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Tuning recombination of carriers during radiative conversion with Cuprum and Ferrum co-doping in the photothermal synergy



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ABSTRACT

Heat induced by solar irradiation can alter crystal structures and interfacial barriers, which may subsequently impact the generation, transport and recombination of photoinduced carriers during the radiative conversion of semiconductors. However, this factor is often ignored in photoreactions. Thus, this study investigates the influence and mechanism of the thermal effect on radiative conversion in photoreactions. We find that when the temperature increases, 1) the radiative absorbance is broadened, 2) the ability of photoinduced electrons to drive reactions is enhanced, and 3) better mobility of photoinduced carriers is achieved. Interestingly, the radiative recombination of ZnO and In_2O_3 decreased and increased, respectively during heating, which resulted in increasing and decreasing photocurrents in the corresponding sample. Furthermore, after co-doping In_2O_3 with Cu and Fe, we reversed the trend of radiative recombination from increasing to decreasing with increasing temperature. Thus, the H₂ production increased by 2.53 times at 250 °C relative to that at 150 °C during the photothermal reaction using Cu3/Fe1–In₂O₃. Finally, we successfully proved that the thermal effect could be converted from a harmful factor into a beneficial role during radiative conversion. This work may inspire more innovative ideas related to the mechanism and utilization of the thermal effect in solar conversion.

1. Introduction

Solar energy, as an abundant and clean renewable energy source, holds promise for large-scale utilization in the future [1]. Current solar energy utilization methods include photovoltaic conversion, solar thermal utilization, photocatalysis, etc. [2–6]. Among these methods, the photocatalytic hydrogen evolution reaction (PC-HER) has become a research hotspot in recent years [7], as it has the potential to address the continuity and stability issues related to the use of solar energy.

However, ultraviolet (UV) light accounts for only 5 % of the entire solar spectrum, with the remaining portion composed of visible (Vis) and near-infrared (NIR) light [8,9]. The mismatch between the energy band structure of semiconductors and the kinetic potential energy required for the HER means general catalysts use light only in the UV–vis range, and the infrared part that accounts for a large proportion of the full spectrum of solar energy is rarely used, which greatly limits the development of photocatalysis technology [10]. Furthermore, in most PC-HERs, to avoid the intensification of radiative recombination caused by high temperature, a temperature-controllable water bath system is

usually used to eliminate the thermal effect generated by the NIR part of sunlight and keep the temperature low [11] [–] [14]. Unfortunately, such conditions may not be the most suitable for a specific catalytic system, and achieving cost-effective industrial production under such conditions is difficult.

To significantly improve the overall efficiency of the full spectrum in photocatalysis and determine the optimal reaction temperature, scholars have made efforts to incorporate heat into photocatalytic systems [15] [–] [18] and are committed to coupling the nonthermal effect with the thermal effect to produce a photothermal synergistic effect and realize full utilization of the solar spectrum. From a thermodynamic perspective, high temperatures can promote an endothermic reaction; from a kinetic perspective, increasing the temperature can simultaneously promote an increase in the endothermic or exothermic reaction rate. This process is called photothermal catalysis (PTC), and it has been observed that PTC can effectively facilitate the migration of carriers, accelerate mass transfer, enhance reaction kinetics, and foster the dissociation of reactants [19,20].

Unfortunately, increasing the temperature is not always beneficial

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for photothermal catalytic reactions, as high temperatures may also reduce PTC efficiency by intensifying particle agglomeration, promoting reverse reactions, enhancing reactant desorption, etc. [21–23]. In other cases, temperature has little effect [21]. The temperature-dependent behavior of photoinduced carriers has been investigated only at a relatively superficial level and has usually been limited to special cases. The general effect of temperature on PTC thus remains unclear. Therefore, there is an urgent need to comprehensively study the influence of temperature on PTC to clarify the internal mechanism and adopt an appropriate temperature regulation strategy for specific reaction systems [24] [–] [26].

In this work, TiO₂, In₂O₃, ZnO and CeO₂ were selected as representative semiconductors. The reasons were as follow: Firstly, these samples were widely used in photochemical applications for their good photoresponse abilities. Secondly, we focused on studying the radiation absorption mechanism which was convenient for our analysis for their simple crystal structures and band structures. Last but importantly, according to our requirements, the physical and chemical properties of samples should be stable to resist to photocorrosion at certain temperature in the photothermal tests, which also made them suitable to investigate photocatalytic reaction mechanisms in this work [27–32]. A series of temperature-based characterization methods were employed to investigate and analyze the radiative conversion mechanism of the four semiconductors in PTC. It was found that increasing the temperature enhanced the PTC activity of the semiconductors through various means, such as by reducing the bandgap, increasing light absorption, shifting the conduction band potential to a more negative position, reducing the electrochemical impedance, and facilitating the migration of photoinduced carriers. However, high temperatures also intensified radiative recombination in In₂O₃, thereby affecting the separation of photoinduced carriers, which differed from the behavior of other semiconductors.

