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Remarkable CO₂ photoreduction activity using TiO₂ nanotube arrays under favorable photothermal conditions driven by concentrated solar light

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Abstract. The photoreduction of carbon dioxide (CO₂) to solar fuels is meaningful in many fields relevant to CO₂ emission control, solar energy conversion and storage, carbon-neutral fuel production, CO₂ conversion and carbon cycle closure. The CO₂ photoreduction on TiO₂ nanotube arrays using concentrated sunlight under favorable photothermal conditions is considered in this work. TiO₂ is a typical catalyst for the process while the reaction rate is still kept at rather poor level, partly because of the mild reaction conditions employed. In this study, the TiO₂ photocatalyst was shaped as nanotube arrays and the current process limitations were tackled by raising the incident light intensity and reaction temperature by using concentrating solar light (concentration ratio between 200 and 800), while jointly increasing the achievable H₂O and CO₂ partial pressure. The results showed that the rate of CO₂ photoreduction on the TiO₂ nanotube arrays was increased by hundred times. The use of concentrated solar light heightens hydrocarbons production rate to thousand $\mu\text{mol g}^{-1} \text{h}^{-1}$ and enriches hydrocarbons products to CH₄, C₂H₄, and C₂H₆. The favorable effects on enhancing the catalyst performance were ascribed to the intensification of reaction conditions. This noticeable breakthrough may represent an important step forward in the deployment of CO₂ photoreduction technologies.

Keywords: CO₂ conversion; photocatalysts; CO₂ photoreduction; TiO₂ nanotube arrays; photothermal; concentrating solar light

Photocatalytic reduction of CO₂ or artificial photosynthesis is an important process as it can readily use sunlight to convert CO₂ into hydrocarbons (solar fuels), which can solve the problems of CO₂ emission mitigation, CO₂ recycling, solar energy storage and carbon-neutral fuels, simultaneously [1]. One of the most attractive benefits of the photocatalytic process relies in the possible reaction achievement under ambient conditions. However, such ambient reaction conditions impose stringent requirements on catalysts performance. Most of the reported reaction rates are still kept at small values (spanning from a few to dozens of μmol·g⁻¹·h⁻¹), especially for the representative commonly used TiO₂ photocatalyst. A large number of photocatalysts and technologies have been developed to carry out the photocatalytic process [2-3]. However, both the solar energy conversion efficiency and the CO₂ conversion rate are still kept at a very poor level. Generally, fast recombination of charge carriers, mismatch between the band gap of photocatalyst and solar radiation spectrum, and unsuitable band-edge position are the key problems [4-6]. Following the guidelines to address the current challenges, researchers are developing more effective photocatalysts and methods for CO₂ photoreduction [7-9].

Among the various possible photocatalysts, TiO₂ (especially shaped as nanotube arrays) has attracted much attention owing to its large surface area, appropriate band-edge position and superior electron transport properties [10-12]. Roy *et al.* [13] have described that free-standing, mechanically robust, TiO₂ nanotube array membranes may enable reaching high CO₂ photoreduction efficiency, wherein CO₂ and water vapor would enter one side of the nanotube array membrane while the produced fuel would exit from the other. However, its wide band gap (3.2 eV) limits the optical response only to UV spectrum (representing about 3-7% of total sunlight). Many efforts have been made to enhance the photocatalytic activity of TiO₂, while the CO₂ conversion efficiency still needs to be further improved. The reported reaction rates are often limited in the range of several to dozens of μmol·g⁻¹·h⁻¹. Regarding the photocatalyst amount (usually lower than 1 g), the total product yield is actually quite small. In order to confirm that the products are really produced from CO₂, Teramura and Tanaka suggested to use isotopically labeled ¹³CO₂ [14]. It is necessary to identify an efficient way to achieve significant breakthrough and advance in the field of CO₂ photoreduction.

The current barrier may be tackled by reactor design optimization and intensification of reaction conditions [15-16]. For the CO₂ photoreduction reaction, the following kinetic rate law has been applied:

$$-r'_{\text{CO}_2} = kI^\alpha \frac{p_{\text{CO}_2} p_{\text{H}_2\text{O}}}{(1 + K_{\text{CO}_2} p_{\text{CO}_2} + K_{\text{H}_2\text{O}} p_{\text{H}_2\text{O}})^2} \quad (1)$$

where r'_{CO_2} represents the rate of CO₂ photoreduction, k the kinetic rate constant, I the sunlight intensity, α the reaction order, K_{CO_2} and $K_{\text{H}_2\text{O}}$ the adsorption equilibrium constants, p_{CO_2} and $p_{\text{H}_2\text{O}}$ the partial pressure of CO₂ and H₂O. According to the equation (1), the light intensity, the reaction temperature and the reactants partial pressure shall have a direct influence on the reaction, but it has not been concerned to date. Most of studies are indeed carried out at ambient temperature.

