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Direct coupling of thermo- and photo-catalytic conversion of CO_2-H_2O to fuels

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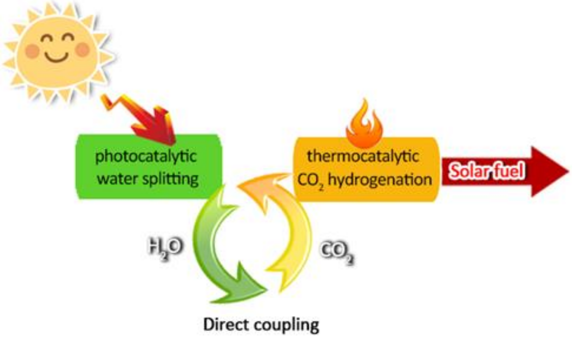
Abstract: Photocatalytic CO_2 reduction into renewable hydrocarbon solar fuels is considered as a promising strategy to simultaneously address the global energy and environmental issues. This article focuses on the direct coupling of photocatalytic water splitting and thermo-catalytic hydrogenation of CO_2 in the conversion of CO_2-H_2O to fuels. Specifically, it was found that direct coupling of thermo- and photo-catalysis over Au-Ru/TiO_2 leads to 15 times higher activity (358 K, with ~99% CH_4 selectivity) in the conversion of CO_2-H_2O to fuels than that of photo-catalytic water splitting. This is ascribed to the promoting effect of thermo-catalytic hydrogenation of CO_2 by hydrogen atoms generated *in situ* by photo-catalytic water splitting.

Conversion of CO_2 to fuels by means of an environmentally friendly solar energy manner not only provides a long-term alternative to the depletion of fossil fuels, but also reduces the net emission of CO_2.[1] Since the first report on the photo-reduction of CO_2 to organic compounds dating back to the mild 1970s,[2] enormous efforts have been undertaken to the development of effective photo-catalysts for CO_2 reduction.[3] However, it is rather difficult to efficiently convert CO_2 to fuels only through photo-catalysis due to the kinetic limitations of multiple e^-/H^+ transfer process and the thermodynamically stable CO_2.[4] Photo-catalysis coupled with other reactions is one of the most effective and distinctive strategies to improve the efficiency of photo-catalysis. For example, natural photosynthesis includes two steps: (a) water splitting to generate protons using solar energy; (b) CO_2 reduction by the generated protons to produce hydrocarbons in Calvin cycle.[5] Inspired by photosynthesis, the ideal route for CO_2 reduction would be the direct utilization of H_2 produced from photo-catalytic water splitting under solar radiation. Wu *et al.* combined photocatalyitc water splitting and hydrogenation of CO_2 reactions into a twin reactor to mimic photosynthesis process, which is more efficient than that of the single photocatalyst system.[5-7] Guan *et al.* directly combined Fe-based or Cu/ZnO catalysts for thermo-catalytic hydrogenation of CO_2 with photo-catalytic water splitting.[8] Recently, MacDonnell *et al.* reported a one-step, gas-phase photo-thermocatalytic process for the synthesis of hydrocarbons from CO_2-H_2O in a flow photo reactor using a Co/TiO_2 catalyst under UV illumination.[9] These preliminary and encouraging results show that the photo-thermocatalytic process is efficient in enhancing the conversion of CO_2-H_2O to fuels using solar energy, and is worthy of further extensive studies.

