High Photothermally Active Fe₂O₃ Film for CO₂ Photoreduction with H₂O Driven by Solar Light

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High photo thermally active Fe₂O₃ film for CO₂ photoreduction with H₂O driven by solar light

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High photo-thermally active Fe₂O₃ film for CO₂ photoreduction with H₂O driven by solar light

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ABSTRACT. A Fe₂O₃ film exhibited very high activity for CO₂ photoreduction with H₂O under high solar light intensity and temperature. The main detected gas products were CH₄, C₂H₄ and C₂H₆ hydrocarbons, simultaneously produced on α -Fe₂O₃ film. The maximum generation rates of CH₄, C₂H₄ and C₂H₆ reached 1470.7, 736.2 and 277.2 $\mu\text{mol}/(\text{g}_{\text{cata}}\cdot\text{h})$, respectively, thus strongly outperforming the performance obtained under standard conditions, and CO₂ conversion reached 0.78%. These results prove the feasibility of the novel approach, and the suitability of iron oxide as a thermally active semiconductor catalyst. The noteworthy performance of Fe₂O₃ film was arising from the beneficial contribution of the highly favorable photo thermal conditions and the formation of Fe₂O₃/Fe₃O₄ Z-scheme system. The study elucidates the feasibility of photo-thermal synergistic catalytic effect for solar energy utilization in CO₂ photoreduction.

KEYWORDS: Photoreduction; photothermal; $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$; CO_2 reduction

Global CO_2 emissions reached 37 gigatons in 2018, which is twice as much as the amount being absorbed back into nature. Solar energy is the most abundant renewable energy resource, holding the answer to reduce CO_2 emissions from fossil fuels. Combining solar energy with CO_2 and H_2O reduction represents the sunshine to liquid vision to produce green liquid fuels.¹ The use of solar energy to convert CO_2 into hydrocarbons can simultaneously achieve CO_2 emission control, carbon cycle closure and solar energy storage. In view of reducing the growing CO_2 emissions contributing to global warming, one possible main approach for reaching this objective is photochemical, and another is thermochemical CO_2 conversion. The former is known as CO_2 photo(electron-)catalytic reduction or artificial photosynthesis based on the photoelectric effect and represents a promising pathway for CO_2 conversion to fuels and chemical commodities using solar energy.^{2,3} The latter is intended to split CO_2 (or H_2O) under extreme high temperatures (often $>1000^\circ\text{C}$) to produce CO (or H_2) that can be further converted to liquid fuels.^{4,5} In addition to the thermochemical route, CO_2 photoreduction is widely developed and under investigation at present. However, due to the wide band gap of semiconductor catalysts, CO_2 photoreduction is usually carried out at room temperature and often only uses short wavelength light in the solar spectrum (thus it can only convert a small portion of the solar spectrum), while most of solar energy is converted into low-grade useless heat during the reaction, which restrains the overall solar energy conversion efficiency. Though much attention has been paid on the topic, it still requires strong research efforts to reach reasonable fuel production range.⁶⁻⁸

