

Solar Fuel Production



Photothermal Conversion of CO₂ into CH₄ with H₂ over Group VIII Nanocatalysts: An Alternative Approach for Solar Fuel Production**

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Abstract: The photothermal conversion of CO₂ provides a straightforward and effective method for the highly efficient production of solar fuels with high solar-light utilization efficiency. This is due to several crucial features of the Group VIII nanocatalysts, including effective energy utilization over the whole range of the solar spectrum, excellent photothermal performance, and unique activation abilities. Photothermal CO₂ reaction rates (mol h⁻¹ g⁻¹) that are several orders of magnitude larger than those obtained with photocatalytic methods (μmol h⁻¹ g⁻¹) were thus achieved. It is proposed that the overall water-based CO₂ conversion process can be achieved by combining light-driven H₂ production from water and photothermal CO₂ conversion with H₂. More generally, this work suggests that traditional catalysts that are characterized by intense photoabsorption will find new applications in photo-induced green-chemistry processes.

How to provide clean, affordable, and reliable energy without causing climate change is a common concern in the world.^[1] The conversion of CO₂, the major component of greenhouse gas, into renewable hydrocarbon fuels by solar energy provides a sustainable way for carbon cycling, and is of significance in solving both energy and environmental issues. Today, solar fuel production by CO₂ conversion is mainly achieved according to two approaches: The first approach is

based on photocatalytic CO₂ conversion over semiconductors, using photoexcited e⁻/h⁺ to drive the simultaneous processes of water photooxidation (at the valence band) and CO₂ photoreduction (at the conduction band).^[2] However, photocatalytic CO₂ conversion remains very inefficient because of the kinetic limitations of multiple e⁻/H⁺ transfer processes and the limited abilities of traditional semiconductors to activate thermodynamically stable CO₂ molecules.^[3] According to recent results,^[2,4] the reaction rates of photocatalytic CO₂ conversion processes using H₂O or H₂ as the hydrogen source are on the order of μmol h⁻¹ g⁻¹, even leaving aside the uncertainty of the carbon source of the final reduction products (the observed products possibly originate from the photoreforming of residual carbonaceous substances rather than the photoreduction of CO₂). The second approach makes use of the dissociation of CO₂ by two-step thermochemical cycles of metal oxide redox pairs (mainly Zn/ZnO, Ce₂O₃/CeO₂, FeO/Fe₃O₄, and SnO/SnO₂); these cycles are driven by the heat obtained from concentrated solar radiation.^[5] However, the very high operation temperature (nearly 2000 °C) and special reactor design are indispensable to realize this reaction. More convenient methods for light-driven CO₂ conversion, especially for water-based CO₂ conversion, a process that mimics photosynthesis, are urgently required.

The recently emerged photothermal effect (or rapid heating) of nanometals inspired us to seek new methods for the production of solar fuels. The photothermal effect of nanometals stems from the dissipation of photon energy into heat. It appears that the remarkable increase in the local temperature of the nanometals results from excitation of the surface plasmon band and the consequential fast thermal relaxation of the exciton, leading to prompt conversion of the light energy into heat.^[6] The photothermal effect, which is induced by surface plasmon resonance (SPR) absorption, has been widely studied for applications in cancer therapy (mainly Au and Pd).^[7] The SPR-induced charge transfer and/or the photothermal effect also enable the effective harvesting of visible and even near-infrared (NIR) light to drive useful reaction processes, such as water splitting,^[8] the decomposition of organic contaminants,^[9] and Suzuki coupling reactions.^[10] Therefore, we were encouraged to face the great challenge of highly efficient utilization of solar energy (mainly 300–2500 nm, photon energy distributed as follows: ultraviolet light: 4%; visible light: 43%; infrared radiation: 53%). Herein, we expand the use of this photothermal effect to nanocatalysts that are based on Group VIII metals (Ru, Rh, Ni, Co, Pd, Pt, Ir, and Fe) for the catalytic conversion of CO₂ with H₂ into CH₄ (Sabatier reaction) and CO (reverse