We note that thermo-catalytic hydrogenation of CO_2 to alkanes, known as "Sabatier reaction", is a mature technology for energy storage.[10] Sabatier reaction can be readily realized under mild conditions. For example, CO_2 conversion and CH_4 selectivity can reach ~100%, respectively, over Ni[11] or Ru[12] based catalysts at atmospheric pressure and a low reaction temperature (~160 ^oC). However, hydrogen is needed in Sabatier reaction. Currently, approximately 95% of total H_2 production is obtained from steam reforming of natural gas and petroleum, which emits unwanted CO_2.[8b] "Green" conversion of CO_2 to fuels requires that hydrogen is produced from renewable sources such as solar energy. Simply using the H_2 that is produced from a separate and standalone photo-catalytic water splitting in conventional Sabatier plants could cause efficiency losses and result in more capital and operating costs. Direct coupling of hydrogen production from photo-catalytic water splitting and photo-reduction of CO_2 is limited by lower efficiency of latter. To mitigate these issues, coupling of photo-catalytic water splitting for hydrogen production and thermo-catalytic hydrogenation of CO_2 could be more efficient than direct photo-reduction of CO_2, especially considering the fact that bifunctional catalysts such as Ru/TiO_2 or Ni/TiO_2 are efficient for both photo-catalytic water splitting[13] and thermo-catalytic hydrogenation of CO_2.[11]



Scheme 1. Direct coupling of photo-catalytic water splitting with thermo-catalytic hydrogenation for the conversion of CO_2-H_2O to fuels.

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Herein, as shown in Scheme 1, we report that direct coupling of photo-catalytic water splitting and thermo-catalytic hydrogenation of CO_2 on a bifunctional Au-Ru/TiO_2 catalyst is efficient for the conversion of CO_2-H_2O to fuels. A CH_4 yield as high as 27.1 μmol g^{-1} h^{-1} can be achieved *via* such a direct photo-thermocatalytic coupling process (DPTCP), which is much higher than that of photo-catalytic water splitting (7.2 μmol g^{-1} h^{-1}). The synergetic effects of photo-catalysis and thermo-catalysis are hereby discussed.

A bifunctional catalyst with both active sites for photo-catalytic water splitting and thermo-catalytic hydrogenation of CO_2 is required for DPTCP (Figure S1-S3 for experimental details). In this study, due to the high stablility and relatively high photocatalytic performance, TiO_2 (P25) provided by Evonik Degussa Co., which contains 80% anatase and 20% rutile, is used for photocatalysis. Ru is used as an active site for thermo-catalytic hydrogenation of CO_2. In order to improve the light absorption of TiO_2, Au nanoparticles (NPs), which is well known for surface plasmon resonance (SPR), is also deposited on TiO_2. Au-Ru/TiO_2 was synthesized using a facile impregnation-reduction method (ESI for experimental details).

Figure S5 shows the X-ray powder diffraction (XRD) patterns of the prepared samples TiO_2, Au/TiO_2, Ru/TiO_2 and Au-Ru/TiO_2. All the samples exhibit a similar XRD pattern as the parent TiO_2 support. The diffraction peaks at 2θ = 27.5°, 36.2°, 41.2° are assigned to (110), (101) and (111) planes of rutile, while other peaks at 2θ = 25.3°, 37.8°, 48.0°, 53.9°, 55.1°, 62.7°, 70.3° and 75.0° are ascribed to anatase. No Au-derived or Ru-derived peak is observed, due to the low loading amount of Au and Ru. The diffraction peaks ascribed to TiO_2 are almost unchanged after Au and Ru loading, suggesting that the presence of Au and Ru do not influence the crystalline structure of TiO_2. The XRD pattern of the Au-Ru/TiO_2 sample after thermo-photocatalytic reaction of CO_2-H_2O is identical to that of the fresh one, which reveals the stability of the catalyst Au-Ru/TiO_2 (Figure S6).

Figure 1 shows the UV-visible diffuse reflection spectra (UV-vis DRS) spectra of TiO_2, Au/TiO_2, Ru/TiO_2 and Au-Ru/TiO_2. All four samples show a strong absorption edge at about 390 nm, corresponding to the band gap absorption of TiO_2. Apparently, loading of Au and Ru does not affect the band gap of TiO_2, which suggests that the deposition of Au and Ru does not lead to their lattice doping in TiO_2. In contrast to the pure TiO_2, the Au/TiO_2 sample exhibits obvious enhancement on light around 570 nm, which is due to the SPR of Au NPs.[14] Meanwhile, after deposition of Ru on Au/TiO_2, the band ascribed to SPR of Au NPs is slightly red-shifted to around 580 nm, implying an interaction between Ru and Au.[15]

