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Efficient CO₂ reduction with H₂O via photothermal chemical reaction based on Au-MgO dual catalytic site on TiO₂

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ABSTRACT

Keywords: Solar fuels Photothermal chemical reaction CO₂ reduction Au MgO Using solar energy for the conversion of H_2O and CO_2 into H_2 , CO, CH₄, and other solar fuels have attracted great interest worldwide. However, the greatest challenge is how to use both the light energy and the heat energy to improve the utilization efficiency of solar energy. Photo-thermal chemical reaction has been used for conversing H_2O and CO_2 into H_2 , CO, CH₄, and other solar fuels and improved by Au and MgO co-loaded TiO₂(AuMgTi). The average yields of CO, H_2 , and CH₄ on AuMgTi were estimated to 45.495 umol/g, 45.072 umol/g, and 6.624 umol/g, respectively. Also, the selectivities of carbon-containing products increased from 29 % to 53.6 % when compared to P25. MgO on the surface of AuMgTi can enhance the chemisorption of CO₂ and initiated the CO₂ reduction reaction to converse CO₂ into CO and CH₄. Au can improve the utilization of visible light through the Localized Surface Plasmon Resonance (LSPR) effect, and reduce the recombination rate of photogenerated carriers due to the existence of the Schottky barrier. Moreover, Au might act as a catalytically active center on the surface to assist in the formation of the intermediate groups and facilitate the reaction. This study demonstrated that the AuMgTi catalyst can effectively utilize full spectrum solar energy for CO₂ reduction by photo-thermal chemical reaction.

1. Introduction

The use of fossil fuels generates large amounts of CO_2 emissions, leading to global warming. Therefore, the development of alternative clean energy sources is urgent [1]. Solar energy is an environmental-friendly, abundant, and effective alternative energy source [2]. The use of solar energy for the conversion of H₂O and CO₂ into H₂, CO, CH₄, and other solar fuels is promising for sustainable development [3].

Semiconductor-based photocatalysis and photoelectric catalytic reactions are the main methods of solar light utilization [4]. Using high-frequency light in the ultraviolet-visible band to excite semiconductors to generate carriers to complete the redox reaction. However, the ultraviolet light only accounts for 5 % of the full spectrum, and most of the solar energy cannot be used, which greatly limits the solar-to-fuel efficiency [5,6]. The solar thermal utilization method is realized through the thermochemical cycle reaction, which can utilize the full-spectrum energy of solar energy [7,8]. But there is a large heat loss in the two-step reaction process, which also reduces the solar-to-fuel efficiency [9].

The energy conversion efficiencies can be improved if the photo and thermal factors can synergize their respective strengths. Most recently, more research studies have been focused on coupling photo and thermal effects in the solar energy conversion reaction and improve solar-to-fuel efficiency. Some studies have suggested that the advantage of photothermal chemical reaction lies in the use of infrared energy that photocatalytic cannot use. The photo-thermal effect in the infrared region of solar energy could promote many catalytic reactions under suitable conditions when catalytic materials with both photo and thermal responses are employed [10-12]. Some studies show that light energy sources could drive reactions because heating under light conditions would accelerate the photocatalytic reduction of H₂O and CO₂ on WO_{2-δ}. However the reaction cannot proceed under dark condition [13]. However, most of the current researches on the photo-thermal chemical reaction basically focus on the light effect or heat effect on the reaction separately. Whether there is any mutual influence between light and heat still needs more in-depth research [11,14].

In addition, the current photo-thermal chemical reactions are mostly used to study CO_2 hydrogenation reactions. At present, the research on the CO_2 reduction with H_2O via the photo-thermal chemical reaction

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faced with the challenges of poor selectivity and low energy conversion efficiency [15,16]. Co-catalysts, such as basic oxides, can effectively improve the selective adsorption of CO_2 on catalyst materials and effectively improve the selectivity of the carbon-containing products [17,18]. In addition, noble metals can maintain stable characteristics at high temperatures. By supporting the noble metal element as a co-catalyst, the reaction energy barrier of CO_2 decomposition can be effectively reduced, thereby increasing the selectivity of carbon-containing products. In addition, noble metals, such as Pd [19], Au [20,21], and Ag [22] have been used to improve the utilization of visible light through the LSPR effect, as well as to reduce the recombination rate of photogenerated carriers due to the existence of the Schottky barrier.

In this work, a simple preparation method was used for co-loading of Au and MgO on P25 material surface. The resulting catalysts were tested for CO₂ reduction with H₂O to produce methane (CH₄) and other fuels under UV and ultraviolet-visible (UV–vis) light by photo-thermal chemical reactions. To the best of our knowledge, no materials containing Au and MgO co-loaded on P25 have so far been reported for the photo-thermal chemical reactions with H₂O and CO₂. The role of Au and MgO in the photo-thermal chemical reaction are explored. The results show that the loading of MgO effectively improves the selective adsorption of CO₂ while the loading of Au reduces the reaction energy barrier of CO₂ decomposition and improves the material's absorption of visible light. AuMgTi increase the selectivity of carbon-containing products from 29 % to 53.6 % of the photo-thermal chemical reaction when compared to P25.

2. Experimental

2.1. Catalysts preparation

Herein, three different samples were prepared: 1.0 wt % MgO loaded on TiO₂(MgTi), 1.0 wt % Au loaded on TiO₂(AuTi), and 1.0 wt % MgO and 1.0 wt % Au co-loaded on TiO₂(AuMgTi). The Au and MgO supported on Degussa P25 TiO₂ were prepared by photo deposition method for Au and co-precipitation method for MgO. For MgO loaded on TiO₂ material, a certain amount of P25 was first dissolved in deionized water under continuous stirring. A magnesium nitrate aqueous solution was then added to the solution followed by NaOH solution to adjust the pH value to 10.5 and ensure the complete precipitation of Mg²⁺. After continuous stirring for 5 h, the mixture was centrifuged and washed several times with deionized water. The obtained target products were then dried in the oven at 363 K for 12 h followed by grinding, annealing in a muffle furnace in an air atmosphere at 723 K and heating rate of 5 K/ min for 12 h. The resulting samples were ground again and sieved to yield MgO loaded on TiO₂ materials.

