radiation response range, leading to enhanced nonthermal effect. Cu doping facilitated the absorption of visibleinfrared light, which was beneficial to the thermal effect and improves the material's photothermal temperature. These

differences are also reflected in the water splitting reaction under different experimental conditions. Fe and Cu double doping coupled the advantages of both, that is, the Fe&Cu- In_2O_3 material with excellent irradiation non-thermal effect and thermal effect was successfully prepared. High photothermal temperature and reactivity in the radiation-driven reaction system were achieved. Furthermore, the impacts of non-thermal and thermal effect on light absorption conversion and target reaction were studied. The reaction temperature played a crucial role in radiation absorption as well as the separation and mobility of photogenerated carriers, consequently affecting the non-thermal effect of radiation. Density functional theory (DFT) calculations further confirmed that the elevating temperature directly influenced the chemical reaction by reducing the energy barrier of the rate-determining step (RDS).

2. EXPERIMENTAL SECTION

2.1. Preparation of the Materials. All chemicals used throughout the experiments were of analytical grade and were purchased and used without further purification. Fe and Cu doped In₂O₃ were synthesized using a solid phase synthesis method. The doping ratio of transition metal in In_2O_2 is 1%. Typically, as for Fe-doped In_2O_2 sample, a certain amount of $Fe(NO_3)_3$ ·9H₂O and InCl₃ were thoroughly mixed with urea in a ceramic crucible, maintaining a mass ratio of $InCl_3/CO(NH_2)_2 =$ 1:10. The crucible was then covered and placed in a muffle furnace, heated to 423.15 K, and held at this temperature for 6 h. Subsequently, the samples were cooled to room temperature and subjected to alternate washing with deionized water and ethanol. If no precipitation was observed upon dropwise addition of AgNO₃ solution to the washed clear liquid, the samples were placed in a muffle furnace and heated to 823.15 K and kept for 4 h. Following calcination, the samples were washed and dried, and then ground to a particle size of 200-mesh to obtain the prepared Cu-doped In₂O₃ sample. For the synthesis of Cu doped and Fe & Cu co-doped In2O3, the Fe(NO3)3.9H2O were replaced by $Cu(NO_3)_2 \cdot 3H_2O$ or the mixture of $Fe(NO_3)_3 \cdot 9H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$ without any other changes. The pure In₂O₃ sample was prepared using the same method without any precursor of transition metal. The samples were denoted as Fe-In₂O₃, Cu-In₂O₃, and Fe&Cu-In₂O₃ for Fe-doped, Cu-doped, and Fe-Cu co-doped In₂O₃, respectively.

2.2. Characterizations of the Materials. X-ray diffraction (XRD) patterns were obtained with a Cu-K α radiation source (K α = 1.54056 Å) operated at 40 kV and 100 mA. Field emission scanning electron microscopy (SEM) images were captured using a Hitachi SU-8010 with an Oxford X-max80 X-ray spectrometer. The light absorption characteristics of the materials were investigated using UV-visible diffuse reflectance spectroscopy (UV-visible DRS) performed with Shimadzu UV-2600i and UV-3600 spectrophotometer (200-1400 nm). Photoluminescence (PL) emission spectra, indicative of electron-hole pair (EHP) recombination in the prepared catalysts, were collected at room temperature on an Edinburgh Instruments FLS 920 instrument with 405 nm excitation light. X-ray photoelectron spectroscopy (XPS) analysis was conducted using a Thermo Scientific K-Alpha spectrometer from Thermo Fisher Scientific. All binding energies were referenced to the C 1s peak (284.80 eV), which served as a reference for determining the adventitious carbon content in the test sample preparation. A Hitachi's HT-7700 120 kV Transmission Electron Microscope (TEM) was used to get the TEM images, and energy dispersive spectroscopy signals were collected by Oxford X-MAXⁿ65-T. Electron paramagnetic resonance (EPR) signals were obtained using an A300 X-band EPR spectrometer produced by Bruker. X-ray absorption fine structure (XAFS) measurements were commissioned at Canada Light Source (CLS) and the data were acquired from the fluorescence signal.

All electrochemical characterizations were conducted using an IVIUMSTAT electrochemical interface in a conventional threeelectrode cell configuration. A platinum plate and an Ag/AgCl/3.5 M KCl electrode were used as counter and reference electrodes. 1 M



Figure 1. XRD patterns between (a) $10-80^{\circ}$ (before and after reaction); (b) $28-33^{\circ}$ and TEM images of (c) In_2O_3 , (d) Fe- In_2O_3 , (e) Cu- In_2O_3 , and (f) Fe&Cu- In_2O_3 .

 Na_2SO_4 solution was employed as the electrolyte, respectively. The ITO loaded with the respective sample was clamped on the platinum sheet electrode clamp serving as a working electrode. The quartz electrolytic cell was positioned on a heater equipped with a K-shaped thermocouple, and a 365 nm LED served as the light source. All tests were carried out at room temperature unless otherwise specified.

2.3. Photothermal Catalysis (PTC) Experiments. 50 mg of samples were ultrasonically dispersing in 7 mL deionized water to form a suspension. Then, the suspension was quickly poured onto a preheated quartz plate and dried at 353.15 K to obtain a catalyst film on the quartz plate. Prior to the reaction, the catalyst film was put into the reaction system and the system was purged with pure argon (Ar) gas to remove any residual impurities. Two types of PTC systems were used in this study to evaluate the performance of all samples, as illustrated in Figures S1 and S3. In the auxiliary heating photothermal catalysis reaction system (abbreviated as AHS), the reaction temperature was controlled by electric auxiliary heating, and a xenon lamp equipped with a short pass filter was used as the light source (spectral distribution can be seen in Figure S2a). A cylindrical stainless-steel reactor with a quartz lining (with a volume of approximately 200 mL) was used for water splitting reaction.

At the beginning of the PTC experiment, Ar gas was fed into the reactor at a flow rate of 100 mL/min for 10 min to remove the residual gas from the reactor. Subsequently, the reactor was heated to the predetermined experimental temperature. Once the desired temperature was reached and stabilized, the gas valve on the reactor was closed, and a specific amount of deionized water was injected into the reactor. Then the xenon lamp was to illuminate the samples for 1 h through the quartz lens. After illumination, the gas valve was opened, and the gaseous products were detected using a gas chromatograph (Agilent 8890 A).