The morphologies of the prepared samples were characterized by transmission electron microscopy (TEM). As shown in Figure 2, TEM image of the as-obtained Au-Ru/TiO_2 reveals that TiO_2 NPs were of around 20-30 nm and the well-dispersed metal nanoparticles (NPs) can be clearly distinguished from TiO_2. Figure 2 (b) also shows the interplanar distances of 0.233 nm, 0.206 nm and 0.360 nm which correspond to the lattice of Au(111), Ru(101) and TiO_2(101) planes, respectively,[14, 16] as well as Au and Ru metal nanoparticles confirmed by the energy dispersive spectroscopy (EDS) mapping (Figure 2 (c-g)). UV-vis DRS and TEM results indicate that Au-Ru/TiO_2 catalyst consists of Au and Ru NPs which are in intimate contact.

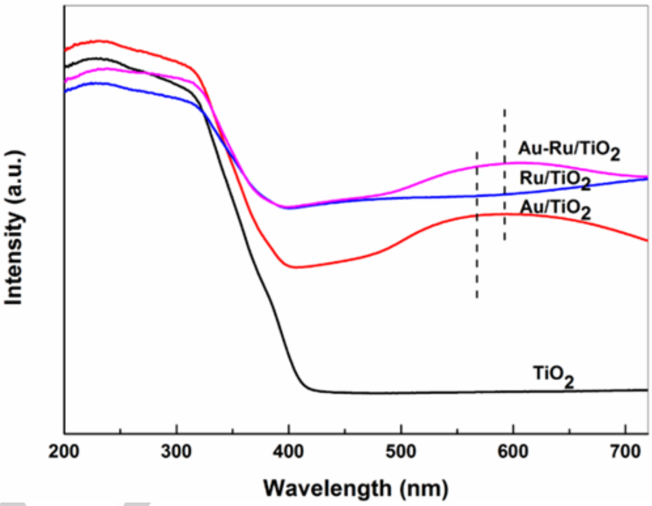


Figure 1. UV-vis DRS spectra of TiO_2, Au/TiO_2, Ru/TiO_2 and Au-Ru/TiO_2.

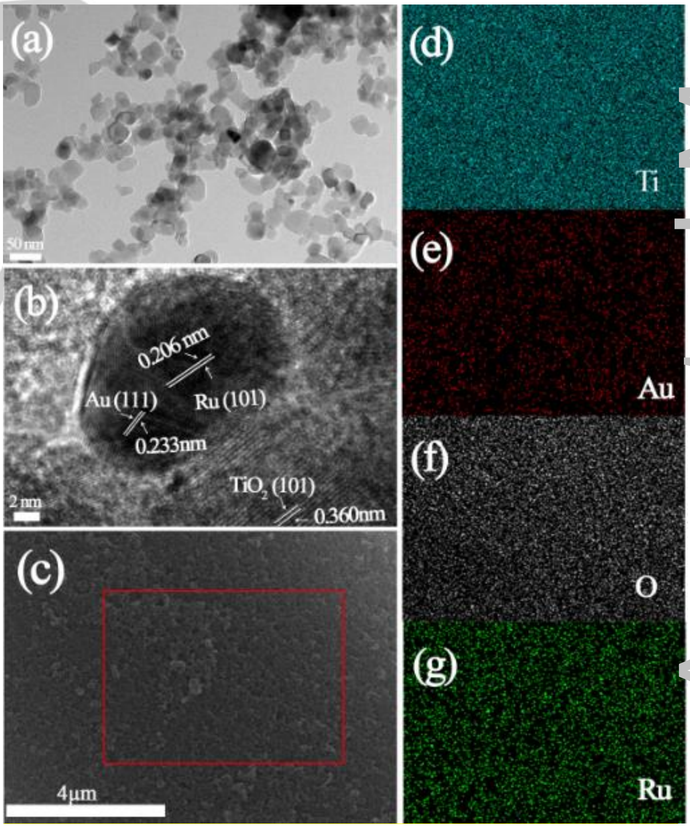


Figure 2. (a) TEM image, (b) High-resolution TEM (HRTEM) image, (c) SEM image and (d-g) EDS elemental mapping of the prepared Au-Ru/TiO_2.