After co-doping In₂O₃ with Cu and Fe, an evident transition from a negative correlation to a positive correlation was observed in the relationship between the photocurrent and radiative recombination with temperature, which enhanced the suitability of In₂O₃ for PTC reactions. In addition, under the irradiation of a 300 W xenon lamp as a solar simulator, the thermal effect on the catalytic activity of modified In₂O₃ was also studied. It was found that under the same light conditions, the higher the temperature was, the higher the hydrogen production rate of Cu/Fe–In₂O₃. The hydrogen production performance at 250 °C was 2.53 times that at 150 °C, revealing a positive correlation between the temperature increase and the hydrogen production performance of Cu/Fe–In₂O₃ and emphasizing the combined benefits of these thermal effects in favor of the PTC-HER in this system.

In conclusion, after investigating the radiation conversion properties of different metal oxides at different temperatures, we found that when the temperature raised, the energy band structures of different samples would change, resulting in changes in their light absorption intensity. At the same time, temperature had different effects on the recombination of different samples, which was also accompanied the changes in the probability of interfacial reaction. The above factors worked together to bring in a comprehensive effect in the integral performance (such as photocurrent) for different samples at different temperatures. Furthermore, in this work, we confirmed that the recombination of carriers during radiative conversion could be tuned with Cu and Fe co-doping, which leaded to a shift in their final performance in the photothermal synergy and enabled materials that were initially unsuitable for hightemperature conditions to be suitable for systems with thermal effects, both the gas phase and liquid phase reaction environments at high temperatures. Actually, in some reactions where sunlight was used, either the thermal effect was ignored or the non-thermal effect was ignored, but the thermal and non-thermal effect actually existed simultaneously [33,34]. This research work on photothermal synergy would help all systems which use sunlight with thermal effect, including gas-phase reaction mode and liquid-phase reaction mode. By giving

these reactions some inspiration on the control and utilization of thermal effects, such as photocatalysis [35,36], photo electrochemistry [37] and photothermal gas-solid two-phase reaction [38,39], they may achieve better performance.

2. Experiments

2.1. Fabrication of materials

In this study, TiO₂ and In₂O₃ were prepared by the sol-gel method, while CeO₂ and ZnO were synthesized by the coprecipitation method. The detailed preparation procedures can be found in the Supporting Information. All chemicals, tetrabutyl titanate ($C_{16}H_{36}O_4Ti$), zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O), hexahydrate cerium nitrate (Ce (NO₃)₃·6H₂O), copper nitrate (Cu(NO₃)₂·3H₂O), and iron nitrate (Fe (NO₃)₃·9H₂O), etc. were purchased from Sinopharm Group Chemical Reagent Co., Ltd. In addition, indium nitrate (In(NO₃)₃) and citric acid (C₆H₈O₇) were purchased from Shanghai Macklin Biochemical Co., Ltd. All these chemicals were analytically pure and used without further purification. All water used deionized water.

2.2. Characterizations

Gas products were detected using a gas chromatography (GC) system (Agilent 8890 A) equipped with a 5A column and a PQ column for the separation of H₂, O₂, and N₂. The GC system used Ar as the carrier gas and was equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). High-resolution Transmission Electron Microscope (HRTEM) micrographs were performed on a Tecnai G2 F20 S-TWIN equipped with field-fired electron guns. Scanning Electron Microscope (SEM) were performed on a JSM-IT800, which is equipped with Energy Dispersive X-Ray Spectroscopy (EDS), the element and content of the sample to be measured can be obtained according to the wavelength and intensity analysis of the element characteristic X-ray. The X-ray diffraction (XRD) analyzer is produced by were performed on a X-pert Powder. XRD patterns were acquired using a Cu-K_{α} radiation source ($K_{\alpha} = 1.540598$ Å) at 60 kV and 60 mA. Diffraction spectra were recorded between 2θ of 20° and 80° at a scan rate of 2° min⁻¹ with a step width of 0.05°.

