



## Enhanced photocatalytic CO<sub>2</sub> hydrogenation with wide-spectrum utilization over black TiO<sub>2</sub> supported catalyst

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### ABSTRACT

Light-driven conversion of CO<sub>2</sub> into chemicals/fuels is a desirable approach for achieving carbon neutrality using clean and sustainable energy. However, its scale-up application is restricted due to insufficient efficiency. Herein, we present a photothermal catalytic hydrogenation of CO<sub>2</sub> into CH<sub>4</sub> over Ru/black TiO<sub>2</sub> catalysts, aiming to achieve the synergistic use of light and heat in solar energy during CO<sub>2</sub> conversion. Owing to the desirable spectral response ability and photothermal conversion performance of black TiO<sub>2</sub>, an efficient combination of photocatalysis and thermocatalysis has been established. The CO<sub>2</sub> hydrogenation was significantly accelerated because of the increased catalyst surface temperature enabled by the photothermal effect of black TiO<sub>2</sub>. Simultaneously, through the *in situ* X-ray photoelectron spectroscopy (XPS) observation, electron-rich Ru nanoparticles was achieved based on the photo-induced excitation, thereby providing more negative hydride to improve nucleophilic attack to the CO<sub>2</sub>, obtaining the CH<sub>4</sub> yield of 93.8%.

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To alleviate the climate change caused by carbon cycle imbalance and reduce the dependence on fossil fuels, conversion of CO<sub>2</sub> into value added chemicals and fuels is one promising choice [1–4]. Considering that solar energy is clean and inexhaustible to a certain extent, photocatalysis is thought to play a crucial role in the future industry system and has been widely investigated [5,6]. Thus, photocatalytic CO<sub>2</sub> conversion is a desirable approach for CO<sub>2</sub> utilization. However, insufficient efficiency limits the application of photocatalytic CO<sub>2</sub> conversion in large-scale industrial production. Although various strategies have been applied to improve the photocatalytic performance, the efficient CO<sub>2</sub> conversion is still a vital challenge.

Photothermal catalysis, which has the potential to utilize the whole solar spectrum, is one desirable choice for this issue [7,8]. During the photothermal catalysis, while the short-wavelength light could be converted into photogenerated electron-hole pairs to drive the photochemical reactions, the long-wavelength light could be converted into heat, accelerating the reaction, especially for the surface endothermic reaction [9,10]. Considering the high efficiency of thermochemical method, the combination of photo-

catalysis and thermocatalysis could strike a balance between energy consumption and conversion efficiency, which has a broad application prospect in CO<sub>2</sub> methanation [11–15].

To achieve desirable synergy between photochemical and thermochemical, the construction design of catalyst is crucial. TiO<sub>2</sub> has been widely applied in photocatalysis [16,17]. However, the photocatalytic activity of TiO<sub>2</sub> is greatly limited due to its poor response ability to visible light [18,19]. To solve this issue, Chen *et al.* prepared TiO<sub>2-x</sub> (black TiO<sub>2</sub>) from TiO<sub>2</sub> by strong reduction treatment, and black TiO<sub>2</sub> exhibits excellent spectral response range and photocatalytic activity [20,21]. Thus, black TiO<sub>2</sub> has attracted increasing attention and been widely applied in photocatalysis such as photocatalytic water splitting. Additionally, because of its inherent black color, black TiO<sub>2</sub> could perform high photothermal conversion ability. Considering the broad spectral response range and excellent photothermal conversion efficiency of black TiO<sub>2</sub> [22–25], it is reasonable to speculate that black TiO<sub>2</sub> could balance the photoelectric conversion and photothermal conversion during the photothermal catalytic CO<sub>2</sub> conversion, giving promising catalytic activity. Therefore, in the present work, supported black TiO<sub>2</sub> was synthesized for light-driven catalytic hydrogenation of CO<sub>2</sub> to CH<sub>4</sub> using ruthenium as the active metal, and the synergic mechanism between photocatalysis and thermocatalysis in the CO<sub>2</sub> conversion was investigated.

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**Table 1**

The CH<sub>4</sub> yield from catalytic conversion of CO<sub>2</sub> over different catalysts (reaction conditions: 0.4 MPa mixture gas-N<sub>2</sub>:H<sub>2</sub>:CO<sub>2</sub> = 4:5:1, 20 mg catalyst, 1 h).