For Au loaded on TiO_2 material, a certain amount of P25 was first dissolved in deionized water under continuous stirring. The mixture was transferred into a self-made container continuously injected by Ar gas at a flow rate of 100 mL/min to create an inert atmosphere. After the addition of certain amounts of anhydrous methanol, the mixture was continuously stirred and ventilated for 2 h. Next, a certain amount of HAuCl₄ was added drop by drop under a high-pressure mercury lamp and continuous illumination for 5 h. After illumination, the same followup drying and grinding treatments of MgTi were used to yield the target catalyst Au supported on TiO_2 .

For Au and MgO co-supported on TiO_2 , two steps were utilized. The first consisted of using the photo deposition method to yield Au loaded on TiO_2 samples. The second dealt with dissolving the samples in a certain amount of deionized water to load MgO by the co-precipitation method.

For photothermal chemical reaction, the catalysts were coated on quartz glass dishes. To this end, 25 mg powdered catalyst and 7 mL deionized water were first mixed under ultrasonic vibration for 10 min to form an ultra-fine particles mixed solution. The as-obtained solution was then poured into a 5 cm diameter quartz glass dish and annealed at 363 K for 3 h to yield catalyst films attached to quartz glass dishes.

2.2. Photothermal chemical reactions

The photothermal chemical reactions were carried out in a self-made reactor. In this system, a quartz dish coated with the catalyst film was placed in a Hastelloy reactor, of which the top was made of a sapphire lens to transmit light. Before reactions, the catalyst was heated to 623 K in Ar atmosphere to remove any surface impurities that can affect the experimental results. To complete the removal of the impurities, some Ar was added into the reactor and heated for 1 h. Gas chromatography (GC) was then applied to monitor the amounts of certain gases until no H_2 , CO, and CH₄ were detected.

The reaction process consisted of first accessing Ar at a flow rate of 100 mL/min to make sure that the reactor was saturated with Ar atmosphere. Secondly, the reactor was heated to 573 K, and the rear valve of the reactor was closed after the temperature stabilized. A certain volume of H₂O was then injected into the reactor through CO₂ gas flow from the front valve of the reactor. Afterward, CO₂ was continuously added at certain pressure by closing the front valve and sealing the reactor. Next, a xenon lamp was turned on to vertically irradiate the catalyst for 1 h, and GC was used to monitor the reaction products. Finally, the heating was turned off and CO₂ was injected into the reactor to cool down.

2.3. Analysis and characterization methods

The crystal structures and morphologies were obtained by X-ray diffraction (XRD), scanning electron microscopy (SEM, FEISIRION-100), high-resolution transmission electron microscopy (HRTEM, FEI Tecnai G2 F20 S-TWIN) coupled with EDXS at an acceleration voltage of 200 kV. The XRD patterns were obtained using a Cu K α radiation source (K α = 1.54056 Å) operating at 40 kV voltage and 200 mA current. The diffraction patterns were obtained over a 2θ range of $10-90^{\circ}$ at intervals of 0.02° and a rate of 4°/min. The optical properties of the samples were characterized by photoluminescence (PL) and UV-vis diffuse-reflectance spectroscopy (UV-vis DRS). The UV-vis DRS were recorded on a Shimadzu UV-2600i spectrophotometer (200-800 nm), and PL patterns were measured on Edinburgh Instrument FLS 920 equipped with a 325 nm excitation source at room temperature. The surface elements were determined by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Fisher Scientific). For the preparation of test samples, adventitious carbon was used as a reference to determine all binding energies of C 1s peak (284.6 eV). The chemical bondings were determined by infrared spectrometry (IR, Nicolet 6700) equipped with a liquid nitrogen-cooled HgCdTe (MCT) detector. The IR data were displayed in absorbance units with a resolution of 4 cm^{-1} using 64 scans. The *in situ* time-resolved diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) studies were carried out in a reaction chamber produced by Harrick Scientific in a Praying Mantis DRIFTS accessory.

2.4. Theoretical calculations

All spin-polarized density functional theory (DFT) [23,24] calculations were conducted by a Vienna ab initio simulation package (VASP) [25,26]. The exchange-correlation interactions were applied by the Perdew-Burke-Ernzerhof (PBE) functional of the generalized gradient approximation (GGA) [27]. The project-augmented wave (PAW) method [28,29] was used to represent the core-valence electron interaction with electrons from the H 1s, C 2s 2p, O 2s 2p, Mg 2s 2p 3s, Ti 3p 3d 4s, and Au 5d 6s shells. The valence electronic states were expanded in plane-wave basis sets with an energy cutoff of 400 eV. The Monkhorst-Pack [30] K-point grid was fixed to $3 \times 3 \times 1$, the convergence threshold for the self-consistent-field iteration was 10^{-4} eV, and geometry optimizations converged for force components less than 0.01

eV/Å.

/Å. photothermal chemical reaction. As shown in Fig. S1(a), the anatase TiO_2 (101) surface was made of

3.2. Crystal structure and morphology

three layer-thick slabs with 3 × 4 surface supercell (Ti₇₂O₁₄₄). The MgOdoped anatase TiO₂ (101) surface was obtained by substituting one of five coordinated Ti atoms with the Mg atom, and the two coordinated O atoms near the Mg atom were removed for charge balance. The Auloaded anatase TiO₂ (101) surface was formed by adding one Au atom on the surface (Fig. S1(c)). The anatase TiO₂ (101) surface with loaded Au and MgO doping was obtained by adding one Au atom on MgO-aTiO₂ (Fig. S1(d)). To minimize the interaction between adjacent slabs, a vacuum layer thickness of 15 Å was chosen along the surface normal direction. The bottom layer was kept fixed, while the top two layers were allowed to relax during the optimization.