X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Scientific K-Alpha. The excitation source was Al K $_{\alpha}$ ray (h ν = 1486.6 eV). All binding energies were referenced to the C 1s peak (284.80 eV), which was used to determine adventitious carbon in the test sample preparation. UV-visible-near infrared diffuse reflectance spectroscopy (UV-Vis-NIR DRS) was performed using UV-Vis-NIR spectrophotometers (200-1400 nm, Shimadzu UV-2600i and UV-3600i Plus) to explore the photo absorption characteristics of the materials. UV-2600i was used to test the absorption spectrum under normal temperature conditions, which can meet the measurement requirements of the spectral absorption range from 200 to 1400 nm. UV-3600iPlus was equipped with the Harrick diffuse reflection high-temperature accessory, which can provide a working cavity temperature of up to 500K temperature conditions. The spectral absorption measurement range was 200-2500 nm. Depending on the test requirements, three types of instruments, FLS 980, FLS 920 and JY HORIBA FluoroLog-3, were used. The Edinburgh Instruments FLS 980 recorded PL emission spectra of four semiconductors at 20-200 °C under 375 nm excitation light. The PL emission and time-resolved photoluminescence (TRPL) spectra at room temperature used an Edinburgh Instruments FLS 920 with a 405 nm excitation light. The PL emission spectrum of the Cu/Fe-modified semiconductor at 20–200 $^\circ C$ used JY HORIBA FluoroLog-3 with a 340 nm excitation light. An inductively coupled plasma atomic emission spectrometer (ICP-AES) (Thermo Fisher iCAP6300) was used to determine the actual contents of Cu and Fe. For this purpose, an acidic mixture including HCl and HNO3 was used for fully dissolving the samples.

2.3. Photoelectrochemical measurements

All photoelectrochemical performance were conducted by a Netherlands electrochemical workstation (Iviumstat A09015) using a three-electrode mode with an Ag/AgCl/KCl sat. as reference counter electrode, a platinum net as counter electrode and the synthesized catalysts as a working electrode. An aqueous 0.5M Na₂SO₄ solution was utilized as the electrolyte. Electrochemical impedance spectroscopy (EIS) was conducted with the frequency of 10 mHz–100 kHz at an overpotential of 1.5 eV. A 365 nm center-wavelength LED ultraviolet lamp was used to acquire the photocurrent response with five light/dark intervals of 30 s. Mott-Schottky (MS) curve analysis was measured at a frequency of 1000Hz.

2.4. measurement of H_2 production

A 15 mg sample was evenly dispersed in 1 ml of deionized water and then treated with ultrasound for 5 min. The mixed suspension was evenly dispersed on a quartz fiber filter membrane with a diameter of 30 mm. The catalyst film was transferred to the quartz scaffold in the reactor. After the reactor was closed, the air valve and mass flowmeter were opened, 100 sccm high-purity Ar was used to exhaust the remaining air in the reactor, and the reactor was heated to the specified temperature. After scavenging for 20 min, the reactor was purged with high-purity Ar at 4 sccm. The 300 W xenon lamp source with a wideband infrared filter (IRCUT 700) (see Fig. S2 for the light source spectrum) was turned on and shined into the reactor through a quartz lens. The filter removed infrared light above 700 nm to avoid interference from the infrared thermal effect on the set reaction temperature. After the temperature of the reactor stabilized, GC (Agilent 8890) was used to detect the product gas, and 6 groups of data were measured continuously. The actual PTC-HER system was shown in Fig. S1.

3. Results and discussion

3.1. Crystal structure and composition

XRD was conducted to characterize the crystal structure of the synthesized semiconductors (Fig. 1a). The diffraction peaks of all semiconductors were sharp and well defined, indicating good crystallinity and purity. According to the Scherrer equation [40], the average grain sizes of the four samples, TiO₂, In₂O₃, ZnO and CeO₂, were 21.8 nm, 13.5 nm, 38.5 nm and 16.1 nm, respectively, and the grain sizes were nanoscale. TiO₂ exhibited a rutile crystal structure, In₂O₃ displayed a cubic spinel crystal structure, ZnO had a hexagonal wurtzite crystal structure, and CeO₂ featured a face-centered cubic fluorite crystal structure.

The XPS spectra in Fig. 1b–f further proved that no impurities were introduced into the semiconductors. Chemically absorbed oxygen-OH (O_C) was detected at approximately 532.00 eV, and lattice oxygen (O_L) was observed at approximately 529.50 eV for all semiconductors (Fig. 1b). Oxygen vacancies (Vo) were observed at binding energies of 530.85 eV, 530.78 eV, and 531.13 eV for In₂O₃, ZnO and CeO₂, respectively. Moreover, the Ce in CeO₂ existed in a mixed valence state



Fig. 1. – (a) XRD patterns of as-prepared TiO₂, In₂O₃, ZnO, and CeO₂ in the original states from 20 to 80°. XPS patterns: (b) O 1s, (c) Ti 2p, (d) In 3d, (e) Zn 2p, and (f) Ce 3d. HRTEM images of (g) TiO₂, (h) In₂O₃, (i) ZnO, and (j) CeO₂; inset: spacing measurements perpendicular to the lattice stripes.

of Ce^{4+}/Ce^{3+} , in which Ce^{4+} was dominant (Fig. 1f). These results indicated that the four metal oxide semiconductors were successfully prepared.