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water–gas shift reaction) for the highly efficient production of solar fuels. These nanocatalysts are generally of a dark grey or black color (Supporting Information, Figure S1). They have much stronger photoabsorption abilities than traditional semiconductor photocatalysts and display a strong photothermal effect. The results of this work indicate that with Group VIII catalysts, reaction rates for the photothermal CO₂ conversion that are several orders of magnitude higher (ca. mol h⁻¹ g⁻¹) than those observed with other photocatalysts can be achieved. The highly efficient CO₂ conversion is due to several features of the Group VIII nanocatalysts, including effective energy utilization over the whole range of the solar spectrum, excellent photothermal performance, and a unique H₂ activation ability (to create active H atoms, which are the key intermediates for CO₂ hydrogenation at low onset temperatures).^[11]

Herein, the intentional use of inert Al₂O₃ as the support instead of photocatalytically active materials such as TiO₂ enabled us to independently investigate the performance of the Group VIII nanocatalysts in photothermal CO₂ conversion. The catalysts were prepared by impregnation of mesoporous Al₂O₃ (BET surface area = 136 m² g⁻¹; see Figure S2) in the precursor solutions of Group VIII metals, followed by calcination at 300 °C for two hours. Further reduction by H₂ was needed for the Ni/Al₂O₃, Co/Al₂O₃, and Fe/Al₂O₃ catalysts (for TEM images of the Group VIII nanocatalysts on Al₂O₃ support, see Figure S3; the particle size of the Group VIII nanocatalysts varied from several nanometers to several tens of nanometers). CO₂ (ca. 2–2.05 mmol) and H₂ (ca. 8.2–8.5 mmol; the molar H₂/CO₂ ratio is slightly larger than 4:1) were mixed as the initial reactants in a batch-type reaction system (Figure S20).

Under photoirradiation, all of the Group VIII nanoparticles were active catalysts for CO₂ conversion (Figure 1 a for the Ru/Al₂O₃ catalyst; for the other catalysts, see Figure S4). Their activities and selectivities are summarized in Table 1. The use of Ru/Al₂O₃ and Rh/Al₂O₃ led to the highest reaction rates, followed by the two cost-efficient catalysts Ni/Al₂O₃ and Co/Al₂O₃. The performance of the Ru/Al₂O₃, Rh/

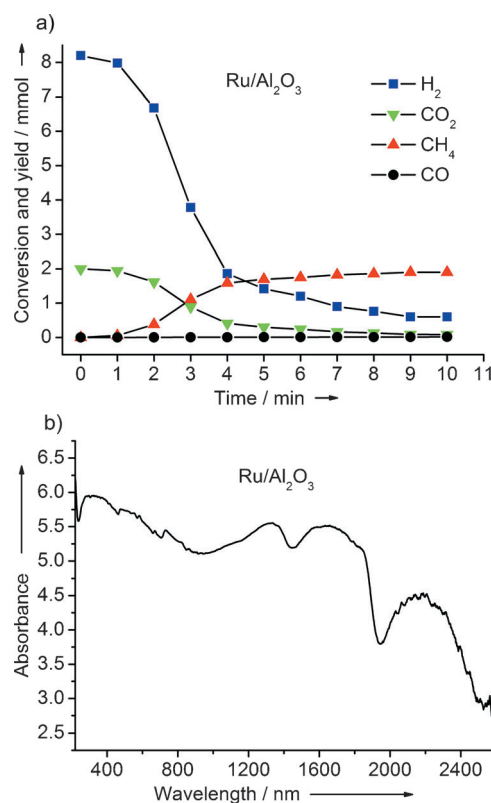


Figure 1. a) Photothermal CO₂ conversion with and b) UV/Vis/NIR spectrum of the Ru/Al₂O₃ catalyst. The reaction was performed in a gas mixture of CO₂ (ca. 2–2.05 mmol) and H₂ (ca. 8.2–8.5 mmol) under irradiation with a 300 W Xenon lamp. The catalyst sample (0.1 g) was spread onto a round air-permeable quartz fiber filter with an area of 7 cm².