At ambient temperature, the concentration of CO₂ is limited by CO₂ solubility if the reaction is carried out in the liquid phase; whereas the vapor pressure of H₂O is limited to several kPa if the reaction is carried out in the gas phase. If the reaction can be carried out at high temperatures (higher than 100°C), the vapor pressure of H₂O can be increased from several kPa to hundreds kPa, and the reaction rate in gas phase should be improved accordingly. Solar light intensity has also a direct influence on the reaction rate, at least before the catalyst ability for light absorption

reaches saturation. The joint action of both increased temperature and sunlight intensity may enhance the reaction rate far above the presently achieved level. Some recent works have reported the feasibility of photothermal catalytic CO₂ reduction [17].

Meanwhile, it is admitted that optical concentration of solar radiation can potentially heighten the temperature and reduce the cost of reactor systems due to a reduction in the device size and components mass (thus saving materials). However, increasing temperature may bring two competing effects. It can reduce the band gap of the semiconductor, which is in favor of broadening light adsorption range; but it can also stimulate the charge recombination and decrease the catalytic efficiency. Thus the global optical concentration effect depends on which mechanism is prevailing under the situation. Nonetheless, optical concentration can potentially reduce the reactor size and catalyst amount for a given fuel productivity.

The effect of solar concentration on the reaction rate of CO₂ photoreduction on TiO₂ catalyst has been tested with a 300W Xe light source in our group [18]. The results showed that light intensity can raise the reaction rate up to about 15 times. However, the output power of Xe light source is not high enough to generate high grade heat and to heat the reactants to high temperature.

In this study, natural sunlight was used as light source and was concentrated by a large Fresnel lens (1 m diameter), in order to obtain high light intensity and temperature conditions for CO₂ photoreduction. The Fresnel lens was made of PMMA material, which can transmit about 93% of solar light without any wavelength selection. Catalytic activity of TiO₂ nanotube arrays was investigated under such favorable photothermal conditions and showed a remarkable improvement. The reaction was carried out with the catalyst exposed to concentrated sunlight, thereby enabling processing at higher temperatures. The results show that reaction conditions intensification greatly enhances the reaction rate by hundred to thousand times. The most attractive asset is that the possible tuning of the processing temperature and pressure can be realized by varying the concentrated sunlight intensity without any other external energy source. Apart from that, as the temperature reached several hundreds of °C, the thermal component of solar energy could also be valorized, which greatly improved the utilization of solar energy. This can potentially provide substantial benefic impact and improve efficiency of photocatalysis and solar-driven CO₂ conversion using both the thermal and quantum components of solar light.

Regarding the photocatalyst synthesis, TiO₂ nanotube arrays catalyst was prepared by anodization method. Generally, it consists of five steps including pretreatment, polishing, anodization, cleaning and annealing. Ti sheets (purchased from Hebei metal Co.) were cut into 20mm x 40mm shapes, and washed in acetone solution for 30 minutes. The sheet surface was polished and smoothed with 7000 meshes sandpaper. The Ti sheet was then cleaned by ultrasonic bath to remove carvings. A chemical polishing solution with ratio of HNO₃:H₂O₂:H₂O:NH₄F(18 wt% solution):CO(NH₂)₂(18 wt% solution) = 5:3:10:1:1 was prepared. The cleaned Ti sheet was put into the solution for a period of time to remove the surface oxidized part. The sheet was then washed with ethanol for several times and immersed in ethanol to avoid random oxidization. The as-treated Ti sheet was placed into the tank face-to-face with a same shaped Pt electrode (distance between the Ti and Pt sheet: 4 cm). The voltage was adjusted to 50 V and the anodization temperature was set at 45 °C. After the anodization step, the TiO₂ nanotube arrays were moved from the tank into an acetone solution, and cleaned by ultrasounds for 30 minutes to remove the electrolyte and surface bundling. The sample was

immediately transferred to the vacuum drying chamber and dried at 60 °C for 12 hours. Finally, the sample was annealed in a muffle at 400 °C for 2 hours with a heating rate of 1 °C/min.