Table 1 summarizes the thermo-catalytic conversion activities of CO_2 with H_2 over TiO_2, Au/TiO_2, Ru/TiO_2 and $Au\text{-}Ru/TiO_2$ catalysts (Figure S1 for experimental details). No product was detected over pure TiO_2 without active sites for thermo-catalytic hydrogenation of CO_2. After the loading of Au, the activities of thermo-catalytic hydrogenation of CO_2 are quite low. While for the Ru/TiO_2 catalyst, CH_4 and C_2H_6 were observed at the reaction temperature as low as 323 K and their yields increase with reaction temperature, reaching $2.69*10^4$ μmol g^{-1} h^{-1} CH_4 and 405 μmol g^{-1} h^{-1} C_2H_6 at 423 K for thermo-catalytic hydrogenation of CO_2 with H_2. In contrast to Ru-based catalysts, Au/TiO_2 shows quite low CO_2 conversion and extremely high selectivity to CO. However, almost no methanation reaction is observed, which is consistent with the low methanation activity on Au as previously reported.[17-19] These results confirm that Ru is essential for thermo-catalytic conversion of CO_2 with H_2. For $Au\text{-}Ru/TiO_2$ catalyst, CH_4 and C_2H_6 were also observed at the reaction temperature as low as 323 K and their yields reaching $1.60*10^4$ μmol g^{-1} h^{-1} CH_4 and 243 μmol g^{-1} h^{-1} C_2H_6 at 423 K. Compared to Ru/TiO_2, the activities decrease slightly after addition of Au on Ru/TiO_2, which is due to partial blocking of Ru by Au as shown in TEM image (Figure 2). These results indicate that $Au\text{-}Ru/TiO_2$ is an active catalyst for the thermo-catalytic conversion of CO_2 with H_2 to alkanes.

Table 1. Catalytic activities of thermo-catalytic conversion of CO_2 with H_2 over TiO_2, Au/TiO_2, Ru/TiO_2 and $Au\text{-}Ru/TiO_2$.[a]

Catalyst	Temperature	Formation rate (μmol $g^{-1}h^{-1}$)		
	(K)	CH_4	C_2H_6	CO
TiO_2	323~423	nd	nd	nd
Au/TiO_2	323	nd	nd	nd
	358	6.1	7.0	nd
	373	7.0	5.4	8.2
	423	2.1	nd	440
Ru/TiO_2	323	82.5	30.7	nd
	358	998	56.1	nd
	373	$1.87*10^3$	96.5	nd
	423	$2.69*10^4$	405	nd
$Au\text{-}Ru/TiO_2$	323	37.3	24.0	nd
	358	356	31.7	nd
	373	972	47.3	nd
	423	$1.60*10^4$	243	nd

[a] Reaction conditions: atmospheric pressure, catalyst: 0.20 g, without light illumination, feed gas: CO_2 (18.02%) + Ar (8.01%) + H_2 (73.97%), flow Rate: 2 mL/min, nd: no detected.