Al₂O₃, Ni/Al₂O₃, Co/Al₂O₃, and Pd/Al₂O₃ catalysts was superior to that of the Pt/Al₂O₃, Ir/Al₂O₃, and Fe/Al₂O₃ catalysts in terms of selectivity for CH₄ production (ca. 99%) and CO₂ conversion (>90%). Only a very small amount of CO was produced by pure Al₂O₃ in control experiments (Figure S4o and Figure S5). In the absence of H₂, photothermal CO₂ conversion cannot occur (Figure S6). Therefore, both the Group VIII catalysts and H₂ are indispensable for highly efficient photothermal CO₂ conversion. As the cheapest noble metal among the Group VIII metals, the Ru nanocatalyst displayed excellent recycling properties (Figure S7). No obvious changes were observed with respect to nanoparticle size and distribution for the Ru as well as Ni nanoparticles after photothermal reactions (Figure S3a–d). The fast decay of the performance of the Pt/Al₂O₃ catalyst in CO₂ conversion is possibly due to a poisoning effect induced by CO.^[12] Under photoirradiation, the maximum reaction rates for the conversion of CO₂ in the presence of Group VIII catalysts were measured to be in the magnitude of mol h⁻¹ g⁻¹ (the carbon source for CH₄ produced over the Ni/Al₂O₃ catalyst was confirmed by labelling experiments with ¹³CO₂; Figure S8). For the current

Table 1: Activities and selectivities of the Group VIII catalysts.^[a]

Sample	Metal loading ^[b] [wt %]	$R_{\max}$ ^[c] [mol h ⁻¹ g ⁻¹]	Conversion ^[d] of CO ₂ [%]	Selectivity ^[d] for CH ₄ [%]	Selectivity ^[d] for CO [%]
Ru/Al ₂ O ₃	2.4	18.16	95.75	99.22	0.78
Rh/Al ₂ O ₃	2.6	6.36	96.25	99.48	0.52
Ni/Al ₂ O ₃	2.1	2.30	93.25	99.04	0.95
Co/Al ₂ O ₃	2.5	0.90	92.58	99.51	0.49
Pd/Al ₂ O ₃	2.0	0.53	93.43	98.64	1.36
Pt/Al ₂ O ₃	2.4	0.47	60.42	15.55	84.45
Ir/Al ₂ O ₃	2.8	0.05	14.94	63.25	36.74
Fe/Al ₂ O ₃	2.4	0.02	7.27	4.04	95.96
TiO ₂	—	9.04×10^{-7}	—	68.23	31.77
Pt/TiO ₂ ^[e]	2.5	8.01×10^{-9}	—	100	0
Ru/TiO ₂ ^[e]	2.5	5.31×10^{-9}	—	100	0

[a] For the reaction conditions, see Figure 1 a. [b] Loading amounts of the Group VIII nanoparticles determined by ICP-OES. [c] $R_{\max}$: the maximum CO₂ reaction rate. [d] Based on the amount of the gas at the end of the reaction (for the reaction duration, see Figures 1 a, S4 a, and S9 a,b). [e] Water (2 mL) was used instead of H₂ as the hydrogen source.

CO₂ conversion by a photocatalytic method using H₂O or H₂ as the hydrogen source, reaction rates that are only on the order of $\mu\text{mol h}^{-1}\text{g}^{-1}$ or even $\text{nmol h}^{-1}\text{g}^{-1}$ have been described.^[2,4] In comparative experiments with a high-surface-area TiO₂ photocatalyst (commercial ST01, BET surface area = $343\text{ m}^2\text{g}^{-1}$) for the CO₂ conversion in the presence of H₂ (Figure S9a) or H₂O (Ru or Pt as co-catalysts; Figure S9b) under the same photoirradiation conditions, CO₂ reaction rates on the order of $\text{nmol h}^{-1}\text{g}^{-1}$ to $\mu\text{mol h}^{-1}\text{g}^{-1}$ were obtained (Table 1). Therefore, the CO₂ reaction rates that are achieved by the Group VIII catalysts through photothermal activation are approximately six orders of magnitude greater than those achieved with photocatalytic methods. A valence-state analysis of some primary Group VIII nanocatalysts (Ru, Rh, and Ni) showed that the active phase should mainly consist of metallic species (for details of the XPS analysis, see Figure S10).