As depicted in Figure S3, the photo-driven photothermal catalysis reaction system (abbreviated as PDS) was constructed using quartz, and the only energy source in this system was a full spectrum xenon lamp (spectral distribution can be seen in Figure S2b). The reaction temperature was maintained by the thermal effect of light irradiation on the catalyst film. The catalyst film was placed on the quartz bracket and the deionized water was placed at the bottom of the quartz reactor. After purging the system with 50 sccm of Ar, the flow rate was adjusted

to 4 sccm, and the xenon lamp was turned on. Once the temperature stabilized, the gas flowing through the reactor was detected by the gas chromatograph.

2.4. Computational Methods. DFT calculations^{31,32} were conducted to determine the reaction energetics, perform charge analysis, and further investigate the reaction mechanism. All spin polarization calculations were performed with the Perdew-Burke-Ernzerhof function of the generalized gradient approximation using the Vienna ab initio simulation package (VASP).³³ The projector augmented wave method was used to represent the core-valence electron interaction with electrons, explicitly including the H 1s; O 2s and 2p; In 5s and 5p; Fe 3p, 3d, and 4s; and Cu 3p, 3d, and 4s shells. The empirical correction in DFT-D3 method with Becke-Jonson damping was used for long-range dispersion corrections.³⁴ The valence electronic states were expanded in plane wave basis sets with an energy cutoff of 400 eV. The integration in the Brillouin zone was performed on a $3 \times 3 \times 1$ *k*-point grid sampled with the Gamma-centered scheme. The convergence threshold for the self-consistent-field iteration was set to 10⁻⁴ eV. Geometric optimizations were considered converged when the force components were less than 0.01 eV/Å. A Bader charge analysis was performed for a qualitative analysis of the charge state of atoms.

Combined with the following XRD results (Figure 1) and surface energy calculations (Table S1), a cubic $In_2O_3(222)$ surface with a threelayer-thick slab was constructed into a 4×2 surface supercell (In₄₈O₇₂) as the calculation model, which was denoted cIn_2O_3 (Figure S4). The top two layers were allowed to relax during optimization, and a 15 Å vacuum layer was set along the surface normal direction to minimize the interaction between periodic images. Dipole correction was applied for calculations involving the slab geometry. Models of Fe doped, Cu doped, and Fe & Cu co-doped In2O3 (abbreviated as Fe-cIn2O3, CucIn₂O₃, and Fe&Cu-cIn₂O₃, respectively) were built to simplify the calculation and discuss the effect of different transition metal doping in In_2O_{32} as can be seen in Figure S5. The effect of temperature on the photothermal catalytic reaction was investigated by calculating the Gibbs free energy (ΔG) of the intermediates under different reaction conditions, and the zero-point energy was also calculated to further correct the total energy.



Figure 2. (a) XPS full spectrum on all samples; fine XPS spectrum of (b) In 3d and (c) O 1s on all samples; (d) Cu 2p and (e) Cu AES on Cu-In₂O₃; (f) Fe 2p on Fe-In₂O₃; (g) Cu 2p, (h) Cu AES, and (i) Fe 2p on Fe&Cu-In₂O₃.

3. RESULTS AND DISCUSSION

3.1. Crystal Structure and Morphology. Various characterization techniques were used to investigate the crystal structure and morphology of the materials before and after PTC. XRD analysis was used to determine the crystal structure of In_2O_3 , and the results are presented in Figure 1a,b. In all In_2O_3 samples, six distinct diffraction peaks at 21.5, 30.6, 35.5, 45.7, 51.0, and 60.7° can be attributed to (221), (222), (400), (431), (440), and (622) crystal face of cubic In_2O_3 , respectively, in accordance with the standard card of PDF#06-0416. Notably, there was no impurity detected in these XRD patterns. Moreover, the lack of Fe- or Cu-related diffraction peaks indicated the absence of new crystal surfaces created by transition metals, which was attributed to the low content of transition metals and the relatively dispersed surface of the material. A comparison of the samples before and after the PTC reaction revealed no significant changes, suggesting that all samples are stable during the PTC process.

As depicted in Figure 1b, a careful analysis of the main peaks at 30.6° corresponding to the (222) crystal face of Fe-In₂O₃, Cu-In₂O₃, and Fe&Cu-In₂O₃ revealed a red shift compared to pure In₂O₃. According to the Prague equation (2d sin $\theta = n\lambda$), red shifts of the diffraction peaks suggest that small-radius ions (Cu²⁺ and Fe³⁺) have been successfully incorporated into the

lattice of In₂O₃ by replacing In³⁺ ions, resulting in the shrink of the lattice spacing.³⁵ In the images of TEM of In_2O_3 , Fe-In₂O₃, Cu-In₂O₃, and Fe&Cu-In₂O₃ (shown in Figure 1c-f), clear and distinct chiaroscuro lattice stripes can be observed with the spacing of 0.293, 0.292, 0.293, and 0.291 nm, respectively, corresponding to the (222) face of In_2O_3 , which agree with the calculated results from XRD (2.933, 2.922, 2.929, and 2.916 Å). Moreover, the grain size of In₂O₃, Fe-In₂O₃, Cu-In₂O₃, and Fe&Cu-In₂O₃, as determined by Scheller equations, was found to be 42.45, 39.14, 34.33, and 35.74 nm, respectively, which is consistent with the results obtained from SEM as shown in Figure S6. The Fe and Cu doping slightly reduced the grain size, shortening the distance for EHP migration from the bulk to the surface, which might enhance the photo response in PTC. Qualitative analysis of element distribution using TEM mapping, as shown in Figure S7, revealed that in addition to In and O elements, transition metal elements (Fe and Cu) were uniformly dispersed in Fe-In2O3, Cu-In2O3, and Fe&Cu-In2O3 samples, indicating successful doping of Fe and Cu into the In_2O_3 lattice.