Entry	Catalyst	Yield of CH <sub>4</sub> (%) <sup>a</sup>	Yield of CH <sub>4</sub> (%) <sup>b</sup>	Yield of CO (%) <sup>c</sup>
1	TiO <sub>2</sub>	ND	ND	ND
2	Black TiO <sub>2</sub>	ND	ND	ND
3	2 wt% Ru/TiO <sub>2</sub>	ND	18.7	0.1
4	2 wt% Ru/black TiO <sub>2</sub>	ND	40.1	0.2
5 <sup>c</sup>	2 wt% Ru/black TiO <sub>2</sub>	ND	ND	ND

ND = not detected.

<sup>a</sup> Without light.

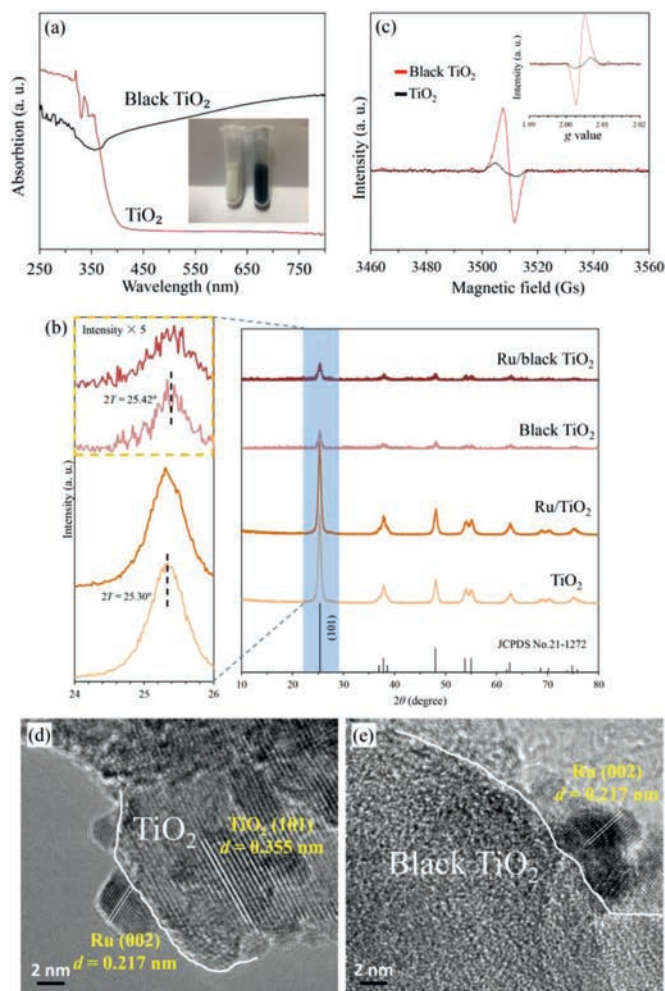
<sup>b</sup> With light.

<sup>c</sup> Without CO<sub>2</sub>.

Firstly, as shown in Table 1, no CH<sub>4</sub> was detected in all entries without irradiation. Considering the high thermodynamic stability of CO<sub>2</sub>, it is difficult to drive the hydrogenation of CO<sub>2</sub> without additional energy input at low temperature. Subsequently, the introduction of irradiation brought significant increase in CH<sub>4</sub> yield (Table 1, entries 3 and 4). Most importantly, the CH<sub>4</sub> yield achieved over 2 wt% Ru/black TiO<sub>2</sub> under irradiation was 40.1%, which was 2 times higher than that achieved over 2 wt% Ru/TiO<sub>2</sub>. Additionally, small amount of CO was also produced in entries 3 and 4. CO species are commonly considered as the important intermediate during the CO<sub>2</sub> hydrogenation. Additionally, we performed the experiments without CO<sub>2</sub> and no carbon containing products were detected, indicating that the injected CO<sub>2</sub> is the sole carbon source. There are two possible reasons for the remarkable improvement of the catalytic activity of Ru/black TiO<sub>2</sub>: (1) The enhancement of CO<sub>2</sub> adsorption capacity; (2) the improvement of spectral response capacity and photothermal conversion efficiency. In order to verify the above conjectures, the CO<sub>2</sub> adsorption capacity and spectral response ability of the catalysts were investigated, and the photothermal conversion performances of the catalysts were evaluated.