HRTEM was used to further observe the morphology and exposed crystal planes of the four semiconductors, as shown in Fig. 1g–j. The majority of the samples consisted of spherical particles with a uniform particle size and excellent dispersion. No obvious agglomeration was observed, and the spacing of the lattice fringes was consistent with the XRD results.

3.2. Influence of temperature on radiative conversion

3.2.1. Energy band structure and radiative absorption

When the photon energy is greater than or equal to the bandgap, electrons in the valence band can be excited to the conduction band, which is the first step in a PTC reaction. UV-Vis-NIR DRS was employed to examine the light absorption of semiconductors at temperatures ranging from 20 °C to 300 °C, as depicted in Fig. 2a-d. The results showed that as the temperature increased, the cutoff wavelength λ_{σ} of the semiconductors exhibited a redshift. Using the Tauc plot method to calculate the bandgap, we found that a higher temperature caused a slight decrease in the bandgap (insets of Fig. 2a-d). The cutoff wavelengths and calculated bandgaps for the four samples (Fig. 2) at different temperatures were shown in Table S1. It is known that temperature not only affects lattice parameters, leading to lattice expansion, but also enhances lattice vibrations (electron-phonon interactions), leading to the relative movement of energy band edges and a smaller bandgap. This effect was generally quantitatively described by the Varshni empirical formula, as follows [41]:

$$E_{g(T)} = E_{g(0)} - \frac{\beta T^2}{T + \gamma} \tag{1}$$

For formula (1), $E_{g(0)}$ is the bandgap energy of the material at a temperature and pressure of zero, β is the bandgap slope at high temperatures, and γ is a parameter related to the Debye temperature.

Increasing the temperature can also improve the intrinsic optical absorption intensity of semiconductors by affecting photon-electron or photon-phonon interactions, which can be divided into direct transition and indirect transition modes. TiO₂, CeO₂, and ZnO are indirect bandgap semiconductors, while In_2O_3 is a direct bandgap semiconductor. The relationships between the absorption coefficients of direct and indirect transition semiconductors and the energies of photons and phonons can be described by formulas (2) and (3), respectively. In particular, phonons participate in the optical absorption process of indirect bandgap semiconductors to maintain momentum conservation [42]. As shown in the insets of Fig. 2a–d, photon-electron and electron-phonon interactions were enhanced when the temperature increased in both direct- and indirect-bandgap semiconductors, and the absorption coefficient α increased with increasing temperature in the UV range.

$$\begin{aligned} \alpha(h\nu) &= A \left(h\nu - E_g \right)^{\frac{1}{2}} \quad h\nu \ge E_g \\ \alpha &= 0 \qquad \qquad h\nu < E_g \end{aligned}$$
 (2)

$$\alpha(h\nu) = A \left[\frac{\left(h\nu - E_g + E_P\right)^2}{\exp\left(\frac{E_P}{k_0 T}\right) - 1} + \frac{\left(h\nu - E_g - E_P\right)^2}{1 - \exp\left(\frac{E_P}{k_0 T}\right)} \right] \quad h\nu > E_g + E_P$$

$$\alpha(h\nu) = A \left[\frac{\left(h\nu - E_g + E_P\right)^2}{\exp\left(\frac{E_P}{k_0 T}\right) - 1} \right] \quad E_g - E_P \le h\nu \le E_g + E_P$$

$$\alpha = 0 \quad h\nu < E_g - E_P$$
(3)

$$E = \int_{200}^{\infty} \alpha(\lambda) \frac{hc}{\lambda} d\lambda$$
(4)

In addition, we found that the radiation absorption performance of narrow-bandgap semiconductors may be more susceptible than that of other semiconductors to temperature changes. Assuming that a light source emits an equal number of photons at different frequencies, we can express the energy *E* required for incident light excitation to produce photoinduced carriers using integral formula (4). Table 1 shows the incremental percentage of energy *E*, ΔE , at 50 °C, 100 °C, 200 °C, and 300 °C compared to that at 20 °C. The order in which the radiation absorption was affected by temperature was as follows: In₂O₃ > CeO₂ >



Fig. 2. – UV–Vis–NIR diffuse reflectance spectra of (a) TiO₂, (b) In_2O_3 , (c) ZnO, and (d) CeO₂ at different temperatures. Insets: the corresponding plots of $(F(R) \cdot h\nu)^{1/2}$ or $(F(R) \cdot h\nu)^2$ versus bandgap energy $(h\nu)$. Mott-Schottky curves of (e) TiO₂, (f) In_2O_3 , (g) ZnO, and (h) CeO₂ under different temperature conditions.

Table 1

The increase in the absorbed photon energy of the four metal oxides at different temperatures.