3. Results and discussion

3.1. Photothermal performance

To study the modification effects of MgO and Au on P25, experiments dealing with the photothermal chemical reaction of CO₂ and H₂O into hydrocarbon fuels were carried out on P25, AuTi, MgTi and AuMgTi materials. As shown in Fig. 1, each material showed stable experimental photothermal chemical reaction, indicating materials maintaining good thermal stability and catalytic effect during the experiments. The yields of the photothermal chemical reaction of P25 are provided in Fig. 1(a). The average yields of CO, H₂, and CH₄ were estimated to 7.651 umol/g, 23.784 umol/g, and 2.069 umol/g, respectively. For comparison, the yields of the photothermal chemical reaction of Au-loaded P25 material are illustrated in Fig. 1(b). The average yields of CO, H₂, and CH₄ were 2.7-fold, 1.3-fold, and 1.8-fold higher than those of P25, respectively. Thus, the loading of Au significantly increased the yield of each product since the Au loading introduced an LSPR effect that made more highenergy electrons participate in the reaction [20,21]. Meanwhile, the Schottky barrier formed at the interface between Au and semiconductor material could effectively separate photogenerated electron-hole pairs and reduce the recombination of photogenerated electron-hole pairs [31]. The latter induced more photoinduced oxygen vacancies to participate in subsequent reactions. Also, Au played the role of a reactive site, further increasing the yield of each product [21,32].

The yields of MgO-supported P25 for photothermal chemical reaction reactions are shown in Fig. 1(c). The average yields of CO, H_2 , and CH4 were 3.4-fold, 1.1-fold, and 1.9-fold higher than those of P25, respectively. In Fig. 1(c), the loading of MgO greatly improved the carbon-containing products, while no significant increase in the production of H₂ as a decomposition product of H₂O was noticed. The reason for this had to do first with the loading of MgO that led to generation of more photo-induced oxygen vacancies to participate in the reaction [33,34]. On the other hand, the loading of MgO led to the absorption of more CO_2 on the material in CO_2 and H_2O atmosphere [35], thereby simultaneously participating in the photothermal chemical reaction reaction and increasing the selectivity of carbon-containing products from 29 % to 52.8 %. The yields of the photothermal chemical reaction of P25 co-loaded with Au and MgO are gathered in Fig. 1(d). The average yields of CO, H₂, and CH₄ were estimated to 45.495 umol/g, 45.072 umol/g, and 6.624 umol/g, respectively. These yields were 5.9-fold, 1.9-fold, and 3.2-fold higher than those of P25, respectively. Also, the selectivity of carbon-containing products increased from 29 % to 53.6 %. The apparent quantum efficiency (AQE) of solar fuels on AuMgTi is 0.0212 % (Table S2 for detailed calculations and Table S3 [36–38]). In Fig. 1(d), the yield of each product greatly improved after co-loading of the two co-catalysts when compared to previous materials. The reason for this had to do with the chemical effect induced by both co-catalysts on the material surface. The loading of Au enhanced the photoresponse performance [21,32], while the loading of MgO led to a strong adsorption capacity of CO₂ on the material [33,34]. The combination of both working together significantly raised the yield of the The XRD characterizations of P25, MgTi, AuTi, and AuMgTi before and after the reaction are illustrated in Fig. 2. All samples showed rutile and anatase crystal forms [39], indicating no obvious changes in crystal form in each material before and after the reaction. Also, the crystal form of P25 did not change by the loading of Au and MgO. On the other hand, no obvious diffraction peaks of Au, AuO, or MgO were observed in the XRD patterns of MgTi, AuTi, and AuMgTi after the reaction due to the low contents of Au and MgO, as well as their high dispersion states [33].

To identify the changes in morphology, the samples were scanned by SEM. In Fig. S2(a) and (b), P25 and AuMgTi showed particle diameters ranging between 20 and 25 nm before the reaction [39]. In other words, the particle size of AuMgTi did not change significantly after the loading of Au and MgO, consistent with the XRD data. In Fig. S2(b) and (d), there is no obvious agglomeration and other changes in the samples after the reaction.

TEM images of AuMgTi after the reaction are displayed in Fig. S3(a) and (b). Numerous small black spots were present on the material surface that might be caused by the loading of MgO or Au [40]. The partial enlarged TEM images of AuMgTi after the reaction are shown in Fig. S3 (c). The measurement of the lattice spacing revealed two crystal forms (rutile and anatase) before and after the cycling reaction, thereby good crystallization. The lattice fringe spacing of 0.350 nm corresponded to the 101 facet of anatase, and that of 0.320 nm was attributed to the 110 facet of rutile (Fig. S3(c)) [41], consistent with the XRD results. In TEM images, the grain size was estimated to about 20 nm, agreeing well with the SEM data. Therefore, the photothermal chemical reaction did not change the crystal forms of P25 and AuMgTi. And no brookite crystal form appeared since the temperature did not reach 873 K. Comparing the TEM images of AuMgTi before the reaction (Fig. S3(k) and (l)), there is no obvious changes in the samples after the reaction (Fig. S3(a)–(c)). However, the lattice fringes of Au and MgO were not visible in the captured images, thereby the energy spectra of larger areas of the material can only be scanned at low magnifications to determine the loading states of Au and MgO [40].

The layered EDXS images of Ti, O, Au, and Mg are summarized in Fig. S3(d)–(j), respectively. The distributions of Au and Mg looked relatively scattered. Therefore, TEM did not directly provide pictures of relevant MgO particles.