The crystal structure of the sample was characterized by XRD (X-ray diffraction) on a X'Pert PRO X-ray diffractometer apparatus (with CuK α source, scanning angle ranging from 20° to 80° (2 θ) with a rate of 0.02°). The surface morphology of the sample was characterized by FESEM (field emission scanning electron microscopy, Hitachi S-4700).

The CO₂ photoreduction with H₂O was performed using an in house-made concentrating sunlight reactor system (Figure 1). The system is composed of a batch reactor, a Fresnel lens (diameter of 1 m) and an auto-tracking system. The Fresnel lens is used to concentrate solar light to the catalyst surface and it is designed with its plano side facing the sun (parallel light source), and the Fresnel surface facing the reactor (focus). Due to the different sun position throughout the day, both the lens and the reactor are fixed on a frame that moves according to the sun position. The auto-tracking system (containing a sensor, a controller, and a motor) is implemented to follow in real time the sun position and to keep the incident sunlight always perpendicular to the catalyst and Fresnel lens surface. The concentrating ratio (CR) is calculated based on the lens area and the catalyst area. The reactor setup can be adjusted in the up and down directions on the track, so that the concentrating ratios can be adjusted. The developed reactor is a stainless steel batch reactor with a quartz glass window of 15 mm thickness above the reactor body, so that the solar light source can enter the reactor and irradiate the catalyst. Experiments thus used real sunlight as light source.

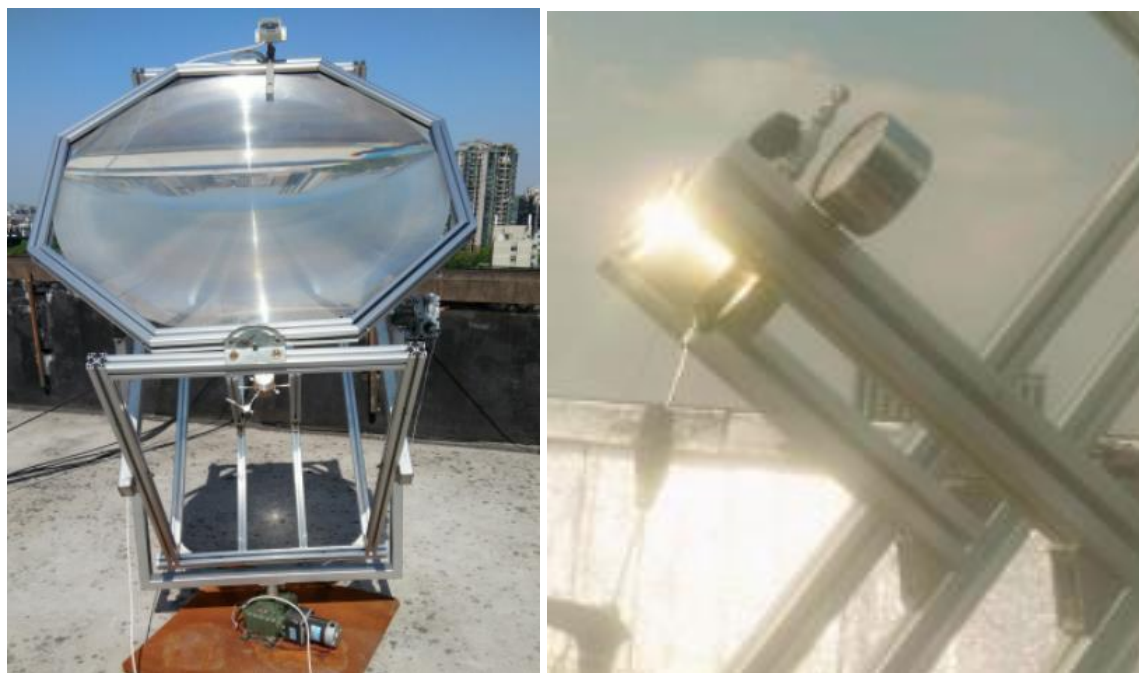


Figure 1. Experimental system including the solar concentrator Fresnel lens (left) and the solar reactor (right)

Before the reaction, the catalyst was first placed into the reactor and fixed with a catalyst support. A thermocouple was placed on the catalyst surface to measure the temperature. The reactor was then sealed. Highly pure N₂ was fed into the reactor for 30 min to remove the impurity gases

from the device, and then highly pure CO₂ was injected into the system to change the gas atmosphere in the reactor. A proper amount of liquid H₂O was injected into the reactor from the side inlet. The auto-tracking system was turned on to follow the sun, concentrate the sunlight, and start the reaction. Gas sampling was carried out after a period of reaction time. The reduced hydrocarbon products were detected by online gas chromatography (GC-2014, Shimadzu) equipped with FID detector and HT-PLOT Q capillary column (Hychrom, 30 m, ID 0.32 mm, Filme 20 μm). Blank experiments were performed to exclude the potential misleading of impurities [18].