3.2. States of Surface Element. The composition and element states of materials play a crucial role in determining their photo response and processing of chemical reaction. Before as shown in Figure 2a, the full spectrum analysis of all samples revealed no significant peaks corresponding to impurity



Figure 3. (a) The normalized Cu-edge K-edge XANES spectra and (b) the Fourier transforms of EXAFS spectra of Cu-In₂O₃ and Fe&Cu-In₂O₃.

elements, except for In, O, transition metals, and the calibration element carbon. In the case of Cu-In₂O₃ and Fe&Cu-In₂O₃, the presence of Cu 2p orbital signal at 930 eV confirmed the successful doping of Cu into the samples. However, the signal of Fe 2p orbital was difficult to distinguish due to its close proximity in energy to the In 3p signal, which falls in the range of 660-700 eV. This overlapping of signals might be the reason behind the obscured Fe 2p signal, as it is likely masked by the dominant In signal. A detailed XPS fine spectrum analysis was conducted to further investigate the valence composition of transition metal elements in the doped samples. As shown in Figure 2b, the In 3d signal exhibited two obvious peaks at 444.3 and 451.8 eV, which can be attributed to In $3d_{5/2}$ and In $3d_{3/2}$, respectively, corresponding to $1n^{3+}$ in $1n_2O_3$. orbit (shown in Figure 2c), two peaks at 529.6 and 531.3 eV were associated with lattice oxygen and chemical absorption oxygen.³⁸ As compared to pure In_2O_{3} , a slight shift of the signal can be observed in both In 3d and O 1s orbits representing the electron transfer after doping, which might be attributed to the stronger electronic binding capability for the transition metals than that of In and the formation of Fe-O-In or Cu-O-In bonds, resulting in the offset of electronic cloud.³⁹ Furthermore, the offset of the electronic cloud can have an impact on the formation energy of oxygen vacancy (V_0) and, subsequently, influence the photo response. Notably, the incorporation of Cu into In_2O_3 , as shown in Figure 2d, is evident by the presence of peaks at 932.9 and 952.6 eV corresponding to $2p_{3/2}$ and $2p_{1/2}$ of $Cu^{0/+}$, and peaks at 934.6 and 955.2 eV corresponding to the $2p_{3/2}$ and $2p_{1/2}$ orbitals of Cu^{2+} .⁴⁰ Additionally, the presence of a satellite peak at around 942 eV in the Cu 2p XPS spectrum also confirms the successful doping of Cu in In_2O_3 .

To further investigate the state of Cu element, auger electron spectroscopy (AES) patterns were analyzed due to the close binding energy of Cu⁺ and Cu⁰. As shown in Figure 2e, peaks at 914.5 and 917.9 eV can be assigned to the rotational energy levels of Cu⁺ and Cu^{0/2+}, respectively.⁴¹ It is worth mentioning that XPS is a surface detection method, and the stronger peaks of Cu⁺ may be attributed to the surface Cu species with charge compensation or incomplete pairing. It is possible that the majority of Cu ions have doped deep into the lattice of In₂O₃, resulting in weak signals of Cu²⁺ in both XPS 2p and AES. In the case of Fe 2p orbital analysis (Figure 2f), the Fe 2p signal is partially obscured by the signal of In 3p, which is the main element of In₂O₃.

However, a discernible peak attributed to $Fe^{3+} 2p_{3/2}$ is still observable near 710 eV, providing evidence for the incorporation of Fe into the In₂O₃ catalyst. The Fe 2p signal is relatively weak and indistinct, and the EPR test was performed to further analyze the composition of transition metal elements (Fe and Cu) in the doped samples. The results of EPR test were presented in Figure S8. In both Fe-In₂O₃ and Fe&Cu-In₂O₃ samples, an obvious absorption peak is observed at approximately g = 4.21. This suggests the presence of Fe³⁺ ions, and Fe atoms have been incorporated into the body-centered cubic lattice of In₂O₃ through substitutional doping.^{42,43} Notably, no noticeable absorption peak is observed near g = 1.99, indicating that the Fe element did not gather in the form of Fe_2O_3 .⁴⁴ This finding aligns with the conclusion that Fe primarily exists in the doped form, with limited presence of iron oxides. In the case of Cu-In₂O₃, a clear absorption peak is observed around g = 2.10, confirming the presence of Cu²⁺ ions,⁴⁵ which is consistent with the XPS results. In Fe&Cu-In₂O₃, absorption peaks corresponding to the transition metals Fe3+ and Cu2+ are observed at approximately g = 4.21 and g = 2.10, respectively, providing further evidence of the dual transition metal doping in Fe&Cu- In_2O_3 .

The XPS spectrum of transition metal elements for Fe&Cu-In₂O₃ sample is presented in Figure 2g. For Cu element, only the binding energy belonging to $Cu^{0/+}$ can be observed in the XPS fine spectrum, while the existence of Cu⁺ can be observed in the Auger spectrum (shown in Figure 2h). This suggests that Cu tends to be doped into In₂O₃ at the surface in a lower valence state. The absence of Cu²⁺ element signals may be attributed to the small amount of Cu doped during the preparation process and the fact that Cu^{2+} elements tend to exist inside the In_2O_3 lattice. In addition, in the Fe&Cu-In₂O₃ sample, the 2p orbital signal of Fe element is also seriously overlapped by the 3p orbital of In element (shown in Figure 2i). Nevertheless, a weak but still discernible peak attributed to $Fe^{3+} 2p_{3/2}$ is observable near 710 eV. This finding, in combination with the results obtained from EPR analysis, suggests that the Cu and Fe co-doped sample was successfully prepared. Comparison of the XPS spectra of transition metal elements before and after the reaction reveals no significant changes in the valence state of the elements and the ratio of different valence states. This further indicates that the doping of Cu and Fe does not compromise the stability of the catalysts in the photothermal synergistic reaction. This observation is consistent with the phenomenon that all materials



Figure 4. Photothermal catalytic water splitting reaction yield performed in the (a) AHS, (b) PDS, and (c) Fe&Cu- In_2O_3 samples in PDS with 600 nm cut-off filter.



Figure 5. (a) UV-vis DRS spectra (inset: determination of the optical band gap) and (b) PL spectra and TRPL spectra of (c) the In_2O_3 , (d) Fe- In_2O_3 , (e) Cu- In_2O_3 , and (f) Fe&Cu- In_2O_3 .

exhibit stable H₂ yields in the photothermal synergistic reaction experiments.