In order to study the effects of light illumination on thermo-catalytic conversion of CO_2-H_2, the activities of conversion CO_2 with H_2 over $Au\text{-}Ru/TiO_2$ catalyst under light illumination at different temperature were measured and are summarized in Table 2 (Figure S1 for experimental details). As shown in Table 1 and Table 2, thermo-photocatalysis activity is much higher than thermo-catalytic activity at the same temperature over $Au\text{-}Ru/TiO_2$ catalyst for the conversion of CO_2 with H_2. These results indicate that light illumination indeed facilitates the thermo-catalytic conversion of CO_2 with H_2 to alkane as previously reported.[20] Liu *et al.* suggested that light illumination could lower the activation energy of thermo-catalytic hydrogenation of CO_2, which is beneficial to thermo-catalytic conversion CO_2 with H_2.[20]

Table 2. Catalytic activities of thermo-catalytic conversion of CO_2 with H_2 over $Au\text{-}Ru/TiO_2$ under light illumination.[a]

Catalyst	Temperature （K）	Formation rate (μmol $g^{-1}h^{-1}$)		
		CH_4	C_2H_6	CO
$Au\text{-}Ru/TiO_2$	323	82.3	11.4	nd
	358	905	22.9	nd
	373	$2.28*10^3$	54.5	nd
	423	$3.06*10^4$	386	nd

[a] Reaction conditions: atmospheric pressure, catalyst: 0.20 g, light source: Hg lamp (150 mW/cm^2), illumination area: 0.8 cm^2, reactor: fixed bed, feed gas: CO_2 (18.02%) + Ar (8.01%) + H_2 (73.97%), flow rate: 2 mL/min, nd: no detected

It is well known that TiO_2-based catalysts are also effective for H_2 production by photo-catalytic water splitting. As shown in Table 3 (Figure S1 for experimental details), under continuous-flow of H_2O/Ar (2 mL/min), 6.3 μmol g^{-1} h^{-1} H_2 was produced at a low temperature of 323 K over $Au\text{-}Ru/TiO_2$ catalyst. As the temperature increased to 358 K, a higher H_2 production rate of 7.2 μmol g^{-1} h^{-1} H_2 was achieved. However, H_2 production rate decreased to 1.9 μmol g^{-1} h^{-1} when the temperature further increased to 373 K. These results indicate that $Au\text{-}Ru/TiO_2$ catalyst is also efficient for H_2 production from water splitting under illumination, but the reaction temperature has a great influence on the H_2 production from photo-catalytic water splitting. In general, elevated temperature does not favor H_2 production from photo-catalytic water splitting due to the increasing rate of charge recombination in the photocatalyst at high temperature.[3] In addition, adsorption of H_2O is another key factor to the performance of H_2 production from water splitting under illumination in a continuous-flow reactor. Bazzo *et al.* reported that the adsorption or even condensation of H_2O and its sufficient concentration on the catalyst surface at low temperatures (< 373 K) are crucial for the stable production of H_2 under light illumination, and the active sites for H_2 production at high temperature such as 423 K were irreversibly consumed.[3]

As mentioned above, $Au\text{-}Ru/TiO_2$ is not only an excellent catalyst for thermo-catalytic conversion of CO_2 with H_2, but also effective for H_2 production from photo-catalytic water splitting under the similar temperature. Apparently, the rate of thermo-catalytic conversion of CO_2 with H_2 is much higher than that of photo-catalytic water splitting for H_2 production. Direct coupling of thermo-catalytic CO_2 hydrogenation with renewable energy for hydrogen production, e.g., photo-catalytic water splitting over the bifunctional $Au\text{-}Ru/TiO_2$ catalyst, represents a viable path for highly efficient conversion of CO_2-H_2O to fuels. In order to confirm this hypothesis, experiments were carried out using a continuous flow fixed-bed reactor with a quartz window under illumination at different temperatures. It is well known that extreme care should be taken in photochemical CO_2 reduction due to the possible carbon residues on catalysts, which are formed from carbon containing precursors.[21] Prior to the test of DPTCP for the conversion of CO_2 and H_2O, the $Au\text{-}Ru/TiO_2$ was pretreated with H_2 and then purged with He without CO_2 under illumination at various temperatures (323-423K), no any carbon containing compound was detected, indicating that the carbon containing compounds are indeed originated from CO_2 in DPTCP. In order to exclude the possible hydrogen residues, CO_2 was then purged without light illumination until no CH_4, CO, C_2H_6 and H_2 were detected at all temperatures studied. Furthermore, there was no carbon containing compound and H_2 detected under H_2O or CO_2/H_2O flow without light illumination. The above control experiments ensure that the carbon containing compounds and H/H_2 products are originated from CO_2 and photocatalytic water splitting.