UV/Vis/NIR spectra indicate that all of the Group VIII catalysts are excellent absorbers over a very broad photoirradiation range that covers ultraviolet light, visible light, and infrared radiation (Figure 1b for the Ru/Al₂O₃ catalyst; for the other catalysts, see Figure S4). The intense absorption implies that a high utilization efficiency of solar energy would be feasible. Monitoring of the catalyst temperature demonstrated that the photoirradiation induced a significant thermal effect (Figure 2 and Figure S11). For almost all of the

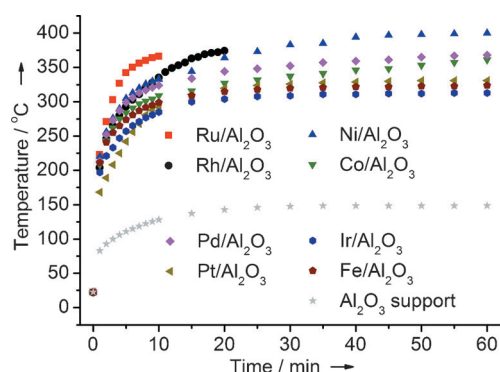


Figure 2. Monitoring of the catalyst temperature.

catalysts, the temperature reached approximately 200 °C within the first minute, whereas the temperature of pure Al₂O₃ support in a control experiment was measured to be approximately 80 °C. Under continuous photoirradiation, Group VIII catalysts maintain a reaction temperature of about 300–400 °C, which is approximately 200 °C higher than that of pure Al₂O₃ support. The excellent photothermal properties in conjunction with the unique activation ability of the Group VIII nanocatalysts favor the highly efficient photo-induced conversion of CO₂. No additional enhancement effects on the CO₂ conversion that are due to the irradiation were observed. We then compared the CH₄ evolution over the Ru/Al₂O₃ catalyst under thermal and photothermal conditions (Figure S12). In both experiments, the onset temperatures were found to be approximately 140 °C. No obvious differences between the CH₄ evolution curves for the two sets

of conditions were found. To investigate whether CO₂ hydrogenation is affected by photocatalytic processes (photoexcitation processes), the CH₄ evolution over the Ru/Al₂O₃ catalyst was measured under irradiation with monochromatic light. With this method, the thermal effect was effectively suppressed (no obvious temperature increase was observed, and the temperature remained at ca. 21–23 °C over the whole experiment). We selected some typical monochromatic light filters (441, 502, 549, 601, and 710 nm) in the visible-light range for this test (for the photon distribution, see Figure S13a). It was found that the CH₄ evolution rate (CO evolution was not observed) was very low (ca. 0.02 $\mu\text{mol}/100\text{ min}$) in the dark, and this evolution rate remained almost unchanged no matter which monochromatic light was used (Figure S13b). This result reflects the fact that photo-induced CO₂ methanation over Ru/Al₂O₃ is not mediated by photocatalysis, but by a photothermal effect. All of these results imply that the mechanism of this process differs from the alleged photocatalytic mechanism,^[13] and that the light-induced thermal effect should dominate the process of CO₂ conversion.

Wide-band-gap semiconductors ($E_g > 3\text{ eV}$), such as Ti-, Nb-, Ta-, Ga-, and Ge-based oxides with adequate redox potentials, constitute the main materials for photocatalytic CO₂ conversion, which are highly dependent upon excitation by ultraviolet irradiation (which only accounts for 4 % of the total solar energy).^[12] In contrast to traditional photocatalytic methods, the photothermal CO₂ conversion over Group VIII catalysts does not require ultraviolet irradiation as the excellent absorption of visible light and infrared radiation (which together account for 96 % of the total solar energy) can effectively drive photothermal CO₂ conversion. In the absence of ultraviolet light, photothermal CO₂ conversion can still proceed over the Ru/Al₂O₃ catalyst (Figure S14). Therefore, Group VIII catalysts are advantageous over traditional photocatalysts because of the highly efficient utilization of solar energy and in particular of the low-energy photons of visible light and infrared radiation.