Firstly, the light response characteristics of the prepared materials were investigated and Fig. 1a shows the UV-vis diffuse reflectance spectra (DRS) of TiO<sub>2</sub> and black TiO<sub>2</sub>. The spectral response ability of black TiO<sub>2</sub> in long wavelength range is much higher than that of TiO<sub>2</sub>. It is possible that, after the hydrogenation at high temperature, the intrinsic symmetry of TiO<sub>2</sub> crystal was broken, forming an amorphous shell on the TiO<sub>2</sub> surface [26,27]. Thus, a secondary narrow bandgap would be introduced into TiO<sub>2</sub>, enhancing the light absorption. Additionally, considering the more significant thermal effect of long wavelength light, the enhanced long wavelength light response ability of black TiO<sub>2</sub> can make black TiO<sub>2</sub> perform better photothermal conversion efficiency under the broad wavelength irradiation. Subsequently, the CO<sub>2</sub> adsorption observation was conducted. As shown in Fig. S1 (Supporting information), the CO<sub>2</sub> adsorption amount of both TiO<sub>2</sub> and black TiO<sub>2</sub> increased with the increase of pressure and the CO<sub>2</sub> adsorption ability of black TiO<sub>2</sub> was better than that of TiO<sub>2</sub>. The enhanced CO<sub>2</sub> adsorption ability of black TiO<sub>2</sub> gives the prepared catalysts better catalytic activity. Furthermore, nitrogen adsorption/desorption isotherms of TiO<sub>2</sub> and black TiO<sub>2</sub> were compared. The Brunauer-Emmett-Teller (BET) specific surface areas of TiO<sub>2</sub> and black TiO<sub>2</sub> are 99.8 m<sup>2</sup>/g and 100.1 m<sup>2</sup>/g, respectively (Figs. S2a and b in Supporting information). The hydrogenation treatment has not brought significant change of specific surface area to black TiO<sub>2</sub>. Thus, it is reasonable to speculate that the enhanced CO<sub>2</sub> adsorption capacity can be attributed to the formation of oxygen vacancy in black TiO<sub>2</sub> [28,29].

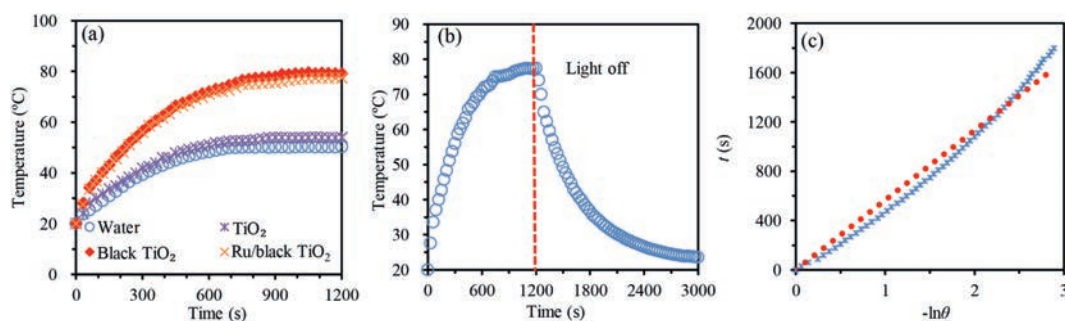
Then, the textural properties were characterized by X-ray diffraction (XRD). As shown in Fig. 1b, the XRD patterns of the catalysts displayed no obvious differences in crystal form compared to the original TiO<sub>2</sub>. However, it is worth noting that the peak intensity of black TiO<sub>2</sub> is significantly lower than that of TiO<sub>2</sub> and the



**Fig. 1.** (a) UV-vis DRS of TiO<sub>2</sub> and black TiO<sub>2</sub>. (b) XRD patterns of TiO<sub>2</sub>, black TiO<sub>2</sub>, 2 wt% Ru/TiO<sub>2</sub> and 2 wt% Ru/black TiO<sub>2</sub>. (c) EPR spectra of TiO<sub>2</sub> and black TiO<sub>2</sub>. (d, e) HRTEM images of 2 wt% Ru/TiO<sub>2</sub> and 2 wt% Ru/black TiO<sub>2</sub>.