3.3. Optical properties and XPS analysis

The optical properties of P25, AuTi, MgTi, and AuMgTi samples were measured in integrating sphere mode by exposure to UV–vis light to detect electronic transitions from their outer molecular layers. As shown in Fig. 3(a), long waves did not induce a large shadowing effect on TiO₂ due to the low loading of Au. However, the loading of Au triggered an obvious bulge in the infrared band though the loading of Au and MgO did not cause a shift in the absorption edge of the samples. The latter was rather caused by the LSPR effect of Au particles, consistent with the literature [20,21]. In other words, the optical absorption capacities of AuTi and AuMgTi enhanced by the loading of Au, conducive to the absorption of light with longer wavelengths to generate high-energy hot electrons, thereby higher yields of Au-loading samples [42,43].

The band gap data of catalysts after transformation are provided in Fig. 3(b) [44]. The intersection of the tangent with the horizontal axis revealed a band gap of about 3.25 eV for P25. This value was close to the reported anatase band gap Eg = 3.20 eV. As a result, the loading of MgO and Au showed no significant influence on the band gap of each material.

The PL spectra of excited P25, AuTi, MgTi, and AuMgTi samples by a 325 nm laser are gathered in Fig. 4. Compared to P25 sample, the





Fig. 1. CO, H_2 and CH_4 production (by mass) of several experiments of photothermal chemical reaction: (a) the P25 samples; (b) the AuTi samples; (c) the MgTi samples; (d) the AuMgTi samples. (e)The comparison for the average production of CO, H_2 and CH_4 production (by mass) of several experiments of photothermal chemical reaction with all samples.



Fig. 2. XRD images: full patterns of all original and after the experiments samples. Each crystal facet is denoted by a black "A"(anatase) or a red "R" (rutile).

fluorescence intensity of MgTi did not significantly change. Meanwhile, AuTi and AuMgTi samples showed smaller and large decreases, respectively. Hence, the loading of Au inhibited the recombination of photogenerated electron-hole pairs. Also, the loading of MgO induced some variation on size of Au particle on TiO₂, reducing the recombination rate of photogenerated electron-hole pairs [45–47]. This can be explained by the transformation of Au into an electron trap, promoting the separation of photogenerated electrons and holes [48,49]. The decline in the recombination rate induced more photo-generated electron-hole pairs that could participate in the photochemical reactions to generate oxygen vacancies, thereby increasing the reaction yields of subsequent products.

To clarify the changes in the valence states of the elements during the reaction and identify the reaction mechanism, XPS was used to study the original P25, AuTi, MgTi, and AuMgTi samples, as well as the three states of AuMgTi before and after illumination reaction. The Ti 2p spectra of various catalysts are summarized in Fig. 5(a). The binding energy of Ti $2p_{3/2}$ in P25 and MgTi was estimated to 458.7 eV, while that of Ti $2p_{3/2}$ in Au and AuMgTi was 458.4 eV. Thus, the loading of Au created defects on the catalyst surface [50]. The Ti 2p spectra of AuMgTi in all three states are presented in Fig. 5(b). The binding energy of Ti $2p_{3/2}$ in the original AuMgTi was recorded as 458.4 eV, while that after illumination declined to 458.1 eV. The binding energy after the reaction was calculated as 458.4 eV, indicating a gain of electrons by Ti⁴⁺ to become Ti³⁺ after illumination. Also, the change in the valence state of

Ti suggested the generation of oxygen vacancies, which then were consumed during the photothermal chemical reaction [51,52]. In O 1s spectrum (Fig. 5(c)), the peaks can be divided into three components at binding energies of 530.0, 531.4, and 532.2 eV, assigned to oxygen associated with O species in the lattice (O_L), O species near the vacancies or defects (O_V), and chemisorbed (O_C) species, respectively [19,53]. In Fig. 5(c), the peak intensity of Ov in O of B state increased. Consequently, Ti—O present on the catalyst surface may be broken after illumination, and the photo-generated electrons formed oxygen vacancies that were consumed during the subsequent reaction. The states of Ti and O both change during the reaction and return to the original state after the reaction. It shows that the AuMgTi has good stability in the reaction.

The Au 4f spectra of AuTi and AuMgTi are displayed in Fig. 5(d). The binding energies of Au $4f_{7/2}$ and Au $4f_{5/2}$ in AuTi and AuMgTi were estimated to 87.2 eV and 83.4 eV, respectively. As a result, Au supported on catalyst surface was based on 0 valence [31,54]. The Mg 1s spectra of MgTi and AuMgTi are presented in Fig. 5(e). The characteristic peak at 1003.7 eV indicated Mg supported on the material surface in the form of Mg²⁺, consistent with the EDX data [55].

3.4. In situ DRIFTS analysis

To further study the reaction mechanism and confirm the roles played by Au, MgO, photo, and thermal energies in the reaction, the asobtained materials were subjected to *in-situ* DRIFTS experiments of nonlight, photothermal chemical cycling, and photothermal chemical



Fig. 4. PL patterns of the samples of P25, AuTi, MgTi and AuMgTi.



Fig. 3. (a) UV-vis DRS spectra of the original samples of P25, AuTi, MgTi and AuMgTi. (b) determination of the optical band gap.



Fig. 5. (a) XPS patterns of the Ti 2p peaks for State A (before irradiation), State B (after irradiation) and State C (after reaction) of AuMgTi. XPS patterns of (b) Ti 2p peaks of the samples for P25, AuTi, MgTi and AuMgTi; (c) O 1s at the various states in the reaction of AuMgTi; (d) Au 4f peaks of the samples for AuTi and AuMgTi; (e) Mg 1s peaks of the samples for MgTi and AuMgTi.

reactions. The specific experimental conditions and procedures are shown in the Fig. S4. For the *in-situ* DRIFTS experiments of photothermal chemical reactions (Fig. S4(a)), after placing the samples in the in-situ cell at 623 K in He atmosphere for 5 h, the temperature was set to 573 K and left to stabilize for a while to collect the background. Next, the gas was switched to a mixed gas atmosphere containing 99 % He and 1 %

 CO_2 , and airflow was used to carry the water injected by the needle tube into the in-situ tank. Finally, the in-situ tank was sealed and the experiment was started after maintaining a certain pressure with illumination. The experiment of non-light was completed under the condition of 573 K without illumination (Fig. S4(b)). For the experiment of photothermal chemical cycling (Fig. S4(c)), after pretreatment for 5 h,



Fig. 6. In situ time-resolved DRIFTS analysis of AuMgTi under the conditions of (a) no light, (b) photothermal chemical reaction, and (c) photothermal chemical cycling.

the sample was irradiated at 298 K in He atmosphere for 1 h. And then the temperature was raised to 573 K to collect the background without illumination.