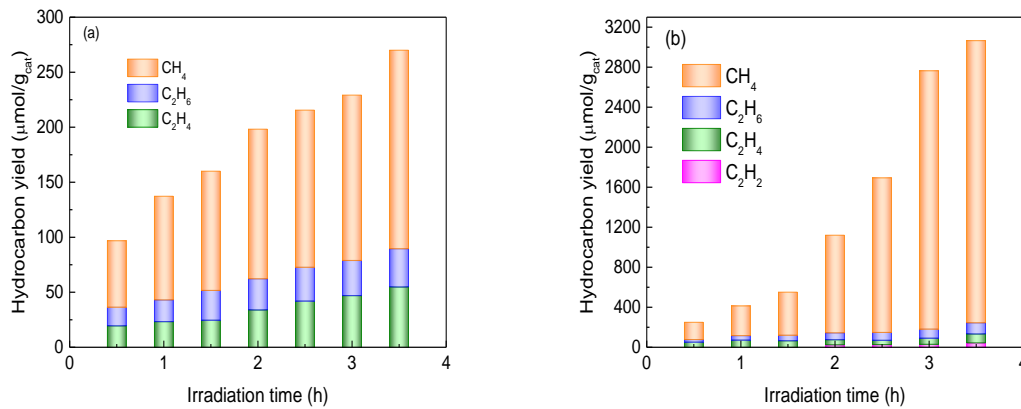
The photocatalytic reduction reaction rate and the CO₂ conversion were calculated by the following equations:

$$r_{C_i} (\mu\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}) = \frac{n_{C_i}}{(w_t \times \text{time})} \quad (2)$$

$$X_{\text{CO}_2} (\%) = \frac{n_{\text{CH}_4} + 2n_{\text{C}_2\text{H}_2} + 2n_{\text{C}_2\text{H}_4} + 2n_{\text{C}_2\text{H}_6}}{n_{\text{CO}_2}} \times 100 \quad (3)$$

Where n_{C_i} is the amount of carbon in each gas species, w_t is the catalyst mass, n_i is the mole amount of gas species i .

Figure 2 summarizes the CO₂ photoreduction results on TiO₂ nanotube arrays under different photothermal conditions and concentrating ratios (CR), and Table 1 reports the gas production rates and CO₂ conversion. According to the results, the high photothermal conditions from concentrating sunlight not only increased the reaction rate, but also enriched the evolved product species. Besides CH₄, both C₂H₄ and C₂H₆ appeared to be detected by the gas chromatograph (GC) in significant amounts (in contrast, C₂H₂ amount was negligible). After 3.5 h of reaction, the total hydrocarbons yield reached about 258 μmol·g⁻¹, 3077 μmol·g⁻¹, 1736 μmol·g⁻¹ and 929 μmol·g⁻¹ under concentrating ratio of 200, 400, 600, and 800, respectively (Figure 2). This result proved that the fuel yield was increased by hundreds of times when compared to that under natural sunlight conditions. Considering the existence of C₂ species, the total CO₂ photoreduction conversion was enhanced.