T (°C)	50	100	200	300
Sample				
In ₂ O ₃	5.71 %	7.66 %	7.73 %	8.74 %
CeO ₂	3.03 %	3.46 %	5.69 %	7.02 %
TiO ₂	1.22 %	1.67 %	2.28 %	2.55 %
ZnO	0.07 %	0.47 %	0.71 %	0.98 %

 $\rm TiO_2 > ZnO.$ Additionally, the bandgaps of these materials were ranked as follows: $\rm ZnO > \rm TiO_2 > CeO_2 > In_2O_3$. The higher sensitivity of $\rm In_2O_3$ to temperature may be attributed to its relatively narrow bandgap.

Furthermore, we found that increasing the temperature was conducive to improving the performance of photoinduced electrons in the PTC-HER. According to double layer theory, the relationship between the space charge layer capacitance and flat band potential is as follows:

$$C^{-2} = \frac{2}{\varepsilon_r \varepsilon_0 e N_D} \left(E - E_{fb} - \frac{kT}{e} \right)$$
(5)

In formula (5), C is the space charge layer, F/cm²; ϵ_r is the relative dielectric constant of the material; and ϵ_0 is the dielectric constant of vacuum, which is 8.854 × 10⁻¹⁴ F/cm. N_D is the average carrier concentration (cm⁻³); e is the unit charge, 1.602 × 10⁻¹⁹C; E is the electrode potential; E_{fb} is the flat band potential; k is the Boltzmann constant, 1.38 × 10⁻²³; and T is the temperature in Kelvin.

According to the MS curves of the four semiconductors within the temperature range of 20–80 $^\circ C$, as shown in Fig. 2e–h, the tangent slope

of the curves decreased with increasing temperature, providing firm evidence that the thermal effect facilitated the generation of a higher concentration of photoinduced carriers. Furthermore, for n-type semiconductors, E_{fb} is close to the conduction band bottom potential (E_{CB}) [43]. As the temperature increased, the tangent intercept of the MS curve increased, indicating that high temperatures were beneficial for shifting the E_{CB} of the semiconductor to a more negative value. The more negative E_{CB} was, the stronger the ability of the photoinduced carriers to drive the reduction reaction, which was beneficial to the HER.

3.2.2. Transmission and conversion of photoinduced carriers

Photoinduced carriers are generated when electrons absorb energy from solar radiation (intrinsic absorption, exciton absorption, free carrier absorption, impurity absorption, plasmon resonance absorption, etc.) [44-47], which means that the radiation energy of photons is transferred and converted into different forms of energy (either used or annihilated). Photogenerated carriers can be transformed into electrical energy, chemical energy, light energy (radiative recombination) or thermal energy (nonradiative recombination or relaxation) [48] [-] [51]. The separation and transmission behavior of photoinduced carriers at different temperatures were investigated by measuring the EIS properties and photocurrent of the semiconductors at 20 °C, 40 °C, 60 °C, and 80 °C. High temperatures promoted the separation and migration of photoinduced carriers. As shown in Fig. 3a-d, the electrochemical impedance of all the semiconductors decreased with increasing temperature, indicating that temperature elevation significantly reduced the migration resistance of the photoinduced carriers and facilitated carrier transport. Moreover, the photocurrent of the TiO₂, ZnO, and CeO₂ samples increased with increasing temperature, as



Fig. 3. – EIS changes of (a) TiO_2 , (b) In_2O_3 , (c) ZnO, and (d) CeO_2 at different temperatures. Photocurrent response curves of (e) TiO_2 , (f) In_2O_3 , (j) ZnO, and (h) CeO_2 at different temperatures. PL spectra of (i) TiO_2 , (j) In_2O_3 , (k) ZnO, and (l) CeO_2 at different temperatures.

shown in Fig. 3e–h, indicating that higher temperatures were favorable for the separation of photoinduced carriers. However, the photocurrent of the In_2O_3 sample showed a negative correlation with temperature, decreasing to 73 % of its original value when the temperature increased from 20 °C to 80 °C.

In the PTC-HER system, the energy conversion efficiency of photogenerated carriers is the key factor affecting catalytic activity. A higher energy conversion efficiency of photogenerated carriers can result in higher HER efficiency. Therefore, the radiative recombination of photogenerated carriers should be as low as possible. PL spectroscopy is commonly used to study the radiative recombination process of photoinduced carriers in semiconductors, which is related to the transfer and separation of carriers. Therefore, temperature-dependent PL tests were also carried out in the range of 20-200 °C. The experimental results (Fig. 3i-l) showed that the radiation recombination of ZnO, CeO₂ and In₂O₃ decreased, stabilized and increased, respectively, when the temperature was increased. Temperature had an inhibitory effect on the radiative recombination of ZnO, making the conditions more conducive to photothermal catalytic reactions. However, the effect of temperature on the radiative recombination of TiO₂ and CeO₂ samples was relatively small. The radiation recombination process of In₂O₃ samples became serious with increasing temperature. Therefore, it was speculated that the decrease in the photocurrent of In₂O₃ with increasing temperature may have been caused by radiation recombination enhancement at high temperatures.