As shown in Table 3, in the case of CO_2-H_2O flow, H_2 and CH_4 are simultaneously produced at the reaction temperature from 323 K to 423 K under light illumination, except that the production of H_2 is much lower than those *via* photo-catalytic water splitting (flowing with only H_2O in Table3) at the same conditions. Theoretically, splitting one mole H_2O forms one mole H_2 and half mole O_2 ($H_2O—H_2 + 1/2O_2$). Unfortunately, even using He as carrier gas for thermal conductivity detector (TCD), O_2 cannot be detected *via* TCD in the photocatalytic water splitting and DPTCP, due to the low sensitivity of TCD for O_2 detection. Because no extra H_2 or reductants provided, the reduction of H_2O to H_2 or CO_2 to CH_4 can only be originated from photo-catalysis. In the control experiments, there was no H_2 and alkane obtained over Au-Ru/TiO_2 without light illumination or under illumination without photocatalyst at 323 K to 423 K, further suggesting the electrons for the reduction of water to H_2 or CO_2 to CH_4 are indeed originated from photo-catalysis. For example, reduction of CO_2 with two photo-generated electrons yields CO ($CO_2 + 2H^+ + 2e^- – CO + H_2O$); reduction of CO_2 with eight photo-generated electrons yields CH_4 ($CO_2 + 8H^+ + 8e^- – CH_4 + 2H_2O$); reduction of H^+ with two photo-generated electrons yields H_2 ($2H^+ + 2e^- – H_2$). In order to provide a quantitative comparison, we used photo-generated electrons for the reduction reactions (R-electrons) to estimate the catalytic activity of different reactions.

R-electrons = 2r (CO) + 8r (CH_4) + 2r (H_2)

where r (CO), r (CH_4), and r (H_2) are the formation rates of CO, CH_4, and H_2, respectively.

As shown in Table 3, 59 μmol g^{-1} h^{-1} R-electrons are reached at 323 K in DPTCP. The R-electrons increase to 218 μmol g^{-1} h^{-1} at 358 K, and decrease to 46 and 33 μmol g^{-1} h^{-1} with further increasing the reaction temperature to 373 K and 423 K, respectively. However, it can be seen from Table 3, the R-electrons of DPTCP (218 μmol g^{-1} h^{-1}) are ~15 times higher than that of photo-catalytic water splitting (15 μmol g^{-1} h^{-1}) under the same intensity of illumination at 358 K. On the other hand, the trend of changing in R-electrons with temperature in DPTCP is the same with that of photo-catalytic water splitting, which implies photo-catalytic water splitting and thermo-photocatalytic conversion of CO_2-H_2O are very different from each other, but they also have some similarities.