The *in-situ* DRIFTS spectra of AuMgTi samples under the conditions of no light, photothermal chemical reaction, and photothermal chemical cycling are shown in Fig. 6(a), (b), and (c), respectively. The CO₂ peak appeared at 1200–1700 cm⁻¹, the water adsorption peak at 1620 cm⁻¹, and the OH adsorption peak at 3500–3800 cm⁻¹ [56]. On the other hand, though the peak of CO₂ appeared earlier with a strong signal (Fig. 6(a)), no obvious change was noticed over time. By comparison, the adsorption peaks of water and -OH looked weak in the beginning but became obvious over time. Therefore, MgO-loaded material adsorbed more CO₂ than water molecules. In the absence of light, the surface groups of the material did not change and the reaction did not proceed.

In Fig. 6(b), the HCO₃⁻ peak appeared at 1234 cm⁻¹ after 2 min reaction [57]. Note that this peak did not exist in Fig. 6(a) and its intensity greatly enhanced over time. As the reaction progressed, the characteristic peaks of 'CO₂⁻ at 1250 cm⁻¹ and 1670 cm⁻¹ weakened significantly, while those of monodentate carbonate(m-CO₃²⁻) and bidentate carbonate (b-CO₃²⁻) underwent only slight changes [19, 57–60]. The adsorption peaks of water and -OH increased significantly over time due to the slower adsorption of H₂O or consumption of more CO₂ as the reaction progressed, thereby vacating some reaction sites for H₂O absorption. Compared to Fig. 6(a) and (b), light played an important role in the photothermal chemical reaction. Without light, HCO₃⁻ groups did not form and the adsorbed groups did not change.

As shown in Fig. 6(c), the CO_2^- characteristic peaks appeared at 1250 cm⁻¹ and 1670 cm⁻¹ after 2 min reaction. The peak intensities continued to decrease until vanishing after 15 min reaction. The reason for this might be due to the oxygen vacancies generated during light exposure, which could quickly adsorb CO_2 after exposure to CO_2 to produce CO_2^- , leading to reaction under heating until full exhaustion.

In Fig. 6(b) and (c), there are characteristic peaks of $m-CO_3^{2-}$ at 1510 $\rm cm^{-1}$ and 1536 $\rm cm^{-1}$. While there is the characteristic peak of m-CO₃²⁻ at 1510 cm⁻¹ in Fig. 6(a). Therefore, these two peaks represent the two adsorption states of m-CO₃²⁻. The peak of m-CO₃²⁻ at 1510 cm⁻¹ is formed by CO₂ adsorbed on the surface with the thermal reaction progresses [57]. This peak all increase with the reaction time in Fig. 6(a), (b) and (c). The peak of m- CO_3^{2-} at 1536 cm⁻¹ may represent the characteristic peak of m- CO_3^{2-} formed by CO₂ adsorption on oxygen vacancies as this peak in the Fig. 6(c) was present at the beginning of the reaction and was gradually consumed as the reaction progressed. During the photothermal chemical cycle experiment, the produced oxygen vacancies after evaluation of light cannot be replenished afterward, causing the disappearance of the peak. In the in-situ DRIFTS experiments of photothermal chemical reaction, the oxygen vacancies could be replenished in time after consumption due to the continuous light exposure, thereby preserving the existence of the related peak. Compared Fig. 6(b) with Fig. 6(c), photo-generated carriers were induced during the photothermal chemical reaction to directly participate in the chemical reaction along with the generation of oxygen vacancies.

In sum, the *in-situ* DRIFTS spectra of AuMgTi samples under different conditions revealed several important points. First, the loading of MgO rendered the adsorption of CO_2 easier on the material than H₂O. Second, the effect of light determined the occurrence of the photothermal chemical reaction and photothermal chemical cycle. Third, both photogenerated carriers during the photothermal chemical reaction directly participated in the reaction, while the oxygen vacancies generated by the reaction indirectly participated in the two reaction pathways.

The *in-situ* DRIFTS spectrum of the photothermal chemical reactions of MgTi and AuMgTi are gathered in Fig. S4(a). Both samples showed characteristic peaks of CO₂ at 1200–1700 cm⁻¹. However, a characteristic peak of HCO₃⁻ appeared at 1234 cm⁻¹ in the spectrum of AuMgTi as the reaction progressed, while the intensity continued to increase. This was different from MgTi sample, indicating that the loading of Au might act as a catalytically active center on the material surface to assist in the quick conversion of the chemical groups and facilitate the reaction.

The *in-situ* DRIFTS spectra of the photothermal chemical reactions of P25 and MgTi are illustrated in Fig. S4(b). The CO₂ peaks in band of MgTi were observed at 1300–1700 cm⁻¹, with no obvious change in their intensities after 5 min and 20 min. The adsorption peak of H₂O was noticed at 1616 cm⁻¹ and showed enhanced intensity. Compared to H₂O, the loading of MgO made the material more suitable for CO₂ adsorption to quickly become saturated.