When the semiconductor absorbs photons with suitable frequencies, photoinduced electron and hole pairs (EHPs) could be generated. The interfacial reaction could be driven by photoinduced EHPs after a series of processes including relaxation, recombination and transfer in bulk and on the interface. In our work, decreasing the EIS radius indicated that increasing temperature was good for reducing the resistance of interfacial reaction when we used In₂O₃ sample. However, according to the temperature-dependent PL tests, the recombination of EHPs seemed to be much more serious. It can be speculated that the negative effects of increased temperature for EHPs recombination were greater than the positive effect of that for interfacial reaction. Because the EHPs recombination happened in several femtosecond while the interfacial reaction of them in some picosecond. The EHPs were much easier to recombine rather than being used in reaction, which further induced the decrease of photocurrent. Therefore, the competition of EHPs between the recombination and reaction may induce the contradictory behavior between the EIS and photocurrent curves of In₂O₃. These results suggested that bare In₂O₃ may not be suitable for efficient PTC-HERs. However, some studies have shown that the introduction of Cu and Fe, two transition metals, may help inhibit photoinduced carrier recombination and improve the catalytic activity and electrical conductivity of semiconductors [52] [-] [55]. Additionally, Cu and Fe doping can generate

impurity levels in the semiconductor bandgap, thereby expanding the radiation response range and promoting radiation absorption in different wavelength ranges. To address the issue of increased radiation recombination in In_2O_3 samples under high-temperature conditions, we chose to modify the In_2O_3 sample by doping with Cu and Fe.

3.3. The transformation of radiative conversion by metal doping

3.3.1. Photothermal catalytic activity

Nine Cu/Fe– In₂O₃ samples with different mass fractions were prepared by the sol-gel method, and the catalytic activity of these samples was tested by a photothermal catalytic water splitting experimental system (Fig. S1). The experimental results were shown in Fig. 4a and b. Among the evaluated samples, Cu/Fe–In₂O₃, containing a mass fraction of 3 % Cu and 1 % Fe, displayed the best catalytic activity and was selected for further investigation. Notably, as the Cu doping amount increased, the valence state of Cu increased, as shown by the XPS and AES results (Figs. S8–9). Higher amounts of Cu doping resulted in worse stability. The detailed preparation and measurement processes of H_2 production can be found in the Supporting Information.

The experimental system shown in Fig. S1 was used to further explore the comprehensive influence of temperature on the PTC-HER activity of Cu3/Fe1–In₂O₃, and the experimental results were shown in Fig. 4c. The H₂ production rate of Cu3/Fe1–In₂O₃ increased with increasing reaction temperature. When the reaction temperature was 250 °C, the H₂ production rate of Cu3/Fe1–In₂O₃ was 46.03 µmol g⁻¹ h⁻¹, which was 2.53 times that at 150 °C. Meanwhile, the Cu3/Fe1–In₂O₃ sample also showed a good stability of performance at 250 °C in 16 h for 8 cycles in continuous experiments (Fig. S3).

While the influence of temperature within the specified range had both beneficial and detrimental impacts on the radiation conversion of semiconductors, the cumulative effect of elevated temperatures on the radiation conversion process of Cu3/Fe1–In₂O₃ in photothermal catalytic reactions was predominantly positive. These results indicate that Cu/Fe modification can improve the catalytic activity of semiconductors and promote energy conversion in photothermal catalytic reactions.

3.3.2. Elemental composition and doping confirmation

The XRD patterns (Fig. S4) of Cu3/Fe1–In₂O₃ exhibited an obvious narrow diffraction peak without an impurity peak, indicting the presence of a highly crystalline structure with a single cubic spinel arrangement and its crystal structure remained stable after reaction. According to Scherrer formula [40], it can be known that the grain size of the Cu3/Fe1–In₂O₃ sample was 12.16 nm, which did not differ from that of In₂O₃ sample. The diffraction peak shifted rightward, indirectly demonstrating Cu and Fe doping. It may be that Cu²⁺ or Fe³⁺ entered the In³⁺ site of the lattice at a smaller radius, forming Cu–O–In or Fe–O–In



Fig. 4. – H_2 production rates of Cu/Fe-In₂O₃ samples: (a) variations in Cu doping ratio and (b) variations in Fe doping ratio. (c) H_2 production rates of Cu3/Fe1-In₂O₃ at different reaction temperatures.