Generally, photo-catalysis mainly includes three steps: generation of electron-hole pairs, separation and migration of photo-generated electrons and holes, redox reactions by photo-generated electrons and holes on catalyst surface.[22] The efficiency of electron-hole pair generation mainly depends on the intrinsic structure of photocatalyst. Meanwhile, effective capture and quick consumption of electrons by reduction reactions will speed up the migration of photogenerated electrons, lower the recombination rate of photogenerated electrons and holes, resulting in a high photocatalytic activity. It is well known that cocatalysts, such as Pt, Ni etc., can effectively capture photogenerated electrons and act as active sites for reduction reactions by the captured electrons.[14, 23] For example, Li *et al.* reported that Pt cocatalyst on CdS can capture electrons efficiently and catalyze proton reduction, i.e., H_2 evolution.[24] As mentioned above, photo-catalytic reduction of CO_2 is more difficult than photo-catalytic reduction of H_2O. Therefore, in the case of DPTCP under CO_2-H_2O flow, it is very likely that most of the captured electrons will preferentially reduce H^+ rather than direct reduction of CO_2. If there is no CO_2 present, reduction of H^+ will lead to H_2 formation with the help of cocatalyst. However, H atoms from H^+ reduction may directly react with CO_2 to form CO or alkanes under CO_2-H_2O flow. Our results show that the Au-Ru/TiO_2 catalyst is highly efficient for thermo-catalytic hydrogenation of CO_2 to alkanes. In addition, illumination facilitates thermo-catalytic hydrogenation of CO_2 (also see Table 2), as reported by literature.[20] Meanwhile, comparison with thermo-catalytic conversion of CO_2 direct with H_2, it is evident that CO_2 can direct react with highly active hydrogen atoms, which are *in situ* generated by photo-catalysis. Although the detailed mechanisms on how the reactive intermediates react with photo-catalytic generated hydrogen atoms are still not clear, we believe that the photo-catalytic generated hydrogen could directly react with CO_2 due to the highly efficient thermo-catalytic hydrogenation of CO_2 over Au-Ru/TiO_2. Rapid consumption of the generated hydrogen by direct thermo-catalytic hydrogenation of CO_2 to produce alkanes greatly accelerates the migration of photogenerated electrons, thus lowers the recombination rate of photogenerated electrons and holes, providing a synergetic effect between photo-catalysis and thermo-catalysis in the direct thermo-photocatalytic reduction of CO_2-H_2O. Recently, MacDonnell *et al.* reported a similar photo-thermochemical process using Co/TiO_2 for both photo-catalytic water splitting and Fischer–Tropsch synthesis.[9] They suggested that the products by photo-catalysis can be consumed in thermal reactions.

Table 3. Activities of photo-catalytic water splitting and the direct coupling of thermo-catalytic hydrogenation of CO_2 and photo-catalytic water splitting for conversion of CO_2-H_2O over Au-Ru/TiO_2.[a]

Feed gas	Temperature (K)	Formation rate (μmol g^{-1} h^{-1})			R-electrons (μmol g^{-1} h^{-1})	AQE(%)
		H_2	CH_4	CO		
H_2O	323	6.30	--	--	13	0.54
H_2O	358	7.20	--	--	15	0.62
H_2O	373	1.90	--	--	4	0.17
H_2O	423	--	--	--	--	--
CO_2+H_2O	323	0.21	7.30	--	59	2.45
CO_2+H_2O	358	0.27	27.1	--	218	9.05
CO_2+H_2O	373	0.49	5.60	--	46	1.91
CO_2+H_2O	423	--	4.05	--	33	1.31

[a] Reaction conditions: atmospheric pressure, catalyst, 0.20 g, light source, Hg lamp, light intensity: 150 mW/cm^2, illumination area: 0.8 cm^2, flow Rate: 2 mL/min

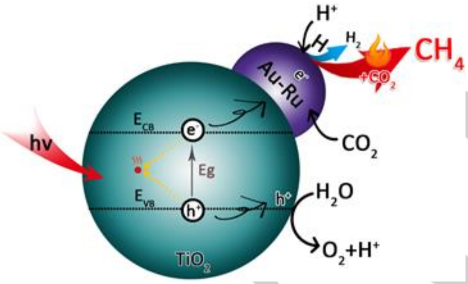
In order to further confirm the synergetic effects between photo-catalysis and thermo-catalysis in thermo-photocatalytic reduction of CO_2-H_2O, photocatalytic water splitting and thermo-photocatalytic conversion of CO_2-H_2O on pure TiO_2 catalysts without thermo-catalytic active sites, such as Ru, were studied. Due to the low phtotocatalytic activity over pure TiO_2, a reactor with greater illumination area (12.5 cm^2) was used (Figure S2 for experimental details). As shown in Table 4, there is no noticeable difference in R-electrons between photo-catalytic water splitting and DPTCP conversion of CO_2-H_2O under the same conditions, implying the important role of the thermo-catalytic hydrogenation of CO_2 to accelerate the migration of photogenerated electrons. This result further confirms the synergetic effect between photo-catalysis and thermo-catalysis in the direct thermo-photocatalytic reduction of CO_2-H_2O.