(101) plane characteristic peak of black TiO<sub>2</sub> shifts to larger diffraction angle, which can be owing to the decrease of the intrinsic material crystallinity and formation of lattice defects [30]. Subsequently, X-ray photoelectron spectroscopy analysis was applied to investigate the 2 wt% Ru/black TiO<sub>2</sub> (Figs. S3 and S4 in Supporting information). In the XPS diagram of O 1s (Fig. S4), it can be seen that the O 1s can be divided into two peaks, among which the peak at 529.52 eV is attributed to the lattice oxygen (O<sub>L</sub>), while the peak at 530.73 eV can be attributed to the oxygen vacancy (O<sub>V</sub>) in black TiO<sub>2</sub> [31,32]. During the high temperature reduction of TiO<sub>2</sub>, part of the oxygen atoms were deprived, causing the decrease of the electron cloud density and thereby increasing the binding energy of O 1s. Additionally, the existence of oxygen vacancies was proved by electron paramagnetic resonance (EPR) measurements. As shown in Fig. 1c, a strong EPR signal (centering at *g* = 2.003) can be observed in black TiO<sub>2</sub> EPR spectra while TiO<sub>2</sub> only exhibits an extremely weak EPR signal [33]. It indicates that lots of oxygen vacancies were produced in black TiO<sub>2</sub>, which accords with the XPS analysis results.

To further investigate the morphology and structure of the catalysts, high-resolution transmission electron microscopy (HRTEM) were conducted. The measured average particle sizes of TiO<sub>2</sub> and black TiO<sub>2</sub> are 22.5 ± 3.0 nm and 28.1 ± 4.7 nm, respectively (Fig. S5 in Supporting information). The agglomeration of the catalysts after calcination at high temperature is one possible reason

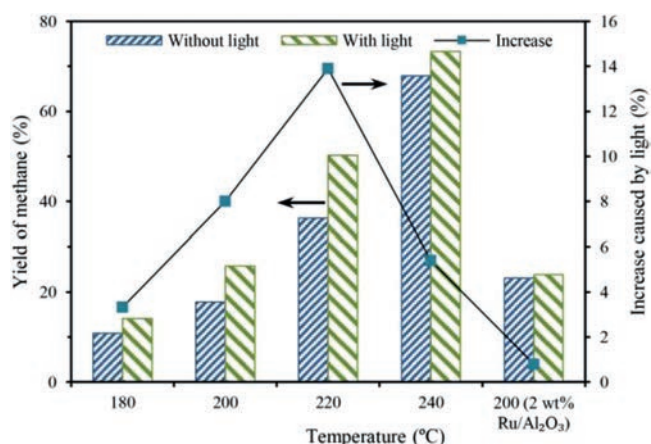


**Fig. 2.** (a) Temperature curves of pure water,  $\text{TiO}_2$ , black  $\text{TiO}_2$  and 2 wt% Ru/black  $\text{TiO}_2$  aqueous solution (200  $\mu\text{g/mL}$ ) under irradiation. (b) The temperature curve of the 2 wt% Ru/black  $\text{TiO}_2$  aqueous solution (200  $\mu\text{g/mL}$ ) for 3000 s. (c) Linear time data versus  $-\ln\theta$  obtained from the cooling period.

for the increase of average particle size. Additionally, as shown in Figs. 1d and e, Ru nanoparticles in the 2 wt% Ru/ $\text{TiO}_2$  and 2 wt% Ru/black  $\text{TiO}_2$  catalysts are loaded on the support surface in the form of small particle and the contact interface between Ru and support can be clearly observed. The lattice fringes belonged to the Ru (002) crystal facet are clearly observed [34]. Owing to the well-contacted interface, efficient photogenerated carriers transferring can be constructed during the reaction. In addition, the lattice fringes of  $\text{TiO}_2$  in 2 wt% Ru/ $\text{TiO}_2$  catalyst are orderly arranged, and the lattice spacing is 0.355 nm, belonging to (101) crystal facet of anatase  $\text{TiO}_2$  [35]. However, it is difficult to observe continuous lattice fringes in 2 wt% Ru/black  $\text{TiO}_2$ . The removal of O during reduction treatment broke the stoichiometric balance of  $\text{TiO}_2$ , forming amorphous phase [20,36]. This result also agrees with the XRD analysis result that the crystallinity of black  $\text{TiO}_2$  has been weakened structurally.