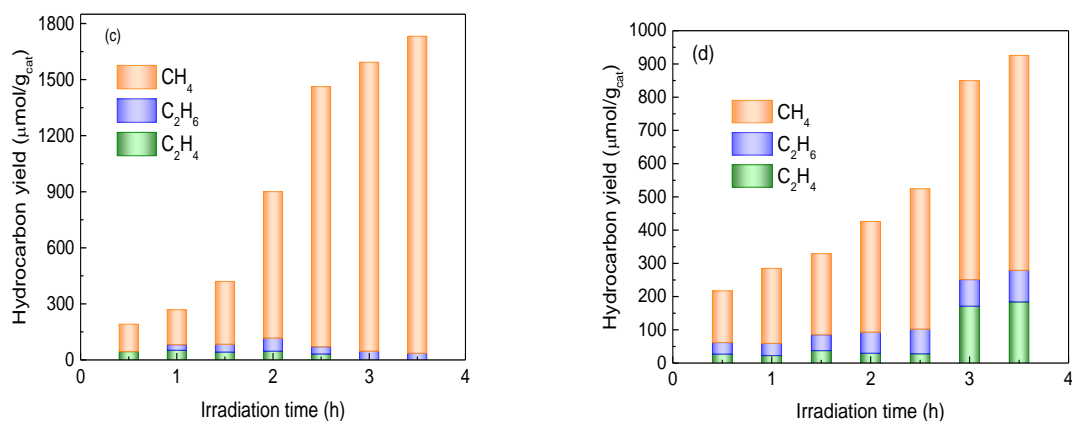


Figure 2. Evolution of the different product yields on the TiO_2 nanotube arrays under different concentrating ratios: (a) CR = 200; (b) CR = 400; (c) CR = 600; (d) CR = 800

Table 1. Gas production rates, CO_2 conversion, and solar-to-chemical energy conversion efficiency

CR	Production rates ($\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$)				CO_2 conversion /%	$\text{STC}^{\text{a}}/\%$		$\text{STC}^{\text{b}}/\%$	
	CH_4	C_2H_2	C_2H_4	C_2H_6		UV	Total	UV	Total
800	310.7	0	57.0	36.5	0.11	0.12	0.0081	0.070	0.0049
600	557.7	0	88.2	35.2	0.18	0.19	0.013	0.11	0.0080
400	861.1	12.0	100.8	53.3	0.27	0.28	0.020	0.17	0.012
200	120.8	0	38.8	33.9	0.06	0.061	0.0042	0.036	0.0025

a. calculated based on Hangzhou irradiation intensity

b. calculated based on AM1.5 spectra and intensity

The temperature of the catalyst surface and the total pressure in the reactor have been recorded (Table 2). The maximum temperature on the catalyst surface reached 474.6°C , 576.3°C , 546.6°C and 532.6°C , and the maximum pressure in the reactor reached 0.43 MPa, 0.90 MPa, 0.70 MPa and 0.80 MPa, respectively. This proves that both the reaction temperature and pressure were efficiently intensified by concentrating sunlight. The intensification of reaction conditions is clearly in favour of the CO_2 photoreduction reaction rate.

Table 2. Recorded temperature of the catalyst surface and total pressure in the reactor

t (h)	CR = 200		CR = 400		CR = 600		CR = 800	
	T($^\circ\text{C}$)	P(MPa)	T($^\circ\text{C}$)	P(MPa)	T($^\circ\text{C}$)	P(MPa)	T($^\circ\text{C}$)	P(MPa)

0.5	357.7	0.28	516.3	0.7	331.1	0.25	532.6	0.6
1.0	474.6	0.35	523.5	0.9	427.7	0.31	436.8	0.8
1.5	423.8	0.4	548.5	0.85	408.1	0.37	474.3	0.55
2.0	364.5	0.43	576.3	0.62	524.5	0.7	455.7	0.46
2.5	354.8	0.38	535.6	0.48	538.6	0.55	350.7	0.42
3.0	376.5	0.33	490.3	0.3	546.6	0.4	405.7	0.38
3.5	446.7	0.36	468.9	0.26	433	0.32	376.8	0.22

To further confirm the results, the effect of water content and initial CO₂ pressure on the reaction performance was also investigated in Figure 3 and Tables 3-4. It can be observed that both parameters have a positive effect on the reaction rate and yield. The reaction rate and hydrocarbon yield increase with the initial CO₂ pressure and H₂O content in the considered experimental range.