3.5. Density functional theory (DFT) calculations and mechanisms

Oxygen vacancies also play a certain role in the photothermal chemical reaction process. The oxygen vacancies formed in various materials obtained by DFT simulations are listed in Table S1. The formation energy of oxygen vacancies in pure TiO_2 was estimated to 3.96 eV. After loading Au nanoparticles, the formation energy of oxygen vacancies significantly reduced to 1.69 eV, similar to that of AuMgTi that declined to 2.38 eV. Thus, the existence of Au could significantly reduce the formation energy of oxygen vacancies [61,62]. The reason for this had to do with Au, which acted as an electron acceptor, where more electrons can be transferred from O near Au toward Au to form oxygen vacancies.

During the adsorption of carbon dioxide to generate CH₄ and other carbon-containing products, a series of intermediate groups and other products may be produced. The intermediate groups and products were determined according to the literature and used to construct the two reaction pathways of carbon dioxide to methane and one of carbon dioxide to monoxide (Fig. S5) [63,64]. The results obtained by combining these intermediate group models with various catalytic materials for calculations are depicted in Fig. 7. From the lowest energy barrier viewpoint, the reaction paths of pure TiO₂, AuTi, and MgTi pointed toward path 1, except for AuMgTi. In Path 1, the highest reaction energy barrier of pure TiO₂ was determined as 0.93 eV, while those of AuTi and MgTi were 0.56 eV and 0.88 eV, respectively. Note that both materials were reduced, suggesting that the support of co-catalyst could reduce the highest energy barrier for facile CH₄ generation. In addition, the CO₂ adsorption energy significantly declined regardless of the loaded material (Au or MgO). Hence, the loading of the co-catalyst enhanced the CO₂ adsorption of the material and facilitated the CO₂ reduction. This agreed well with the experimental results showing that carbon-containing products possess obvious output and selectivity improvement after loading. Comparison of the energy barriers of various materials for pathways from CO* to CO showed improvement in energy barriers after the loading of the co-catalyst. This meant increased difficulty of CO* transformation to CO, where more CO* may lead to the formation of CH₄. Compared to the direct conversion of CO* intermediates into CO, the energy of CO* intermediate conversion to HCO* looked lower regardless of the material. Also, more CH₄ should theoretically be generated but the formation reaction of CH₄ required 8 electrons while that of CO required only 2 electrons. As a result, the formation of CO was easier to carry out. This may also explain why the output of CO was still higher even if the adsorption of CO₂ was facilitated.

Based on the above investigation, photothermal chemical reaction of CO_2 with H_2O over the AuMgTi catalyst under irradiation with Xenon lamp was likely to take place according to Fig. 8. According to the in-situ DRIFTS experiments of photothermal chemical reactions, the loading of MgO increased the amount of chemisorbed CO_2 to form active magnesium carbonate species, which is believed to be more reactive than the linear CO_2 molecule [65]. With excitation, holes (h⁺) in the valence band of TiO₂ are generated. Part of holes in the valence band of TiO₂ reacts with H₂O to form O₂ and H⁺. The other part reacts with lattice oxygen to form oxygen vacancies which has been verified by XPS analysis. Due to the loading of Au, the formation energy of oxygen vacancies on the surface of TiO₂ is reduced (Table S1). It leads that more



Fig. 7. The whole reaction process of two reaction pathways to methane and one to monoxide for (a) anatase TiO₂ (101), (b) Au-anatase TiO₂ (101), (c) MgO-anatase TiO₂ (101), and (d) Au-MgO- anatase TiO₂ (101).



Fig. 8. Reaction mechanism for photothermal chemical reactions of CO_2 with H_2O on AuMgTi.

oxygen vacancies can be generate and consumed for CO_2 reduction on the surface of AuMgTi. At the same time, high-energy hot electrons are generated due to the LSPR effect excited by visible light on the surface of Au particles. The high-energy hot electrons on Au can participate in the reduction reaction of CO_2 to produce carbon-containing products.

4. Conclusions and future outlooks

Intensive research studies were successfully carried out to improve the selectivity of CO_2 reduction in the presence of H_2O during photothermal reaction after Au and MgO loading. The photodeposition and impregnation methods were used to prepare the AuMgTi samples, and 5 groups of photothermal experiments were performed. The average yields of CO, H_2 , and CH_4 on AuMgTi were estimated to 45.495 umol/g,

45.072 umol/g, and 6.624 umol/g, respectively. The yields were 5.9fold, 1.9-fold, and 3.2-fold higher than those of P25, respectively. Also, the selectivities of carbon-containing products increased from 29 % to 53.6 % when compared to P25. The roles played by Au and MgO in the reaction were investigated, the reaction mechanisms were further studied by combined characterization and calculations. XRD, SEM, and TEM results showed that the loading of Au and MgO did not significantly change the comparative areas, sintering characteristics, crystal form, and structure of P25. EDXS and XPS revealed the successful loading of Au and MgO on P25 surface with high dispersion. The PL and UV-vis characterizations confirmed that Au loading did not only improve the response characteristics of P25 to visible light by LSPR effect but also acted as an electron acceptor to enrich the photo-generated electrons on the surface with Au. The latter effectively reduced the recombination rate of photo-generated electron-hole pairs, thereby generating more photo-generated holes to participate in the photoreaction and form more oxygen vacancies. The DFT calculations showed that oxygen vacancies were more likely to be generated near Au, while the energy barrier effect diminished for the formation of oxygen vacancies. Au and MgO reduced the adsorption energy of CO₂, as well as the energy barrier of CH₄ generation pathway. Under these conditions, TiO₂ loaded by Au and MgO showed good photothermal reaction performances. In sum, these findings look promising for future if efforts are made to enhance both optical and thermal steps by utilized materials and additional studies of the photothermal chemical reaction should be carried out to study the mechanism, enhance solar fuel production and improve the selectivity of carbon-containing products.

Author statement

Wenhui Huang: Conceptualization, Data curation, Formal analysis,
Methodology, Validation, Investigation, Writing - Original Draft.
Li Zhang: Investigation, Methodology, Software, Validation.