Table 4. Activities of photo-catalytic water splitting and direct coupling of thermo-catalytic hydrogenation of CO_2 and photo-catalytic water splitting for the conversion of CO_2-H_2O over TiO_2.[a]

Feed gas	Temperature	Formation rate ($\mu mol\ g^{-1}\ h^{-1}$)			R-electrons ($\mu mol\ g^{-1}\ h^{1}$)
	(K)	H_2	CH_4	CO	
H_2O	323	6.1	--	--	13
H_2O	358	8.7	--	--	18
H_2O	373	9.1	--	--	19
H_2O	423	12.0	--	--	24
CO_2+H_2O	323	1.3	0.6	2.7	13
CO_2+H_2O	358	2.1	1.9	2.6	25
CO_2+H_2O	373	2.6	3.2	1.3	34
CO_2+H_2O	423	2.0	5.7	1.5	53

[a] Reaction conditions: atmospheric pressure, catalyst: 0.60 g, light source: Hg lamp, light intensity: 150 mW/cm^2, illumination area: 12.5 cm^2

Based on the above results, a model of enhanced conversion of CO_2-H_2O to alkanes over bifunctional catalyst Au-Ru/TiO_2 *via* direct coupling of thermo-catalysis hydrogenation and photo-catalysis water splitting can be proposed and shown in Scheme 2. Notably, rapid consumption of the *in situ* photo-catalytic generated hydrogen by direct thermo-catalytic hydrogenation of CO_2 over the same bifunctional catalyst is beneficial to the efficiency of CO_2 conversion.



Scheme 2. Schematic illustration of synergetic effects between photo-catalysis and thermo-catalysis in direct thermo-photocatalytic reduction of CO_2-H_2O over Au-Ru/TiO_2.

In summary, we presented here a facile strategy for highly efficient conversion of CO_2-H_2O to alkanes *via* direct coupling of photo-catalytic water splitting and thermo-catalytic hydrogenation of CO_2. The improved catalytic efficiency of CO_2-H_2O conversion to alkanes is attributed to the promoting effect of thermo-catalytic hydrogenation of CO_2 with highly active hydrogen atoms generated *in situ* by photo-catalysis, which can greatly reduce the recombination rate of photogenerated electrons and holes. This example presents a conceptually promising process for alkane production using CO_2 and solar energy. Furthermore, the direct coupling of photo-catalysis with thermo-catalysis process presented herein may be further extended to other hydrogenation reactions, such as ammonia synthesis or CO_x to methanol etc., with hydrogen *in situ* derived from solar energy.

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Keywords: CO_2 conversion • photo-catalysis • coupling • thermo-catalysis • hydrogenation

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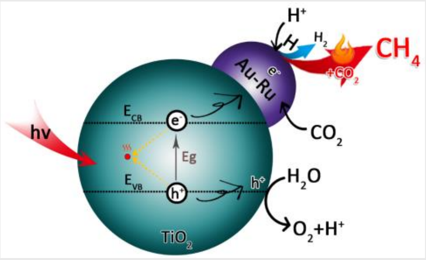
Entry for the Table of Contents

COMMUNICATION

An activity of direct coupling thermo- and photo-catalysis over Au-Ru/TiO_2 leads to 15 times higher activity (358 K, with ~99% CH_4 selectivity) in the conversion of CO_2-H_2O to fuels than that of photo-catalytic water splitting, which is ascribed to the promoting effect of thermo-catalytic hydrogenation CO_2 with hydrogen atoms generated *in situ* by photo-catalytic water splitting.



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Direct coupling of thermo- and photo-catalytic conversion of CO_2-H_2O to fuels