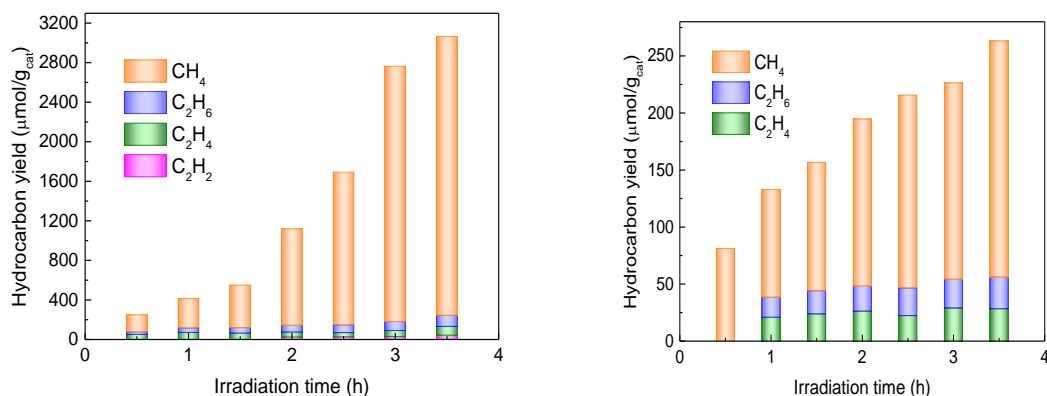


Figure 3. Gas species production yields on the TiO₂ nanotube arrays (CR = 400) under 0.05 MPa CO₂ partial pressure, 2 ml H₂O (left) and 0.1 MPa CO₂, 0.2 ml H₂O (right)

Table 3. Formation rate of CO₂ photoreduction related products under different water volumes (CR = 400)

Water volumes ml	CH ₄ μmol·g ⁻¹ ·h ⁻¹	C ₂ H ₂ μmol·g ⁻¹ ·h ⁻¹	C ₂ H ₄ μmol·g ⁻¹ ·h ⁻¹	C ₂ H ₆ μmol·g ⁻¹ ·h ⁻¹	Total μmol·g ⁻¹ ·h ⁻¹
0.8	1166.1	2.7	210.9	231.4	1611.1
0.2	162.3	0	20.9	17.5	200.7

Table 4. Formation rate of CO₂ photoreduction related products under different CO₂ partial pressures (CR = 400)

CO ₂ partial pressure Mpa	CH ₄ μmol·g ⁻¹ ·h ⁻¹	C ₂ H ₂ μmol·g ⁻¹ ·h ⁻¹	C ₂ H ₄ μmol·g ⁻¹ ·h ⁻¹	C ₂ H ₆ μmol·g ⁻¹ ·h ⁻¹	Total μmol·g ⁻¹ ·h ⁻¹
0.05	287.3	0	58.5	27.6	373.4

CO₂ photoreduction is a process enabling solar energy conversion and storage, thus solar-to-fuel energy conversion efficiency is a key performance output for this application. In this regard, solar-to-chemical energy conversion efficiency (STC) has been defined as follows:

$$\text{STC} = \frac{\text{Output energy as chemical product}}{\text{Energy of incident solar light}} = \frac{r \cdot \Delta G_r}{P_{\text{sun}} \cdot S} \quad (4)$$

where r , ΔG_r , P_{sun} and S are the production rate of the chemical specie of interest (mol/s), the Gibbs energy of the reaction (J/mol), the energy flux density of concentrated sunlight (W/m²), and the area of the reactor (m²), respectively.

Here, the STC was calculated based upon two standards. One is the real light intensity measured at experimental days; another is the ASTM-G173 AM1.5 global tilt (AM1.5G) spectrum, and the solar energy flux density is 1 kW·m⁻², as a reference. The standard Gibbs energies of CO₂ reduction to methane (CH₄), acetylene (C₂H₂), ethylene (C₂H₄), and ethane (C₂H₆) are +818, +1472, +1331 and +1467 kJ mol⁻¹, respectively, at 298 K. The resulting STC are listed in [Table 1](#). The maximum STC on the TiO₂ nanotube arrays under different concentrating ratios can reach about 0.28% based on UV part and 0.02% based on total incident sunlight.

Interestingly, in some figures, it can clearly be observed a sharp increment of hydrocarbons yield around 1.5-2.5 h. As the reaction conditions are not changed with the reaction time, it is reasonable to infer that the sharp increment is originated from the catalyst properties. Figure 4 shows XRD patterns of the catalyst before and after reaction under different concentrating ratios. As a reference, a P25 TiO₂ sample from Degussa company was also analyzed. XRD shows that after annealing at 400 °C, TiO₂ nanotube arrays have mainly the structure of anatase phase (Figure 4a). Under a concentrating ratio of 200, the catalyst keeps the characteristic peaks of anatase TiO₂ phase, and some of the catalyst samples are partly converted into rutile phase such as in the case of the reaction under higher concentration ratios (CR = 400 and 600, Figure 4b).