It is interesting that the low-cost Ni/Al₂O₃ catalyst was even more active than some noble-metal catalysts (Pd, Pt, and Ir). This implies that the Ni/Al₂O₃ catalyst is a promising candidate for practical use in future artificial photo-induced CO₂ conversion systems. In further investigations, increasing the loading amount of Ni on Al₂O₃ (for XRD and TEM results, see Figure S15, S16) demonstrated that a 7.3 wt % Ni/Al₂O₃ catalyst achieved comparable activity to a 2.6 wt % Rh/Al₂O₃ catalyst, and CO₂ conversion reached 90 % within 15 minutes (Figure 3a and Figure S4a). Both temperature variation and CO₂ conversion showed similar tendency when increasing the loading amount of Ni. (Figure 3). Obviously, more catalytically active sites and heat-gathering centers will be created with an increase in the amount of Ni on the Al₂O₃ support, which leads to remarkably enhanced CO₂ conversion. Aside from the catalytic abilities of the nanometals, some other factors (mainly the design of the reactor) interfered with the increase in CO₂ conversion efficiency with an increasing in the loading amount of Ni from 7.3 % to 12.9 %. For example, the gas flow rate (controlled by the vibration of the gas circulation pump; Figure S20) has

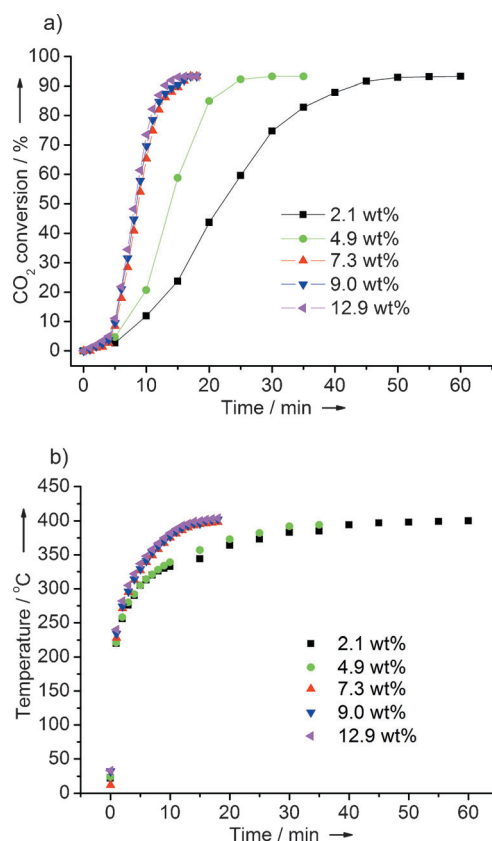
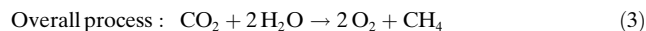
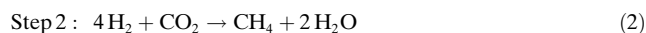


Figure 3. a) CO₂ conversion with and b) temperature monitoring of Ni/Al₂O₃ catalysts. For the reaction conditions, see Figure 1 a.

reached its maximum for the present batch-type reaction system. Although increasing the loading amount of Ni will lead to an increase in the number of catalytically active sites, the limited flow rate restricts the amount of reactant gas that can be supplied and thus hampers the increase in the reaction rate of CO₂ conversion. However, the reaction speed of CO₂ conversion might be further increased by using a different reaction system (such as a flow-type reaction system). The use of Ni/Al₂O₃ catalysts with larger Ni particle sizes (ca. 20–100 nm, obtained from the H₂ reduction of Al₂O₃ supported NiO nanoparticles produced by ball milling) led to a slight decrease in reaction temperature as well as CO₂ conversion (Figure S17). This might be caused by the change in photothermal conversion owing to the different size of the Ni particles and the decrease in the number of catalytically active sites. Using commercial TiO₂ (P25, BET surface area = 57 m² g⁻¹) as a support remarkably enhanced CO₂ conversion with Ni nanocatalysts (Figure S18). This support effect should be the subject of future studies.