As aforementioned that the increase of catalytic activity of Ru/black  $\text{TiO}_2$  can also be attributed to the enhanced photothermal conversion ability, therefore, the photothermal conversion performances of Ru/ $\text{TiO}_2$  and Ru/black  $\text{TiO}_2$  were compared. Firstly, surface temperatures of the prepared catalysts under irradiation were directly observed based on IR temperature measuring device. As shown in Fig. S6 (Supporting information), the rising rate of the surface temperature of 2 wt% Ru/black  $\text{TiO}_2$  was significantly higher than that of 2 wt% Ru/ $\text{TiO}_2$  under irradiation. After 300 s, the surface temperature of 2 wt% Ru/black  $\text{TiO}_2$  reached 283.7  $^{\circ}\text{C}$ , while the temperature of 2 wt% Ru/ $\text{TiO}_2$  was only 223.1  $^{\circ}\text{C}$ . It can be seen from Fig. S7 (Supporting information) that the overall temperature of reaction system raised gradually during the reaction due to the photothermal conversion effect of the catalyst.

Furthermore, the photothermal conversion efficiency of 2 wt% Ru/black  $\text{TiO}_2$  was evaluated. The materials were dispersed in aqueous solution with water as the negative control. Initial temperature of the solution and room temperature were controlled at 20  $^{\circ}\text{C}$ . The solutions were irradiated under the Xe lamp and the lamp was turned off after 1200 s, and the temperature change was observed for 3000 s (Figs. 2a and b). The highest temperature of 2 wt% Ru/black  $\text{TiO}_2$  aqueous solution is 79.6  $^{\circ}\text{C}$  while the temperature of  $\text{TiO}_2$  aqueous solution is only 53.8  $^{\circ}\text{C}$  (Fig. 2a). It is worth noting that the highest temperature of 2 wt% Ru/black  $\text{TiO}_2$  solution is slightly lower than that of black  $\text{TiO}_2$ . Considering that near-infrared (NIR) absorption ability has marked impact on photothermal conversion [37], UV-vis-NIR DRS of the catalysts were conducted. As shown in Fig. S8,  $\text{TiO}_2$  displays poor NIR response and the loading of Ru improve its NIR absorption. However, there is no significant difference between the spectra of black  $\text{TiO}_2$  and Ru/black  $\text{TiO}_2$ , which means that the intrinsic NIR absorption of black  $\text{TiO}_2$  is higher than that of Ru NPs. Therefore, the photothermal conversion capacity of black  $\text{TiO}_2$  is slightly higher than that of Ru/black  $\text{TiO}_2$ . The photothermal conversion efficiency ( $\eta$ ) can



**Fig. 3.** The yield of  $\text{CH}_4$  from catalytic conversion of  $\text{CO}_2$  at different temperatures (reaction conditions: 0.4 MPa mixture gas- $\text{N}_2$ : $\text{H}_2$ : $\text{CO}_2$  = 4:5:1, 20 mg 2 wt% Ru/black  $\text{TiO}_2$ , 1 h, 100  $\text{mW/cm}^2$ ).