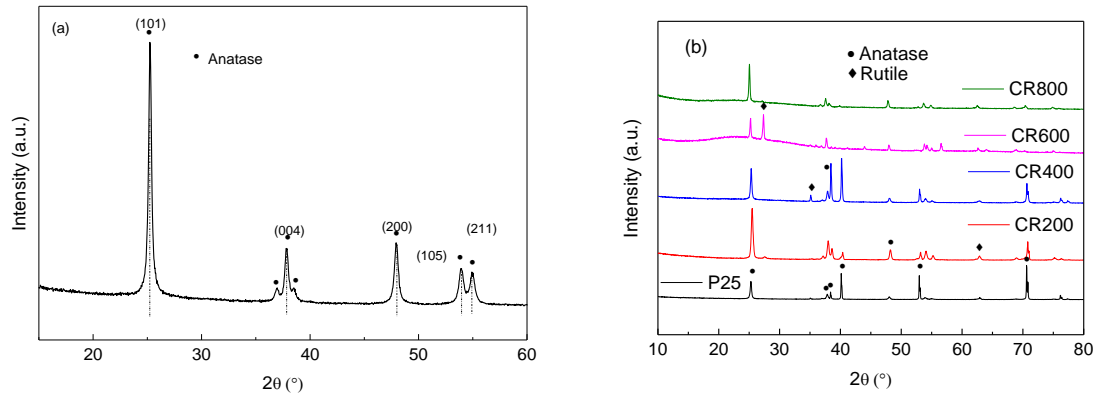


Figure 4. XRD patterns of TiO₂ nanotube arrays (a) before and (b) after reaction

Figure 5 displays SEM images of TiO₂ nanotube arrays catalyst before and after reaction under different concentration ratios. Viewed from top, the TiO₂ nanotube arrays show regular tube shape with some covers. The diameters of the tubes are in the range of 50-100 nm. After reaction, the shape of tubes has been transformed. Under concentration ratio of 400, the tubes change into well shaped cubic crystals, while under concentration ratio of 600, the tubes seem to be melted down, and they form a porous material with smooth external surface. These results mean that the reaction conditions also have an influence on the properties of the TiO₂ nanotube arrays catalyst. The phase and morphology transformation of the catalyst can be beneficial to the catalytic performance [19-20].