Zheng Li: Investigation, Software.

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Declaration of Competing Interest

The authors report no declarations of interest.

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Appendix A. Supplementary data

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References

- [1] Y.P. Yuan, L.W. Ruan, J. Barber, S.C.J. Loo, C. Xue, Hetero-nanostructured suspended photocatalysts for solar-to-fuel conversion, Energy Environ. Sci. 7 (12) (2014) 3934–3951.
- [2] W.G. Tu, Y. Zhou, Z.G. Zou, Photocatalytic conversion of CO₂ into renewable hydrocarbon fuels: state-of-the-art accomplishment, challenges, and prospects, Adv. Mater. 26 (27) (2014) 4607–4626.
- [3] C. Liu, B.C. Colon, M. Ziesack, P.A. Silver, D.G. Nocera, Water splittingbiosynthetic system with CO₂ reduction efficiencies exceeding photosynthesis, Science 352 (6290) (2016) 1210–1213.
- [4] A. Fujishima, K. Honda, Electrochemical photolysis of water at a semiconductor electrode, Nature 238 (5358) (1972), 37-+.
- [5] J.X. Gao, L.L. Tang, Z.Z. Shen, Y.M. Dong, Z.Y. Wang, J.Z. Lyu, J. Li, H.Q. Yu, Efficient solar-light conversion for optimizing the catalytic ozonation of gaseous toluene with PdO_x-LaFeO₃, Appl. Catal. B-Environ. 288 (2021).
- [6] Q. Wang, K. Domen, Particulate photocatalysts for light-driven water splitting: mechanisms, challenges, and design strategies, Chem. Rev. 120 (2) (2020) 919–985.
- [7] A. Haeussler, S. Abanades, A. Julbe, J. Jouannaux, B. Cartoixa, Two-step CO₂ and H₂O splitting using perovskite-coated ceria foam for enhanced green fuel production in a porous volumetric solar reactor, J. CO2 Util. 41 (2020).
- [8] W.C. Chueh, C. Falter, M. Abbott, D. Scipio, P. Furler, S.M. Haile, A. Steinfeld, High-flux solar-driven thermochemical dissociation of CO₂ and H₂O using nonstoichiometric ceria, Science 330 (6012) (2010) 1797–1801.
- [9] J.M. Naik, C. Ritter, B. Bulfin, A. Steinfeld, R. Erni, G.R. Patzke, Reversible phase transformations in novel Ce-substituted perovskite oxide composites for solar thermochemical redox splitting of CO₂, Adv. Energy Mater. 11 (16) (2021).
- [10] Nanostructured indium oxide coated silicon nanowire arrays: a hybrid photothermal/photochemical approach to solar fuels, J. ACS Nano (2016) 9017–9025.
- [11] G.B. Chen, R. Gao, Y.F. Zhao, Z.H. Li, G.I.N. Waterhouse, R. Shi, J.Q. Zhao, M. T. Zhang, L. Shang, G.Y. Sheng, X.P. Zhang, X.D. Wen, L.Z. Wu, C.H. Tung, T. R. Zhang, Alumina-supported CoFe alloy catalysts derived from layered-double-hydroxide nanosheets for efficient photothermal CO₂ hydrogenation to hydrocarbons, Adv. Mater. 30 (3) (2018) 8.
- [12] X. Meng, W. Tao, L. Liu, S. Ouyang, J.J.A.C. Ye, Photothermal conversion of CO₂ into CH₄ with H₂ over group VIII nanocatalysts: an alternative approach for solar fuel production, Angew. Chemie 126 (43) (2014).
- [13] D. Liu, C. Wang, Y. Yu, B.H. Zhao, W. Wang, Y. Du, B. Zhang, Understanding the Nature of Ammonia Treatment to Synthesize Oxygen Vacancy-Enriched Transition Metal Oxides, 2019.
- [14] J.Y. Yan, C.H. Wang, H. Ma, Y.Y. Li, Y.C. Liu, N. Suzuki, C. Terashima, A. Fujishima, X.T. Zhang, Photothermal synergic enhancement of direct Z-scheme behavior of Bi₄TaO₈Cl/W₁₈O₄₉ heterostructure for CO2 reduction, Appl. Catal. B-Environ. 268 (2020).
- [15] S.N. Habisreutinger, L. Schmidt-Mende, J.K. Stolarczyk, Photocatalytic reduction of CO₂ on TiO₂ and other semiconductors, Angew. Chem.-Int. Edit. 52 (29) (2013) 7372–7408.
- [16] A. Corma, H. Garcia, Photocatalytic reduction of CO₂ for fuel production: Possibilities and challenges, J. Catal. 308 (2013) 168–175.
- [17] Q.Y. Li, L.L. Zong, C. Li, J.J. Yang, Photocatalytic reduction of CO₂ on MgO/TiO2 nanotube films, Appl. Surf. Sci. 314 (2014) 458–463.