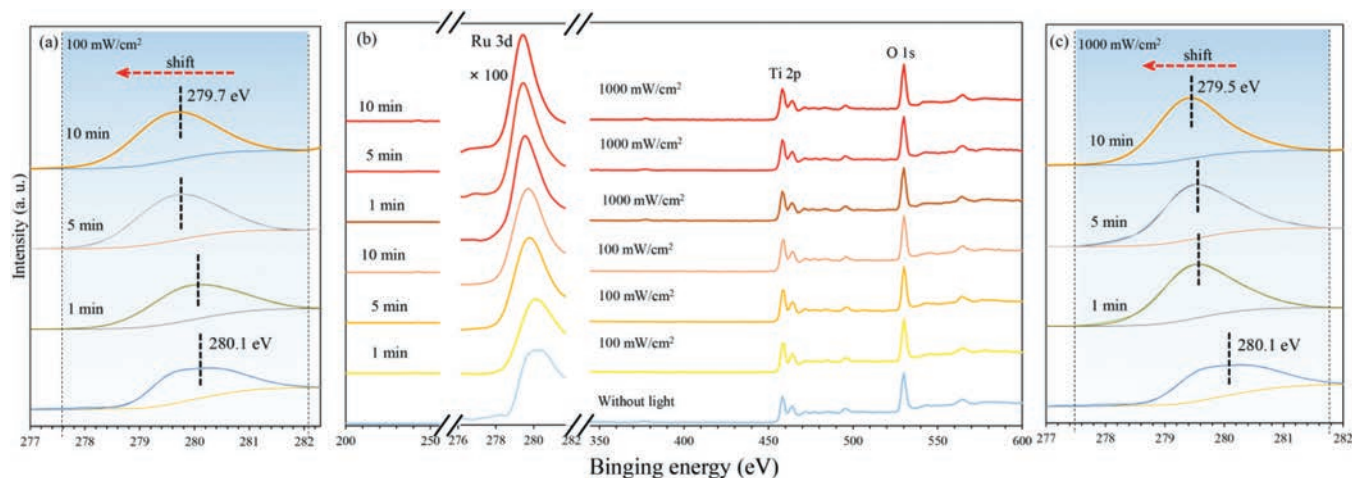
be calculated based on Eq. 1 [37–39]:

$$\eta = \frac{hA(\Delta T_{\text{max,mix}} - \Delta T_{\text{max,H}_2\text{O}})}{I} \quad (1)$$

where  $h$ ,  $A$ ,  $I$ ,  $\Delta T_{\text{max,mix}}$  and  $\Delta T_{\text{max,H}_2\text{O}}$  represent the heat transfer coefficient, the container surface area, the total energy Ru/black  $\text{TiO}_2$  nanoparticles absorbed, the temperature change of the 2 wt% Ru/black  $\text{TiO}_2$  suspension and water at the maximum stable temperature, respectively. Based on the fitting parameters of the cooling period in Fig. 2c, the  $\eta$  value of 2 wt% Ru/black  $\text{TiO}_2$  is calculated to be 37.9%. The calculation details can be seen in the Supporting Information. Owing to the efficient photothermal conversion based on black  $\text{TiO}_2$ , strong heat center can be produced on the catalyst surface under irradiation, improving the substances ( $\text{CO}_2$  and  $\text{H}_2$ ) activation and accelerating the reaction [40].

Subsequently, to verify the participation of photogenerated carriers during the  $\text{CO}_2$  conversion, the irradiation intensity was decreased to 1 sun (100  $\text{mW/cm}^2$ ) and a series of experiments at different temperatures were conducted. The experiments were carried out at 180, 200, 220 and 240  $^{\circ}\text{C}$ , respectively. As shown in Fig. 3, the methane yield increased with the increase of temperature, which indicates that the increase of reaction temperature is conducive to the methanation of  $\text{CO}_2$ . Most importantly, the  $\text{CH}_4$  yields increased at all temperatures after the introduction of light and highest synergy was obtained at 220  $^{\circ}\text{C}$ , which means that intrinsic excitation process of the catalysts may played an important role during the reaction.

Considering the large band gap of  $\text{Al}_2\text{O}_3$ , Ru/ $\text{Al}_2\text{O}_3$  was prepared to avoid the excitation of catalyst and its catalytic performance was observed to further confirm the effect of photogener-



**Fig. 4.** *In situ* high-resolution XPS spectrum of 2 wt% Ru/black TiO<sub>2</sub>. (a) Ru 3d<sub>5/2</sub> of 2 wt% Ru/black TiO<sub>2</sub> obtained under irradiation (100 mW/cm<sup>2</sup>); (b) survey spectrum; (c) Ru 3d<sub>5/2</sub> of 2 wt% Ru/black TiO<sub>2</sub> obtained under irradiation (1000 mW/cm<sup>2</sup>).

ated carriers. As displayed in the Fig. 3, the CH<sub>4</sub> yield showed no significant increase over Ru/Al<sub>2</sub>O<sub>3</sub> after the introduction of light. Thus, it is reasonable to speculate that, during the hydrogenation of CO<sub>2</sub> over Ru/black TiO<sub>2</sub>, not only the heat input generated from photothermal conversion but also the photogenerated carriers promote the conversion of CO<sub>2</sub>. The role photogenerated carriers played during CO<sub>2</sub> conversion were investigated in mechanism discussion section.