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3 Recently, the photothermal concept has been developed to effectively use the long
4 wavelength solar light. Some metals are doped into the photocatalyst system to generate the hot
5 charge carriers for CO₂ photoreduction via plasmatic effect.^{9,10} Meanwhile, there may exist a more
6 direct and simple way to achieve the same goal. Indeed, the low grade or low temperature heat,
7 generated from long wavelength light can be raised and upgraded by using concentrated solar light
8 technology. Although CO₂ reduction is a photoelectron catalytic reaction with minor influence of
9 reaction temperature, it can be expected that such a temperature rising could improve the reaction
10 extent by favoring thermodynamics, even exhibiting a photo-thermal synergistic catalytic effect.
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14 To achieve this goal, a high thermally active and stable semiconductor catalyst is required, as
15 it is recognized that temperature rising will influence the properties of the semiconductor catalyst,
16 by enhancing the charge recombination in the semiconductor, in turn decreasing the photocatalytic
17 activity. Iron is one of the most common elements in the earth's crust. Iron oxide in the α -phase
18 (α -Fe₂O₃) with a band gap of 2.2 eV has good thermal stability and the capability to absorb photons
19 in the visible spectral range; hence it attracts increasing attention in the CO₂ photoreduction field
20 as a semiconductor photocatalyst.^{11,12} Iron oxide can also be found in different oxidation states,
21 being involved in the form of Fe₂O₃/Fe₃O₄ or Fe₃O₄/FeO redox pairs at high temperatures, which
22 is in favor of solar thermochemical splitting of CO₂.^{13,14} Therefore, iron oxide is expected to be a
23 suitable candidate catalyst for the CO₂ reduction process. Nevertheless, the low conduction band
24 (CB) bottom level of α -Fe₂O₃ implies photogenerated electrons with low energy, which is
25 unfavorable for carrying out reduction reactions with CO₂ and H₂O. Thus, single α -Fe₂O₃ cannot
26 meet the demand of CO₂ photoreduction. Thus, it is desirable to unveil a suitable way to promote
27 α -Fe₂O₃ in CO₂ photoreduction and related photocatalytic processes.¹⁵
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3 In the present study, high photo thermal reduction of CO₂ with H₂O was achieved with a
4 Fe₂O₃ film using a home-made concentrating solar light reactor system. It was found that Fe₂O₃
5 film can be partially reduced to form Fe₂O₃/Fe₃O₄ heterojunctions under the high intensity light
6 irradiation and high temperature conditions, which greatly promoted the efficiency of CO₂
7 reduction.
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15 The Fe₂O₃ film was prepared by anodization method. The concentrating light reactor system
16 involving Fresnel lens was transmission type. Detailed description of the experimental set-up can
17 be seen in Supporting Information. Figure 1 displays the results of CO₂ photoreduction under given
18 photo thermal conditions (Figure 1a shows the result under nature light at room temperature,
19 Figure 1b-d show the results under high temperature achieved by concentrating solar light). The
20 Fe₂O₃ film exhibits a normal performance at room temperature. CH₄ is detected as the main
21 product, which is consistent with the results of previously reported systems.^{16,17} About 3.14
22 μmol/g_{cata} yield is obtained after 3 h reaction. Under high light intensity and temperature
23 conditions, in addition to CH₄, C₂H₄ and C₂H₆ are also detected as the main gas products.
24 Noticeably, all the hydrocarbon compounds yields are boosted from a few μmol/g_{cata} to several
25 hundreds of μmol/g_{cata}. After 3 h reaction, the maximum CH₄ yield can reach 1652.1 μmol/g_{cata},
26 along with 52.3 μmol/g_{cata} of C₂H₄ and 167.9 μmol/g_{cata} of C₂H₆. The total amount of hydrocarbons
27 based upon single carbon atoms reaches 2092.5 μmol/g_{cata}. The maximum conversion of CO₂
28 reaches 0.47%. The global conversion is thus about 700 times higher than that obtained under
29 nature light and room temperature. Therefore, the CO₂ photoreduction behavior of Fe₂O₃ film
30 catalyst is significantly improved by highly concentrated sunlight photo-thermal conditions. Since
31 the increase of the reaction rate was substantial at the light concentrating ratio (CR) of 600, the
32 reasons for the reaction rate boosting under this condition need to be elucidated.
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X-ray diffraction (XRD) analyses were performed for the fresh and used Fe_2O_3 film catalysts, as shown in Figure 2. The fresh Fe_2O_3 film shows typical $\alpha\text{-Fe}_2\text{O}_3$ characteristic peaks of (400) and (440) face, indicating that the Fe_2O_3 catalyst prepared by anodization method has a regular structure (such as nanotubes).¹⁸ After reaction, Fe_3O_4 phase clearly appears on the XRD patterns and coexists with $\alpha\text{-Fe}_2\text{O}_3$ phase, which indicates that $\alpha\text{-Fe}_2\text{O}_3$ was partially reduced to Fe_3O_4 phase. The more active the catalyst, the clearer the change of the film crystal phase.

X-ray photoelectron spectrometry (XPS) was further performed. XPS spectra were recorded to determine the oxidation states of Fe at the surface of the thin film of $\alpha\text{-Fe}_2\text{O}_3$ and the results are shown in Figure 3. In Figure 3A related to the fresh catalyst, three peaks can be observed directly or by deconvolution on the Fe 2p_{3/2} curve of fresh $\alpha\text{-Fe}_2\text{O}_3$ film at about 710.4 eV, 713.1 eV and 718.8 eV respectively. After reaction (Figure 3B), the peak at 718.8 eV was weakened to be nearly vanished, while the other two peaks moved to low binding energy (about 705.8 eV and 708.8 eV). According to previous reports, the peak position of Fe 2p_{3/2} is between 710.6 and 711.2 eV, and the area of Fe 2p_{3/2} peak is greater than that of Fe 2p_{1/2}. The Fe 2p_{3/2} peak has also been associated with a satellite peak located approximately 8 eV higher than the main Fe 2p_{3/2} peak for $\alpha\text{-Fe}_2\text{O}_3$, and Fe 2p_{3/2} of Fe_3O_4 does not have a satellite peak.^{19,20} Therefore, the presence of the satellite peak at 718.8 eV in the Figure 3A confirms the existence of $\alpha\text{-Fe}_2\text{O}_3$; and after reaction, the weakening of the satellite peak implies the reduction of $\alpha\text{-Fe}_2\text{O}_3$. Furthermore, the peak position of Fe 2p_{3/2} moves downward after reaction, which can be attributed to the formation of Fe^{2+} 2p_{3/2} of Fe_3O_4 .²¹ The XPS spectra thus indicate the reduction of $\alpha\text{-Fe}_2\text{O}_3$ to Fe_3O_4 during the reaction.