The XAFS (XANES/EXAFS) techniques were employed to further explore the local structures and the states of transition metal elements in doped samples. The normalized Cu K-edge XANES spectra of Cu-In₂O₃ and Fe&Cu-In₂O₃ are shown in Figure 3a. Both spectra show similar shapes, indicating similar chemical states of Cu in these two samples. When compared with the spectra of Cu-foil, Cu₂O, and CuO, noticeable differences can be observed, suggesting distinct chemical and crystal states of Cu in Cu-In2O3 and Fe&Cu-In2O3 as compared to Cu metal and Cu oxides. Moreover, the absorbing edge positions of Cu-In2O3 and Fe&Cu-In2O3 are closest to that of CuO, indicating a tendency for Cu to exist as Cu^{2+} in In_2O_3 samples.⁴⁶ An evident pre-edge peak is also observed at around 8970 eV, which might arise from electric dipole transitions between core shell orbitals and hybrid orbital, and this absorption intensity is influenced by the asymmetry lattice structure of the core element (Cu).⁴⁷ Interestingly, in Fe-doped samples, as shown in Figure S9a, these pre-edge peaks are also

observed (see details in Supporting Information), suggesting that the transition metal (Fe) may enter the lattice of In_2O_3 and induce lattice distortion.

As demonstrated in Figure 3b, the EXAFS analysis yields similar results, that Cu elements are in similar chemical and crystal conditions in Cu-In2O3 and Fe&Cu-In2O3, suggesting that the doping of the second transition metal (Fe) has minimal influence on the first one (Cu), and that the same doping element may show similar properties in both single- and doubledoped samples. At bond lengths about 1.5 and 3.4 Å, two obvious peaks corresponding to Cu-O and Cu-In are observed, which are closer to In-O and In-In bonds in pure $In_2O_3^{48}$ than Cu–Cu and Cu–O bonds in Cu metal or oxides. Similar bond lengths are also observed for Fe in both Fe-In₂O₃ and Fe&Cu-In₂O₃ (Figure S9b). These indicate that the transition metals were incorporated into the lattice of In2O3 with the formation of Cu-O-In and Fe-O-In bonds. Moreover, the ARTEMIS programs of IFEFFIT have been utilized to fit the EXAFS data. The fitting was done for $\chi(R)$ between R = 1-4 Å, including Cu–O, Cu–In, Fe–O, and Fe–



Figure 6. Mott-Schottky plots of In₂O₃, Fe-In₂O₃, Cu-In₂O₃, and Fe&Cu-In₂O₃ tested at (a) 1000 and (b) 3000 Hz.

In correlations. Figure S10a,b, respectively, shows the Fourier transforms curves of Cu K-edge, Fe K-edge EXAFS spectra for Fe&Cu-In₂O₃, along with the best fitting results, which also clearly shows the two obvious peaks of Cu (Fe)-O and Cu (Fe)-In. The obtained best fitting parameters (Table S3) provide valuable insights into the local coordination environments of Cu and Fe in Fe&Cu-In₂O₃. The first nearest neighbor around Cu or Fe are oxygen atoms fitting with 3 and 6 coordination numbers, respectively, with Cu-O bond lengths of 1.97 Å to Fe-O bond lengths of 1.99 Å. The near edge data for Cu and Fe resemble those of CuO and Fe₂O₃, indicating the oxidation states of Cu²⁺ and Fe³⁺ in the doped sample. However, for Cu or Fe oxide compounds, the second nearest neighbor is Cu-Cu or Fe-Fe, respectively, which is different with the doped sample that the second nearest neighbor can be Cu–In (3.28 Å), Fe–In (3.67 Å), exhibiting 6 coordination numbers. These observations align with prior studies on Fe and/or Cu-doped In_2O_3 .^{49,50} The combination of XAFS results, TEM data, XRD patterns, XPS spectra, and EPR results collectively suggests that Cu and/ or Fe atoms are incorporated into the ${\rm In^{3+}}$ sites within the ${\rm In_2O_3}$ lattice.

3.3. Performance of PTC Experiments. For all In₂O₃ samples, PTC water splitting reactions were performed in two different reaction systems, auxiliary heating system (AHS) and photo-driven system (PDS), as shown in Figures S1 and S3. In the AHS, all samples were tested at temperatures of 473.15, 523.15, 573.14, and 623.15 K, respectively. As the temperature increased, the hydrogen yields showed a significant enhancement, with the highest H₂ production observed at 623.15 K, which is also the maximum temperature that the reaction system can reach. At this temperature, the H₂ yields for In_2O_3 , Fe- In_2O_3 , Cu-In₂O₃, and Fe&Cu-In₂O₃ were found to be 16.1, 25.6, 10.3, and 28.6 μ mol·g⁻¹·h⁻¹, respectively, as shown in Figure 4a. This can be ascribed to several factors according to the subsequent characterizations. The temperature rise contributes to enhanced light absorption, as evidenced by the results depicted in Figure 9a. Additionally, it leads to a reduction in the recombination of photogenerated carriers, as illustrated in Figure 9b-d. Furthermore, the elevated temperature effectively lowers the energy barrier for the RDS in the reaction process, as demonstrated in Figure 11. Moreover, when comparing different samples, it was observed that Fe-In2O3 and Fe&Cu-In2O3 showed superior performance at the same temperature, while $Cu-In_2O_3$ exhibited a lower H_2 yield compared to In_2O_3 . This



Figure 7. Band structure of $\rm In_2O_3,~Fe-In_2O_3,~Cu-In_2O_3,~and~Fe&Cu-In_2O_3.$

observation aligns with their respective absorption intensities in the UV short-wavelength region, as shown in Figure 5a. It suggested that the change of short-wavelength light absorption intensity caused by Fe or Cu doping significantly affects the water splitting reaction. In this system, temperature was controlled as a variable, and the H₂ yield showed a clear positive correlation with short-wave light absorption intensity, also indicating that short-wave light may dominate the reaction processing. In the meantime, temperature showed an influence on H₂ production, which suggested that in real solar energy utilization systems, the thermal effect of solar energy could have a great impact on the reaction rate.