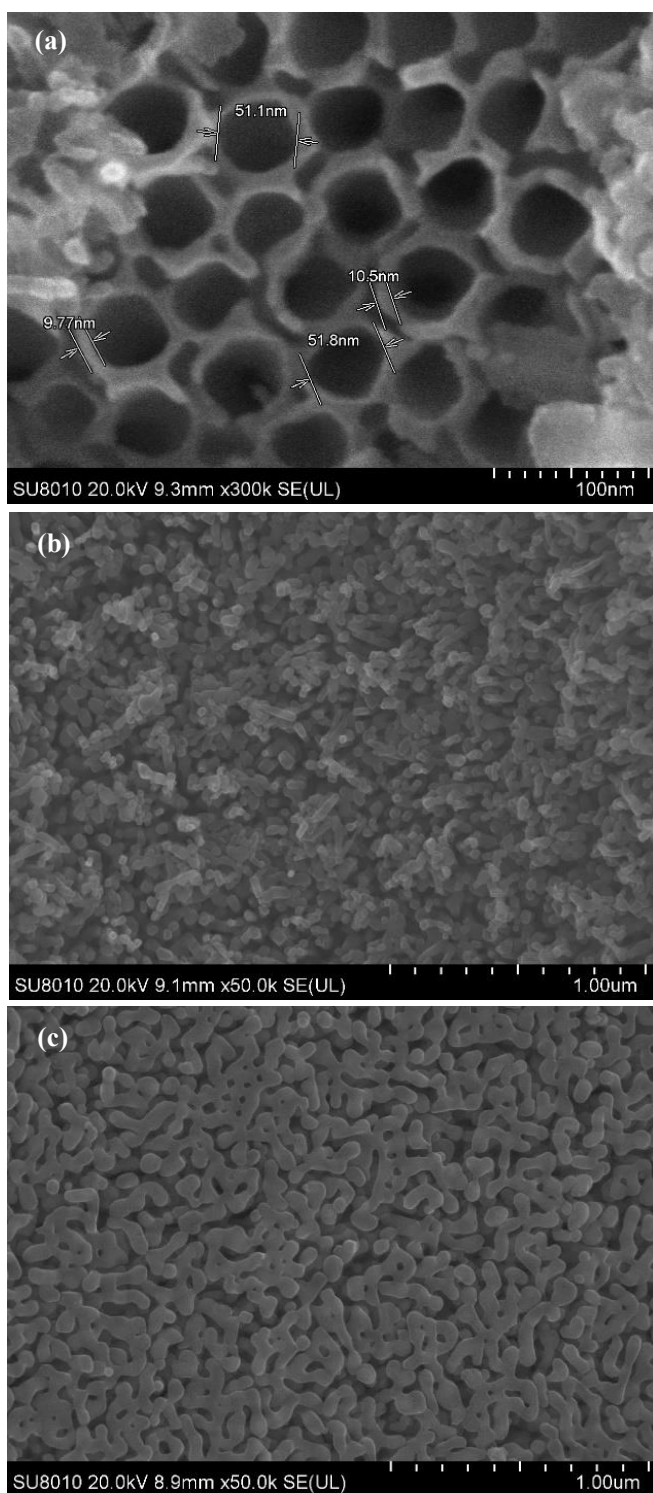


Figure 5. SEM images of TiO_2 nanotube arrays before and after reaction: (a) fresh; (b) after reaction with CR = 400; (c) after reaction with CR = 600

The outstanding reaction rate confirmed the beneficial impact of concentrating solar light on CO₂ photoreduction performance. It is meaningful to decompose the contributions of different factors. According to the activity tests and catalyst characterization, light intensity, temperature, pressure, and catalyst properties can contribute together to increase the reaction rate. Among them, the temperature effect is not direct, as without light, no CO₂ thermo-reduction reaction would happen in the investigated temperature range, and the reaction is still photocatalytic when the temperature increases. The blank experiment (i.e., the reaction carried out under high temperature without any light irradiation) confirms that the light is the main driving force for the reaction. The contribution of thermal effect is thus considered to be related to the heating of both CO₂ and H₂O while simultaneously raising the partial pressure of the two reactants (thereby raising the maximum pressure in the reactor to about 0.9 MPa). Concentrating solar light also has an effect on the catalyst properties since a phase change is occurring during the initial reaction time, which might be seen as an activation step for the catalyst. Part of TiO₂ is converted into rutile phase in the initial stage, and the mechanism for the activation step might be originated from the formation of heterojunctions between anatase and rutile TiO₂, which can be beneficial to the activity [21-22].

All the contributions can be reflected in the reaction kinetics. Therefore, the reaction kinetics has been investigated based on the reaction rate obtained under different conditions. As the temperature and reaction pressure have been recorded, the only unknown parameter is the reaction order related to the light intensity, which is considered to decrease with the light intensity increment, and at very large light intensity, it is close to zero [23-24]. The large concentrating ratio of solar light guarantees that the reaction order related to light intensity can be assumed as zero. The reaction kinetics of the CO₂ photoreduction can thus be processed and the reaction rate constants can be obtained by regression, as listed in Table 5. The obtained reaction rate law is as follows:

$$-r'_{\text{CO}_2} = 5.05 \times 10^6 \exp\left(-\frac{34980}{RT}\right) \frac{p_{\text{CO}_2} p_{\text{H}_2\text{O}}}{(1+0.45p_{\text{CO}_2}+0.91p_{\text{H}_2\text{O}})^2} \quad (5)$$

The obtained activation energy is about 35.0 kJ/mol, which may suggest that besides the photocatalytic effect, there should be a thermally activated effect under the reaction conditions.

Table 5. Reaction rate parameters obtained by regression

A	Ea (kJ/mol)	K _{H₂O} (MPa ⁻¹)	K _{CO₂} (MPa ⁻¹)	α	R ²
(5.05±0.5)×10 ⁶	35.0±0.1	0.91	0.45	0	0.90

In summary, the beneficial role of a concentrating solar light reactor system in enhancing CO₂ photoreduction activity has been demonstrated. It not only increases the incident light intensity and reaction temperature, but also solves the problem of the mismatch between CO₂ and H₂O concentration during the CO₂ photoreduction process. The intensification of reaction conditions as well as the formation of rutile/anatase TiO₂ heterojunctions have greatly increased the reaction rate by hundreds and even thousands of times, which is of major interest for lowering the critical barriers to progress in the field of CO₂ photoreduction. On the basis of the present average reaction rate achieved in this work and the advances in the attained performance, it should be relevant to reconsider the suitable processing conditions for improving the CO₂ photoreduction process using both the thermal and quantum components of solar light. The proposed

photothermal process should decrease the critical barriers to progress in the field of CO₂ photoreduction as it reconsiders the suitable reaction conditions for enhancing noticeably the performance of CO₂ photoreduction with H₂O.

Conflict of interest

The authors declare no competing financial interest.

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Data Availability Statement

The data that supports the findings of this study are available within the article.

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