Ideally, CO₂ conversion should mimic the photosynthesis of green plants by using abundant and stable H₂O instead of H₂ as the hydrogen source for CO₂ conversion to realize the sustainable production of solar fuels and to maximize the conversion of solar energy into chemical energy. However, photocatalytic CO₂ conversion is far less efficient in terms of reaction rates and the efficient utilization of solar energy. Future studies on water-based CO₂ conversion and solar fuel production should be based on more flexible strategies for

solar-energy utilization than photocatalysis. Based on the results of this work, we propose that water-based solar fuel generation can be achieved by a two-step process [Eq. (1)–(3)], which combines photo-driven H₂ production through



water splitting and photothermal CO₂ hydrogenation (Figure 4). H₂ production could be realized through different

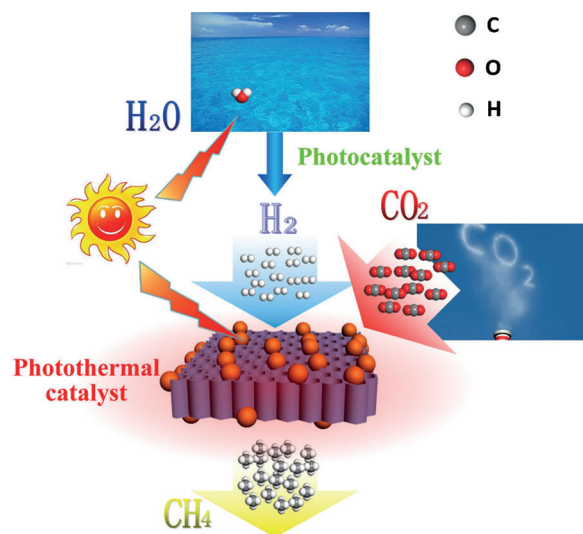


Figure 4. Two-step water-based CO₂ conversion driven by solar energy.

light-driven methods, including photocatalysis,^[14] photoelectrochemistry,^[15] photothermal effects,^[5a,b,16] and photobiology.^[17] Then, the generated H₂ will be used as a hydrogen source for photothermal CO₂ methanation. For example, according to recent results on the photocatalytic production of H₂ through water splitting in the absence/presence of a sacrificial reagent, the H₂ evolution rate is on the order of μmol h⁻¹ g⁻¹ to mmol h⁻¹ g⁻¹.^[14d] Given that all of the H₂ was used for photothermal CO₂ conversion, the overall reaction rate for two-step water-based CO₂ conversion can still be expected to be higher than that of the direct CO₂ photo-reduction by water over semiconductor photocatalysts. Therefore, the two-step method should become more efficient and technically feasible in the future. After combustion of CH₄ (the primary component of compressed natural gas), the generated CO₂ can be recycled^[18] for continuous methanation. In theory, zero carbon dioxide emission can be realized if a rationally designed carbon cycling system can be implemented (Figure S19).

In summary, the outstanding CO₂ conversion efficiency highlighted herein is based on two predominant features of the Group VIII nanocatalysts, namely 1) the highly efficient utilization of solar light and excellent photothermal performance, and 2) a unique activation ability for the hydro-

genation of CO₂. The progress in the development of technologies for the light-driven H₂ production through water splitting and the highly efficient photothermal CO₂ hydrogenation reported herein illustrate the feasibility of overall water-based CO₂ conversion. It should be noted that catalytic CO₂ hydrogenation covers a wide range of reaction processes. Aside from the production of solar fuels, hydrogenation of CO₂ can also produce other useful chemical feedstocks.^[19] Future work should focus on exploring diversified reaction pathways for photothermal CO₂ conversion. Studies of photothermal catalysis in general and new reaction mechanisms as well as of potential synergism between light and thermal effects, in particular, will create new opportunities for chemical science and technology.

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