To explore the comprehensive utilization of solar non-thermal and thermal effects on all samples, a series of experiments were performed in the PDS using a full-spectrum xenon light as the only energy source. Throughout the experimental procedure, the xenon light power was adjusted, and the surface temperature of the catalyst and the rate of hydrogen production during the reaction were measured and recorded, the results are shown in Figure 4b. For all samples, both the H₂ yields and the temperature were increasing with rising light intensity. Specifically, In₂O₃, Fe-In₂O₃, Cu-In₂O₃, and Fe&Cu-In₂O₃, all obtained the highest yield at the highest light intensity tested (3.63 W/cm²), with values of 3.78, 3.95, 1.27, and 6.59 μ mol· g⁻¹·h⁻¹, respectively. Furthermore, the photo-to-thermal conversion temperature at the same light intensity followed



Figure 8. (a) EIS and (b) transient photocurrent results of In₂O₃, Fe-In₂O₃, Cu-In₂O₃, and Fe&Cu-In₂O₃,



Figure 9. (a) UV-vis-NIR DRS spectra; (b) PL spectra; (c) EIS and (d) transient photocurrent results of Fe&Cu-In₂O₃ tested at different temperatures.

the order of Fe-In₂O₃ < In₂O₃ < Fe&Cu-In₂O₃ < Cu-In₂O₃, which is consistent with the long-wavelength light absorption intensity, indicating that long-wavelength light contributes significantly to the photo-to-thermal conversion temperature. Similar to the results obtained in the AHS, Cu-In₂O₃ showed the lowest H₂ yields. This could be attributed to the suppression of short-wavelength light absorption caused by Cu doping. Additionally, the narrow band gap and low conduction band position of Cu-In₂O₃, as illustrated in Figure 7, may thermodynamically hinder the water splitting reaction, thereby

further contributing to the observed lower H_2 yields. While the H_2 production rate of Fe-In₂O₃ showed an obvious decline, even falling below that of pure In₂O₃. This might be attributed to the reduction in long-wavelength light absorption caused by Fe doping, leading to lower reaction temperatures and ultimately limiting the PTC water splitting reaction. Regarding Fe&Cu-In₂O₃, the synergistic enhancement of absorption due to Fe doping at shorter wavelengths and Cu doping at longer wavelengths leads to the highest H_2 yields in both AHS and PDS, as well as achieving elevated temperatures in PDS.



Figure 10. The reaction energy profiles of two reaction paths on (a) cIn_2O_{31} (b) Fe- cIn_2O_{32} (c) Cu- cIn_2O_{32} and (d) Fe&Cu- cIn_2O_{32} .

In the PDS system, to elucidate the contributions of thermal and non-thermal effects in the PTC reaction, a combination of xenon light with a 600 nm cut-off filter and a 365 nm LED light was employed to drive the water splitting reaction on Fe&Cu- In_2O_3 . In this reaction system, the photons with the wavelength greater than 600 nm do not possess enough energy to excite the catalysts for non-thermal effects, and the thermal effect of the LED light is comparatively restricted. Hence, it can be considered that the non-thermal effect all come from the LED light, and the filtered xenon light only affects the reaction through the thermal effect. As depicted in Figure 4c, a noticeable decline in temperature was observed upon the application of filtered xenon light, concomitant with a substantial reduction in H₂ yield to negligible levels. As the intensity of LED light increased, the H₂ yields also increased, providing further evidence that the water splitting reaction is predominantly driven by short-wavelength light-excited EHPs, while temperature elevation is facilitated by full-spectrum light.

3.4. Radiation Absorption Properties: Optical Performance and Electrochemical Characterizations. In an ideal solar fuel production system, solar energy serves as the primary energy source for both fuel production and thermal energy output, making the photo response of the material a critical factor in solar energy utilization. UV-vis DRS was used to investigate the optical absorption properties of all In₂O₃ samples, as shown in Figure 5a. In₂O₃ exhibited a broad absorption range from 200 to 600 nm, which could be attributed to the intrinsic absorption characteristics of the semiconductor. Within this range, the semiconductor can be excited by photons, generating EHPs for the water splitting reaction. After transition metal doping, the absorption edges displayed an apparent redshift, indicating a narrowing of the band gaps (E_g) of In_2O_3 . The band gaps of all samples were further calculated by the Kubelka–Munk function (inset of Figure 5a). Specifically, the band gaps of In₂O₃, Fe-In₂O₃, Cu-In₂O₃, and Fe&Cu-In₂O₃ were 2.87, 2.73, 2.41, and 2.67 eV, respectively. This suggests that the transition metal doping effectively narrows the band gap of In_2O_3 , with Cu doping showing a better performance than Fe doping. A narrower band gap signifies that the material is capable of absorbing more short-wave light, thereby providing more energy for the water splitting reaction. However, upon examining the absorption intensity within a range shorter than 400 nm, Cu doping was observed to suppress light absorption, while Fe doping enhanced it. For short-wave light absorption, Cu doping showed an extension on light response range but a suppressed intensity. In contrast, Fe doping showed enhancement in both range and intensity, indicating that Fe-In₂O₃ may have a better water splitting reaction performance due to better light response.

The majority of absorbed solar energy that is not converted into chemical energy will be converted to thermal energy, resulting in an increase in the temperature of the solar energy utilization system. Therefore, the absorption of long-wavelength light has a significant influence on the photo-to-thermal conversion performance. In this spectrum, different transition metals show totally different performance. Cu doping shows an obvious enhancement in the long-wavelength spectrum, which could be attributed to d-d electron transfer⁵¹ and the presence of defect sites (such as V_0).^{52,53} For Fe&Cu-In₂O₃ sample, the short- and long-wavelength spectrum absorption were enhanced simultaneously, indicating that this sample may possess superior water splitting performance, while also exhibiting a higher photo-to-thermal conversion temperature.