There is a sharp increase in gas yields between 1.5h and 2h in Figure 1c. Before 1.5h, the reaction rate is lower than $400 \mu\text{mol}/(\text{g}_{\text{cata}} \cdot \text{h})$, whereas after 2h, the reaction rate is clearly higher than $600 \mu\text{mol}/(\text{g}_{\text{cata}} \cdot \text{h})$. As the reaction conditions do not change, some materials properties change may

happen on the α -Fe₂O₃ catalyst during the reaction progress. CO₂ photoreduction was then carried out under the same conditions but stopped at 2 h reaction. The activity and XRD pattern of the used catalyst are presented in Figure 4. The resulting activity is still poor. Only CH₄ and C₂H₄ are detected. The total hydrocarbon yield is below 200 $\mu\text{mol/g}_{\text{cata}}$. Meanwhile, the characteristic peaks of Fe₃O₄ appear, which indicates that α -Fe₂O₃ has been reduced. These results confirm that the formation of Fe₃O₄ is not occurring at the end of the reaction but rather at the initial stage of the reaction. The formation of Fe₃O₄ in the initial stage may act as an activation step for α -Fe₂O₃ film during CO₂ photoreduction.

Considering that the reaction conditions may be not optimal, further experiment was carried out at concentrating ratio of 600 while reaction temperature was controlled at about 500 °C. The result is shown in Figure 5. In the initial 3 h period, the hydrocarbons yield increases slowly, and then at 4 h, the yield boosts to reach even higher values. If the initial 3 h is considered as the activation stage, the reaction rate of CH₄, C₂H₄ and C₂H₆ between 3 h and 4 h would reach 1470.7, 736.2 and 277.2 $\mu\text{mol}/(\text{g}_{\text{cata}}\cdot\text{h})$, respectively. The total hydrocarbons yield rate reaches 3497.5 $\mu\text{mol}/(\text{g}_{\text{cata}}\cdot\text{h})$ and the CO₂ conversion reaches 0.78%. The solar energy to hydrocarbons efficiency can be calculated to be about 0.05% (Table S1).

From the above results, it can be stated that the activity of CO₂ photoreduction is first improved by the photo-thermal conditions and then by the change of catalyst properties. The latter reason may be more important. It is known that the CB potential of α -Fe₂O₃ (0.28 eV vs NHE) is more positive than the CO₂/CO₂⁻ (-1.7eV), which is unsuitable to reduce CO₂. The CO₂ reduction is often realized by forming heterojunctions or yielding a Z-Scheme system with some other semiconductors such as g-C₃N₄. Here, the effect may happen between the α -Fe₂O₃ and Fe₃O₄. Although the band gap of Fe₃O₄ in bulk phase can be lower to 0.1eV, many studies also have

shown that the band gap of Fe_3O_4 can reach from 2.2 eV to 3.08 eV in nanoparticles shape. The Fe_3O_4 may form a Z-scheme system with Fe_2O_3 which could achieve higher negative potential and realize the CO_2 reduction with H_2O .^{15, 22-24} The schematic illustration of reaction mechanism of Fe_2O_3 film is represented in Figure 6.

In summary, we reported for the first time a highly efficient photo-thermal pathway for CO_2 photoreduction. The study demonstrated that the high photo thermal conditions involving concentrated sunlight can effectively activate the Fe_2O_3 film catalyst by forming $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ junctions, thereby enabling to obtain much higher hydrocarbons yield than current level, thus outperforming the conventional approach. The catalyst characterization suggests that the formation of $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ Z-scheme system may account for the high catalyst activity. This method can improve the efficiency of solar energy conversion by utilizing both short and long wavelengths in the solar spectrum, and thus helps for the progress of CO_2 photoreduction.

FIGURES

Figure 1. CO₂ photoreduction behavior of Fe₂O₃ film under different concentrating ratios (CR).

a) nature light (CR=1, 50 °C; b) CR=400, 450 °C; c) CR=600, 560 °C; d) CR=800, 680 °C

Figure 2. XRD patterns of Fe₂O₃ film before and after reaction under different concentrating ratios (CR)

Figure 3. XPS patterns of fresh (A) and used (B) Fe₂O₃ film catalysts

Figure 4. CO₂ photoreduction behavior and XRD pattern of Fe₂O₃ film after 2h light irradiation under concentrating ratio of 600

Figure 5. CO₂ photoreduction performance of Fe₂O₃ film at CR=600 and temperature=500 °C

Figure 6. Schematic illustration of reaction mechanism of Fe_2O_3 film

ASSOCIATED CONTENT

Supporting Information. A listing of the following files are available free of charge.

Experimental details and additional figures, tables and (PDF)

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Notes

The authors declare no conflict of interest.

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