bonds, resulting in the reduced lattice spacing and the shift to the right of the XRD diffraction peak. The results of ICP tests (Fig. S5) demonstrated that Cu3/Fe1–In₂O₃ consists of 3.1 wt% Cu and 0.93 wt% Fe, indicating that Cu and Fe were successfully doped into In₂O₃ according to the set mass fractions. In the HRTEM images (Fig. S6), no Cu and Fe lattice fringes were observed on the surface of Cu3/Fe1–In₂O₃, the lattice spacing was approximately 0.294 nm, less than that of In₂O₃, and the crystal morphology remained stable after the reaction. The EDS mapping results (Fig. S7) further indicated that Cu and Fe were uniformly doped in the In₂O₃ sample.

The XPS and AES results of Cu/Fe–In₂O₃ (Fig. S8–10) showed that all of the In in the samples had a +3 valence state, and the O1s orbital spectra showed the presence of lattice and chemisorbed oxygen. As the Cu doping amount increased, some Cu adopted a high valence state (+1), and some Cu even transformed to a higher valence state (+2). Fe was also successfully doped into the In₂O₃ substrate, showing a +3-valence state, and an Fe³⁺ $2p_{3/2}$ orbital signal was observed in samples with high Fe doping.

3.3.3. Energy band structure and radiative absorption

The radiation absorption properties of Cu3/Fe1–In₂O₃ were analyzed by UV–Vis–NIR DRS (Fig. 5a). The bandgap of Cu3/Fe1–In₂O₃ was smaller than that of bare In₂O₃, and the spectral response of Cu3/Fe1–In₂O₃ was improved to varying degrees in the UV and Vis light ranges, greatly increasing the number of photoinduced carriers. Notably, doping with Cu and Fe mainly affected the radiation absorption intensity of In₂O₃ in the UV and Vis regions, respectively.

The UV–Vis–NIR DRS results of Cu3/Fe1–In₂O₃ in the temperature range of 20–200 °C (Fig. 5b) further showed that increasing the temperature increased the light absorption of the semiconductor, indicating further enhancement of the excitation of photoinduced carriers. With increasing temperature, the light absorption of Cu3/Fe1–In₂O₃ in the UV and Vis regions was enhanced simultaneously. Among the regions, the enhancement in the UV range was more obvious, accompanied by a redshift of the absorption edge. These observed temperature-dependent radiation absorption properties of Cu3/Fe1–In₂O₃ were consistent with those of bare In₂O₃ (Fig. 4b).

3.3.4. Transmission and conversion of photoinduced carriers

To determine the impact of Cu and Fe doping on the separation and migration efficiency of photoinduced carriers, PL spectra of In_2O_3 and Cu3/Fe1–In₂O₃ samples were measured in the range of 425–650 nm under excitation with a 405 nm light source, as shown in Fig. 6a. The results revealed that the luminescence intensity of Cu3/Fe1–In₂O₃ was weaker than that of the original In_2O_3 , indicating that Cu and Fe introduction effectively suppressed electron-hole recombination.

The lifetime of photoinduced carriers in semiconductors was also an important factor affecting the energy conversion efficiency of the PTC- HER [56]. By comparing the signal index fitting results of the TRPL spectra of In_2O_3 and $Cu_3/Fe_1-In_2O_3$ samples within 0–60 ns (Fig. 6b and c), it was found that the average lifetimes of photoinduced carriers in In_2O_3 and $Cu_3/Fe_1-In_2O_3$ were 7.763 ns and 9.484 ns, respectively. This finding suggested that Cu and Fe co-doping not only effectively suppressed the radiative recombination of photoinduced charge carriers in In_2O_3 but also prolonged the lifetime of photoinduced charge carriers, increasing the probability of photoinduced charge carriers participating in chemical reactions and thus improving the energy conversion efficiency of the PTC-HER.

To investigate the effect of temperature on the recombination process of photoinduced carriers in Cu3/Fe1–In₂O₃, we tested the temperature-dependent PL spectra of Cu3/Fe1–In₂O₃, which was found to be the exact opposite of those for the original In₂O₃. The PL spectra of the Cu3/Fe1–In₂O₃ sample were recorded in the range of 375–680 nm under excitation by a light source at various temperatures (20–300 °C), as shown in Fig. 6d.

The results showed that the radiative recombination of Cu3/ Fe1–In₂O₃ decreased with increasing temperature, indicating that the introduction of Cu and Fe effectively inhibited the radiative recombination of In₂O₃ at high temperature and made it more suitable for PTC reactions.