After EHPs were generated, the recombination greatly impacted the efficiency of the water splitting reaction. PL spectroscopy was used to explore the recombination of photoinduced EHPs. All In₂O₃ samples were examined in the region from 450 to 750 nm under 405 nm light excitation at room temperature. As shown in Figure 5b, a wide PL signal was observed for In2O3, Fe-In2O3, Cu-In2O3, and Fe&Cu-In2O3 samples. An obvious and similar peak can be observed at about 550 nm for all samples, indicating that In_2O_3 can be excited by 405 nm light to produce EHPs and the doping of transition metals did not significantly alter the recombination behavior of In₂O₃. For Cu-In₂O₃ and Fe&Cu-In₂O₃, a weaker peak was observed at approximately 550 nm, demonstrating that Cu doping can reduce the recombination rate of EHPs and improve the light response of the materials. As for Fe doping, the PL signal also showed a decrease but the decline was not that obvious.

To explore the photoinduced EHP lifetime, time-resolution photoluminescence (TRPL) spectra were acquired under the excitation of a 405 nm laser, as shown in Figure 5c-f. The emission lifetimes were calculated by double exponential fitting, and the functions were shown in Supporting Information. In the case of the Cu-In₂O₃ sample, the emission lifetimes (τ_{av} = 52.57 ns) were much longer than that of pure In_2O_3 ($\tau_{av} = 2.56$ ns) and Fe-In₂O₃ (τ_{av} = 5.35 ns). Notably, the Fe&Cu-In₂O₃ sample showed the longest emission lifetime (τ_{av} = 58.94 ns) among all the samples, which is one order of magnitude higher than that of In_2O_3 and Fe-In₂O₃. The doping of transition metals may introduce impurity energy levels into the bang gap of In_2O_3 . The suitable impurity energy levels can serve as capture centers for photogenerated electrons that will significantly extend the lifetime of EHPs. The better performance of Cu doping might be attributed to the fact that Fe has a closer valence to In than Cu doping, resulting in less influence on the electron cloud.

Electrochemical tests were conducted to further study the band structure, and the Mott–Schottky curves of the materials were tested at frequencies of 1000 and 3000 Hz. The results are shown in Figure 6. The slopes of the straight lines for all samples were found to be positive, indicating that the In_2O_3 samples modified by transition metal still exhibited n-type semiconductor behavior. According to the Mott–Schottky equation in Supporting Information, the material's carrier density is negatively correlated with the slope of the straight line. Fe doping and Cu doping have different effects on the carrier density, in which Fe doping increased the carrier density of the semiconductors, whereas Cu doping showed an adverse effect.

Furthermore, the flat band potentials of In₂O₃, Fe-In₂O₃, Cu- In_2O_3 , and Fe&Cu-In_2O_3 were calculated to be -0.38, -0.45, -0.27, and -0.44 eV (vs Ag/AgCl), namely -0.17, -0.24, -0.06, and -0.24 eV (vs NHE). Combined with the results of the diffuse reflectance absorption spectrum (DRS) and the flat band potential, the conduction band potential can be estimated,⁵⁴ and then the band structure of the catalysts can be obtained. As shown in Figure 7, In₂O₃ exhibited a suitable band structure. Moreover, transition metal doping was found to significantly shorten the band gap, thereby expanding the photoresponse range and providing more EHPs for driving chemical reactions. Additionally, transition metal doping also had an impact on the conduction band position. Fe doping made the conduction band position more negative, shortening the band gap of In₂O₃ and improving the reduction ability of photogenerated electrons, which might be an important factor to promote the water splitting reaction. While Cu doping shortened the band gap most significantly, making it have the highest photothermal temperature, which can be explained by several factors. The introduction of Cu dopant results in increased absorption of a wider range of solar radiation, including both visible and near-infrared regions, as shown in Figure 5a. The modified electronic band structure of Cu-doped sample facilitates efficient charge carrier generation upon photon absorption, more electrons are excited by the absorbed photons from the valence band to the conduction band. After being excited to higher energy states, the generated charge carriers undergo relaxation processes such as non-radiative recombination, where they lose excess energy and reach thermal equilibrium with the lattice. The transfer of energy from charge carriers to the lattice vibrations generates phonons, which represent thermal energy. These processes may contribute to the conversion of photogenerated charge carriers into thermal energy, leading to a higher photothermal temperature by Cu doping. However, in the meanwhile, the position of conduction band moved down apparently, becoming very close to the hydrogen potential of water splitting. This weakened the reducibility of the electrons generated by photoexcitation, which is not conducive to the decomposition of water and hydrogen evolution. It can be concluded that although Cu doping alone had the broadest photo-response range, it showed poor activity in the photothermal synergistic water splitting reaction due to the weakened reducibility of photogenerated electrons. Fe and Cu double doping combined the advantages of Fe doping and Cu doping, which not only shortened the bandgap but also maintained a relatively negative conduction band position. This allowed Fe&Cu-In₂O₃ to respond to wider solar spectrum under the same illumination conditions, while also being able to generate photogenerated carriers that were suitable for water splitting.

Electrochemical impedance spectroscopy (EIS) and transient photocurrent experiments were performed to further investigate the carrier characteristics of In2O3, Fe-In2O3, Cu-In2O3, and Fe&Cu-In₂O₃. As shown in Figure 8, transition metal Fe or Cu doping reduced the carrier transfer resistance in In₂O₃, which is favorable for the water splitting reaction. Moreover, the Fe&Cu- In_2O_3 sample has the smallest transfer resistance, indicating the synergistic effect of Fe and Cu doping. Transient photocurrent measurements were performed using a 365 nm LED lamp as the excitation light, the current density increased significantly upon light illumination, indicating that the light excited the semiconductor to generate photogenerated carriers and photocurrent through the external circuit, while the rapid recombination of EHPs after turning off the light caused an instant drop in photocurrent. All samples produced significant photocurrents under illumination, and the photocurrent intensity was related to the light absorption intensity of the samples near 365 nm in the UV-vis-NIR DRS spectrum. Concretely, Fe-In₂O₃ had the strongest light absorption and showed the highest photocurrent intensity, while Cu-In₂O₃ showed the weakest photocurrent due to its relatively low light absorption near 365 nm. Moreover, although pure In_2O_3 had better light absorption than Cu- In_2O_3 , its photocurrent was close to that of Cu-In₂O₃ due to higher carrier recombination. The Fe&Cu-In2O3 sample exhibited a higher photocurrent intensity owing to its improved light absorption and reduced photocarrier recombination.