According to the above results and the reported CO<sub>2</sub> hydrogenation mechanism, the functionary mechanism of photogenerated carrier was proposed (Fig. S9 in Supporting information). Due to the low Fermi level of Ru and the well-contacted interface between Ru nanoparticle and black TiO<sub>2</sub> nanoparticle (Fig. 1f), it is reasonable to speculate that the photogenerated electrons would be gathered in Ru nanoparticles, forming electron-rich Ru surface. Furthermore, *in situ* high-resolution XPS was carried out. As displayed in Fig. 4, the binding energy of Ru 3d<sub>5/2</sub> shows a significant decrease after the introduction of light. In addition, with the gradual increase of irradiation intensity and irradiation time, the binding energy of Ru 3d<sub>5/2</sub> displayed a further shifting tendency.

Considering that the increase of electron density can enhance the shielding effect of electron clouds, which would decrease the binding energy of Ru 3d core level, it is reasonable to speculate that an electron injection process is achieved during the reaction. In contrast, the introduction of light caused the increase of O 1s binding energy (Fig. S10 in Supporting information), indicating that oxygen is in electron deficient state, which could be owing to the photogenerated holes. It is worth noting that the activation of H<sub>2</sub> is essential for the CO<sub>2</sub> hydrogenation. The formation of electron-rich Ru surface can provide more negative hydride, thus enhancing the nucleophilic attack reactivity of the hydride to the carbon center of CO<sub>2</sub> [41,42]. Besides, the light with larger wavelength could be converted into heat due to the photothermal conversion, further improving the CO<sub>2</sub> conversion. It is one promising way to achieve efficient hydrogenation of CO<sub>2</sub> using light as the only driving force based on the synergy between photocatalysis and thermocatalysis.

Additionally, a series of Ru/black TiO<sub>2</sub> catalysts with different Ru loading amount were prepared and the circulation stability test was carried out. The CH<sub>4</sub> yield increased with the increase of Ru loading amount and 93.8% of CH<sub>4</sub> yield was achieved within 2 h over 5 wt% Ru/black TiO<sub>2</sub> (Fig. S11 in Supporting information). The H<sub>2</sub>-temperature programmed desorption (TPD) was carried out to investigate the adsorption strength between the ad-

sorbed hydrogen and catalysts. As displayed in Fig. S12 (Supporting information), all tested catalysts displayed two significant hydrogen desorption peaks. The desorption peaks around 270 °C could be ascribed to the weakly adsorbed hydrogen on Ru surface and the peaks at high temperature (around 340 °C) could be ascribed to the strongly adsorbed hydrogen on the surface of black TiO<sub>2</sub> caused by hydrogen spillover [43–45]. Such spillover could do contribution to the hydrogenation of CO<sub>2</sub>. Additionally, no significant decrease in CH<sub>4</sub> yield was observed during the stability test of 5 wt% Ru/black TiO<sub>2</sub> (Fig. S13 in Supporting information). The XRD patterns of the collected catalysts after stability test display similar XRD patterns (Fig. S14 in Supporting information) and no high temperature phases such as rutile TiO<sub>2</sub> were produced after reaction, indicating that the catalyst can maintain desirable stability under the current reaction conditions.

In summary, a black TiO<sub>2</sub> supported catalyst was constructed for the photothermal catalytic CO<sub>2</sub> hydrogenation. Owing to the introduction of oxygen vacancies, the CO<sub>2</sub> adsorption ability of the black TiO<sub>2</sub> supported catalyst was significantly enhanced, improving the CO<sub>2</sub> conversion. The wide spectral response range and high photothermal conversion efficiency of black TiO<sub>2</sub> brought desirable catalytic performance for photocatalytic hydrogenation of CO<sub>2</sub> to the prepared Ru/black TiO<sub>2</sub>. Additionally, based on the well-contacted interface between Ru nanoparticle and black TiO<sub>2</sub> nanoparticle, an electron injection process was achieved to form electron-rich Ru metal nanoparticles, further improving the hydrogenation of CO<sub>2</sub>. This study opens the step for full wavelength range utilization of solar energy in light-driven conversion of CO<sub>2</sub>.

#### 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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## Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ccl.2021.07.046.

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