Finally, it was further verified that Cu and Fe co-doping suppressed the radiation recombination of In_2O_3 and prolonged the lifetime of photoinduced carriers at high temperatures by conducting photoelectrochemical measurement tests. Specifically, EIS and photocurrent measurements of Cu3/Fe1–In₂O₃ related to the transmission behavior of photoinduced carriers were performed in the temperature range of 20–80 °C. The EIS spectrum in Fig. 6f revealed that with increasing temperature, the carrier migration resistance and transmission resistance of Cu3/Fe1–In₂O₃ at the liquid–solid interface still decreased, consistent with the results for bare In_2O_3 .

As shown in Fig. 3f, the photocurrent of the In_2O_3 substrate decreased with increasing temperature and was negatively correlated with temperature, while Fig. 6e showed that the photocurrent of Cu3/Fe1–In₂O₃ increased with increasing temperature and was positively correlated with temperature. Since the photocurrent signal is a macroscopic manifestation of carrier separation and transfer characteristics, the above experimental results indicated that the correlation of the photoelectric response of In_2O_3 with temperature shifted from negative to positive, and the carrier response of In_2O_3 to temperature was effectively changed from negative to positive by co-doping with Cu and Fe.

In short, the photothermal promotion mechanism of Cu/Fe can be summarized as follows: Firstly, the UV–Vis–NIR diffuse reflectance spectra (Fig. 5) illustrated that the band gap of Cu3/Fe1– In_2O_3 (2.25 eV) was smaller compared with bare In_2O_3 (2.60 eV), which was attributed to the enhancement of the radiative absorption intensity of



Fig. 5. – (a) UV–Vis–NIR diffuse reflectance spectra of bare In₂O₃ and Cu3/Fe1–In₂O₃. (b) UV–Vis–NIR diffuse reflectance spectra of Cu3/Fe1–In₂O₃ at different temperatures.



Fig. 6. – (a) PL spectra of bare In_2O_3 and Cu3/Fe1– In_2O_3 . Time-resolved PL emission decay spectra of (b) bare In_2O_3 and (c) Cu3/Fe1– In_2O_3 . (d) PL spectra of Cu3/Fe1– In_2O_3 at different temperatures. (e) Photocurrent response curves of Cu3/Fe1– In_2O_3 at different temperatures. (f) EIS changes of Cu3/Fe1– In_2O_3 at different temperatures.

In₂O₃ by Cu– Fe in the UV and visible regions, respectively, leading to a significant increase in the number of photoinduced carriers. Secondly, the experimental results of variable-temperature PL and TRPL (Fig. 6a–d) illustrated that the introduction of Cu and Fe effectively suppressed the recombination of the EHPs and prolonged the lifetimes of the EHPs, respectively, which increased the probability of the photo induced carriers to participate in the chemical reactions. Last but not least, the introduction of Cu/Fe helped to reduce the transport impedance of EHPs in interfacial reactions (Fig. 6f), which improved the separation and migration efficiency of the photo induced carriers and thus raised the energy conversion efficiency of PTC-HER. Furthermore, we verified that co-doping Cu and Fe can tune recombination of carriers during radiative conversion, which resulted in a transformation of the photoelectric performance of In₂O₃ in the photothermal synergy, as evidenced by the reversal of the photocurrent (Fig. 6e). As mentioned above, we verified that co-doping Cu and Fe can tune the recombination of carriers during the radiation conversion process, so that the thermal effect can be converted from a harmful factor to a beneficial effect in the photothermal synergy.

4. Conclusion

In summary, by applying a series of temperature-dependent characterization methods and experimental verifications, we explored the effects of temperature on the energy band structure, radiation absorption, and photoinduced carrier behavior of semiconductors. All the experimental results showed that increasing the reaction temperature was conducive to enhancing the light absorption of semiconductors, promoting the separation and migration of photoinduced carriers and enhancing the ability of photoinduced carriers in the reduction reaction.

However, in some cases, high temperatures may also decrease the performance of photoinduced carriers in PTC by inducing some negative effects. For example, In_2O_3 undergowent a serious radiative recombination phenomenon at high temperature, which caused a sharp decrease in the number of photoinduced carriers, resulting in a 73 % drop in photocurrent of In_2O_3 at 80 °C. Subsequent experiments demonstrated

that through co-doping of Cu/Fe transition metal, the severe radiative recombination of In_2O_3 at high temperature can be repaired, the lifetime of photoinduced carriers can be prolonged by 22 %, the photocurrent will reverse to be positively correlated with temperature, and the rate of H₂ production can be improved by 2.53 times at 250 °C relative to that at 150 °C. All these effects indicated that the catalyst may be modified by Cu/Fe transition metal co-doping to make it more suitable for PTC synergistic system. This study helped elucidate the temperature-dependent behavior of photoinduced carriers in semiconductors and provided valuable guidance for the design of highly efficient photothermal catalytic materials.

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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Appendix A. Supplementary data

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