3.5. Impact of Thermal Effect on Solar Radiation Absorption. In the photothermal synergistic reaction, solar radiation increases the surface temperature of the catalyst through the thermal effect, thereby facilitating the reaction progress by coupling the non-thermal and thermal effect. However, the underlying mechanisms remain unclear and controversial. To explain the increase in final product yields with the elevating temperature, here the effects of temperature on the radiation absorption conversion of Fe&Cu-In₂O₃ were investigated. The absorption spectra at different temperatures are revealed in Figure 9a. As the temperature increases, the basic shape of the light absorption curve does not show noticeable change, indicating that the radiation response of the material has not changed fundamentally. It also shows that the structure of the catalyst reveals minimal changes even at elevated temperature, which is believed to be a key factor for the stable reaction yield observed after multiple cycles. In contrast to the unchanged shape, the intensity of light absorption has shown variations. The light absorption of Fe&Cu-In₂O₃ has been further improved, but this improvement is dependent on the wavelength. Specifically, the improvement of short-wavelength photo response is not obvious, indicating that the intrinsic absorption intensity of the semiconductor is not substantially influenced by temperature. However, the increase in temperature does cause a slight red shift in the absorption edge, expanding the radiation response range of Fe&Cu-In₂O₃, which may be due to the subtle changes in the semiconductor band structure at different temperatures.^{55,56} For the long-wavelength photo response, it has been significantly enhanced as the temperature rises.

Similarly, the PL spectra of Fe&Cu-In₂O₃ were obtained at different temperatures using 405 nm light excitation, as shown in Figure 9b. Remarkably, the PL intensity showed a negative correlation with temperature, gradually weakening with the rising temperature. It suggested that higher temperatures reduced the radiative recombination rate of carriers, promoting carrier separation and being more conducive to the chemical

reaction. In the case of Fe&Cu-In₂O₃, the increasing temperature expanded the light absorption range, promoted longwavelength light absorption, and inhibited carrier recombination, thus providing more available photogenerated carriers for chemical reactions, which played a role in the non-thermal effect of radiation. This also happens to explain why the hydrogen yield increases with temperature. Consequently, maintaining a certain high catalytic temperature in the photothermal synergistic reaction has a positive impact on radiation absorption conversion. Fe&Cu-In₂O₃ has not only high catalytic activity and suitable band structure due to Fe doping but also has the promotion of photothermal temperature induced by Cu doping. Therefore, it demonstrated the highest H₂ yield in water splitting reaction utilizing solar radiation as the only energy source.

The results of carrier migration and transient photocurrent tested at different temperatures are summarized in Figure 9c,d. In the EIS test, the impedance of the high frequency band is dominated by the carrier transfer resistance. As the test temperature rises, the radius of the semicircle of the Nyquist curve gradually decreases, indicating that the carrier transfer resistance has a negative correlation with temperature. A similar trend is observed in the transient photocurrent test. Under the irradiation of the same light source, the intensity of photocurrent increases with the temperature, which is consistent with the results of radiation absorption curve and carrier recombination at different temperatures. The light absorption of Fe&Cu-In₂O₃ is enhanced, while the carrier recombination rate and carrier transfer resistance decrease, which is also reflected in the increase of photocurrent. Therefore, in the photothermal synergistic reaction, with the same other reaction conditions, the promotion of the radiation absorption conversion of the material by the increasing temperature may be the key factor to increase the H_2 yield of the water splitting reaction.

3.6. Mechanisms Analysis. The charge distributions of atoms near the doping sites on all established cIn_2O_3 -based models were analyzed by Bader charges calculation. As shown in Figure S11, M1 and M2 are transition metal doping sites. The charge changes of all surrounding atoms are listed in Table 1. It

Table 1. Changes in Charge before and after Surface Doping of $c\mathrm{In}_2\mathrm{O}_3$

	In ₂ O ₃	Fe-In ₂ O ₃	Cu-In ₂ O ₃	Fe&Cu-In ₂ O ₃
M1	1.565	Fe	Cu	Fe
M2	1.561	1.559	1.557	Cu
01	-1.009	-1.003	-1.003	-0.997
O2	-1.016	-0.996	-0.872	-0.893
O3	-1.077	-1.076	-0.995	-1.045
04	-1.038	-1.035	-0.957	-0.986
05	-1.071	-1.083	-1.045	-1.053
06	-1.083	-1.075	-1.075	-1.076
07	-1.083	-1.084	-1.083	-1.058
08	-1.074	-1.083	-1.04	-0.943

can be seen that after being doped with transition metal on the M1 site, the surrounding O atoms all show electrons loss, indicating that the transition metal ions Fe and Cu have stronger electron attraction ability than the In ion, leading to electrons transfer, which is also consistent with the phenomenon observed from XPS. The strong attraction of doped metals for electrons may generate trapping sites for electrons in radiative non-

thermal conversion, facilitating the separation of photogenerated electron-hole pairs.

On the basis of the previous work, metal oxides may interact with surface adsorbed species during the reaction process, and lose O to form surface oxygen vacancies, thus providing new pathways for water splitting reactions.⁵⁷ The surface V_{Ω} formation energy of In₂O₃-based catalysts was calculated and is presented in Table S2. On the In_2O_3 surface, there are two possible reaction pathways depending on whether oxygen vacancies are generated and consumed during the reaction.⁵⁸ Specifically, for the two distinct pathways, as shown in Figure S12, there are five key steps along with a total of six main intermediate groups in the photothermal catalytic watersplitting process. The initial step involves the adsorption and dissociation of water (H_2O) into hydroxyl and hydrogen atom (*OH + *H). Subsequently, one hydrogen atom dissociates from the OH group and combines with the previous H atom to form a H₂ molecule, while an oxygen atom remains bonded to the O2 site, forming *O. In the following steps, the activated *O can undergo two reaction tendencies. The first tendency is to adsorb and dissociate the second water molecule and leave hydroxyl, oxygen, and hydrogen atoms on the surface (*O + *OH + *H). This is followed by the second H_2 evolution in step 4 (*O + *OH + *H \rightarrow *O–O + H₂ \uparrow) and the O₂ evolution in step 5 (*O–O \rightarrow * + O₂↑). The second tendency involves the generation of surface V_0 and the release of O_2 (step 8: *O \rightarrow $V_0 + O_2$). The V_0 participates in the water splitting and the second H₂ evolution in step 10 (*OH($V_{\rm O}$) + *H \rightarrow * + H₂ \uparrow). To explore the process of H₂O splitting reaction before and after doping, the two reaction paths (path I and path II, shown in Supporting Information) were calculated on the four catalysts models. The results are demonstrated in Figure 10, in which the red line is the RDS of the reaction path. For cIn_2O_3 , Fe- cIn_2O_3 , and Fe&Cu-cIn₂O₃, due to the energy barrier of the second, H_2 generation step (step 4) in Path I is more difficult than the H_2 generation step (step 10) on oxygen vacancies in Path II, the water splitting reaction tends to go through by Path II, in which the RDS is the first H₂ evolution step (step 2: $*OH + *H \rightarrow *O$ + H₂↑).

Compared with the pure CIn_2O_3 , the doping of transition metal Fe or Cu both improves the desorption of H₂ on the catalyst surface, lowers the energy barrier of the RDS, promoting the reaction. For Cu element doping, owing to the lowest $V_{\rm O}$ formation energy, it further reduces the energy barrier of step (8) while improving the generation of H_2 on the catalyst surface (step 2). However, the too low V_0 formation energy makes its reducing ability weaker, which is not conducive to the generation of H_2 on V_0 (step 10), so that the reaction path becomes Path I, and the RDS becomes step (4). The RDS energy barriers of splitting water to produce hydrogen, are 3.50, 3.67, and 3.36 eV of Fe-cIn₂O₃, Cu-cIn₂O₃, and Fe&Cu-cIn₂O₃, respectively, which is consistent with the photothermal synergistic reactivity in the corresponding samples. Also, the Cu-In₂O₃ sample has a lower RDS energy barrier, but its poor reactivity might be attributed to its inappropriate energy band structure (relatively low conduction band and high valence position).

In addition, the increasing temperature caused by thermal effect also affects the reaction progress by changing the energy barrier of key steps in the water splitting reaction pathway. As can be seen in Figure 11, on the one hand, the energy barriers of H_2O adsorption steps (step 1, 3, 9; H_2O adsorbed in dissociation form) increase, showing that the H_2O adsorption



Figure 11. The Gibbs free energy of two reaction paths on cln2O3, Fe-cln2O3, Cu-cln2O3, and Fe&Cu-cln2O3.

on surface active sites weakens as the temperature rises. On the other hand, the energy barriers of hydrogen evolution step and product desorption step (step 2, 4, 5, 10) decrease. While in Path I and Path II, the RDS is step (4) and step (2), respectively. The

rising temperature reduces the energy barrier of the RDS to varying degrees, which has a direct promotion effect on the whole water-splitting process, and also explains that the H_2 yield gradually increases as the temperature increases. Fe&Cu-In₂O₃ exhibits the lowest RDS energy barrier, which is also consistent with the phenomenon that it owns the best reactivity at all experimental temperatures. For all catalysts here, the thermal effect plays a positive role by lowering the energy barrier of the RDS (shown in Figure S13). In other word, under the same other conditions, the radiation thermal effect enhanced, the photothermal synergistic water splitting reaction will also be promoted.

To sum up, as shown in Figure 12, it is thought that both Fe doping and Cu doping effectively promote the absorption of



Figure 12. Conceptual illustration of the mechanism.

solar radiation, albeit with differing effects on different wavelength ranges of light. Fe doping greatly expands the radiation response range, enhances the intrinsic absorption intensity of In2O3, and promotes the non-thermal effect. Cu doping promotes the absorption in the visible-infrared region, which is beneficial to the thermal effect and improves the material's photothermal temperature. This difference is further evident in the water splitting reaction conducted under varying experimental conditions. When the reaction temperature is kept constant, Fe doping shows superior hydrogen production rate. However, once light radiation is used as the only energy source, the Fe-doped samples exhibit limitations in the water splitting reaction due to their comparatively lower photothermal temperature. Fe&Cu-In₂O₃ combines the promotion of shortwavelength absorption by Fe doping and long-wavelength absorption by Cu doping to couple the non-thermal and thermal effect of radiation, achieving a higher reaction temperature and optimal water splitting reaction yield simultaneously.

4. CONCLUSIONS

Here, the advantages of Fe doping and Cu doping are synergistically combined in Fe&Cu- cIn_2O_3 , which is prepared with excellent radiation non-thermal and thermal effect, achieving an enhanced photothermal synergistic water-splitting reactivity for hydrogen production in the radiation-driven reaction system. Spectral experiments prove that the ultraviolet-visible light with higher energy in the radiation spectrum is mainly used to drive the chemical reaction, while long-wavelength radiation predominantly affects reaction through the thermal effect. To promote the non-thermal effect, it is crucial to

optimize the energy band structure of semiconductors to meet the thermodynamic requirements of the water splitting reaction and reduce the carrier recombination while expanding the radiation response range. The thermal effect affects the material's radiation absorption and the migration of photogenerated carriers by altering the temperature, thereby affecting the non-thermal effect. Additionally, the change of temperature can also directly affect the chemical reaction by reducing the energy barrier of the RDS. Therefore, in the process of designing and synthesizing photothermal synergistic materials, it is important to not only consider the non-thermal effect or thermal effect but also comprehensively consider the interaction of the two, so as to get a higher photothermal temperature while promoting the non-thermal effect, achieving efficient coupling of solar light and heat, and lay the foundation for the construction of future photothermal comprehensive utilization system.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.3c07041.

More calculational tests and details, water splitting reaction path I and path II, schematic diagrams of two photothermal catalytic reaction systems, spectral distribution of the xenon lamp, the surface models of all catalysts, and EXAFS data fitting results (PDF)

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Author Contributions

L.Z. and X.-H.Z. conceived, designed, conducted the experiments, and co-wrote the manuscript. L.Z. carried out DFT calculations and analyzed the data. H.-F.M. conducted a part of optical characterizations. J.-N.H. performed a part of PTC experiments. S.-N.Y. conducted EPR test characterization. Z.-H.Z. revised the manuscript. C.-Y.X. revised the manuscript and provided critical feedback. Y.-W.Z. received the funding for the

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Notes

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