- Journal of CO2 Utilization 55 (2022) 101801
- [18] X. Feng, F.P. Pan, H.L. Zhao, W. Deng, P. Zhang, H.C. Zhou, Y. Li, Atomic layer deposition enabled MgO surface coating on porous TiO₂ for improved CO₂ photoreduction, Appl. Catal. B-Environ. 238 (2018) 274–283.
- [19] C.Y. Xu, W.H. Huang, Z. Li, B.W. Deng, Y.W. Zhang, M.J. Ni, K.F. Cen, Photothermal coupling factor achieving CO₂ reduction based on palladiumnanoparticle-loaded TiO₂, ACS Catal. 8 (7) (2018) 6582–6593.
- [20] M. Tahir, B. Tahir, N.A.S. Amin, Synergistic effect in plasmonic Au/Ag alloy NPs co-coated TiO₂ NWs toward visible-light enhanced CO₂ photoreduction to fuels, Appl. Catal. B-Environ. 204 (2017) 548–560.
- [21] S.J. Yu, A.J. Wilson, J. Heo, P.K. Jain, Plasmonic control of multi-electron transfer and C-C coupling in visible-light-driven CO₂ reduction on au nanoparticles, Nano Lett. 18 (4) (2018) 2189–2194.
- [22] M.G. Mendez-Medrano, E. Kowalska, A. Lehoux, A. Herissan, B. Ohtani, D. Bahena, V. Briois, C. Colbeau-Justin, J.L. Rodriguez-Lopez, H. Remita, Surface modification of TiO₂ with Ag nanoparticles and CuO nanoclusters for application in photocatalysis, J. Phys. Chem. C 120 (9) (2016) 5143–5154.
- [23] W. Kohn, L.J. Sham, Self-consistent equations including exchange and correlation effects, Phys. Rev. 140 (4A) (1965), 1133-.
- [24] P. Hohenberg, W. Kohn, Inhomogeneous electron gas, Phys. Rev. B 136 (3B) (1964). B864-+.
- [25] G. Kresse, J. Furthmuller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, Phys. Rev. B 54 (16) (1996) 11169–11186.
- [26] G. Kresse, J. Furthmuller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, Comput. Mater. Sci. 6 (1) (1996) 15–50.
- [27] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, Phys. Rev. Lett. 77 (18) (1996) 3865–3868.
- [28] G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmentedwave method, Phys. Rev. B 59 (3) (1999) 1758–1775.
- [29] P.E. Blochl, Projector augmented-wave method, Phys. Rev. B 50 (24) (1994) 17953–17979.
- [30] H.J. Monkhorst, J.D. Pack, Special points for Brillouin-zone integrations, Phys. Rev. B 13 (12) (1976) 5188–5192.
- [31] A. Wang, S.J. Wu, J.L. Dong, R.X. Wang, J.W. Wang, J.L. Zhang, S.X. Zhong, S. Bai, Interfacial facet engineering on the Schottky barrier between plasmonic Au and TiO₂ in boosting the photocatalytic CO₂ reduction under ultraviolet and visible light irradiation, Chem. Eng, J. 404 (2021) 9.
- [32] J.L. Zhuang, C.J. He, K.L. Wang, K.X. Teng, Z.Q. Ma, S.T. Zhang, L.M. Lu, X.B. Li, Y. H. Zhang, Q. An, Nanoscopically-optimized carrier transportation and utilization in immobilized AuNP-TiO₂ composite HER photocatalysts, Appl. Surf. Sci. 537 (2021) 8.
- [33] M. Manzanares, C. Fabrega, J.O. Osso, L.F. Vega, T. Andreu, J.R. Morante, Engineering the TiO₂ outermost layers using magnesium for carbon dioxide photoreduction, Appl. Catal. B-Environ. 150 (2014) 57–62.
- [34] L.J. Liu, C.Y. Zhao, H.L. Zhao, D. Pitts, Y. Li, Porous microspheres of MgO-patched TiO₂ for CO₂ photoreduction with H₂O vapor: temperature-dependent activity and stability, Chem. Commun. 49 (35) (2013) 3664–3666.
- [35] S.J. Xie, Y. Wang, Q.H. Zhang, W.P. Deng, Y. Wang, MgO- and Pt-promoted TiO₂ as an efficient photocatalyst for the preferential reduction of carbon dioxide in the presence of water, ACS Catal. 4 (10) (2014) 3644–3653.
- [36] M. Sayed, F.Y. Xu, P.Y. Kuang, J.X. Low, S.Y. Wang, L.Y. Zhang, J.G. Yu, Sustained CO₂-photoreduction activity and high selectivity over Mn, C-codoped ZnO coretriple shell hollow spheres, Nat. Commun. 12 (1) (2021).
- [37] Y. Nie, W.N. Wang, Y. Jiang, J. Fortner, P. Biswas, Crumpled reduced graphene oxide-amine-titanium dioxide nanocomposites for simultaneous carbon dioxide adsorption and photoreduction, Catal. Sci. Technol. 6 (16) (2016) 6187–6196.
- [38] A. Raza, H.L. Shen, A.A. Haidry, L.H. Sun, R. Liu, S.S. Cui, Studies of Z-scheme WO₃-TiO₂/Cu₂ZnSnS₄ ternary nanocomposite with enhanced CO₂ photoreduction under visible light irradiation, J. CO2 Util. 37 (2020) 260–271.
- [39] Y.W. Zhang, C.Y. Xu, J.C. Chen, X.H. Zhang, Z.H. Wang, J.H. Zhou, K.F. Cen, A novel photo-thermochemical cycle for the dissociation of CO₂ using solar energy, Appl. Energy 156 (2015) 223–229.
- [40] C.J. Wang, Y.L. Zhao, H. Xu, Y.F. Li, Y.C. Wei, J. Liu, Z. Zhao, Efficient Z-scheme photocatalysts of ultrathin g-C₃N₄-wrapped Au/TiO₂-nanocrystals for enhanced visible-light-driven conversion of CO₂ with H₂O, Appl. Catal. B-Environ. 263 (2020) 13.
- [41] Y.N. Gao, H. Wang, J. Wu, R.H. Zhao, Y.F. Lu, B.F. Xin, Controlled facile synthesis and photocatalytic activity of ultrafine high crystallinity TiO₂ nanocrystals with tunable anatase/rutile ratios, Appl. Surf. Sci. 294 (2014) 36–41.
- [42] Y. Shi, J. Wang, C. Wang, T.T. Zhai, W.J. Bao, J.J. Xu, X.H. Xia, H.Y. Chen, Hot electron of Au nanorods activates the electrocatalysis of hydrogen evolution on MoS₂ nanosheets, J. Am. Chem. Soc. 137 (23) (2015) 7365–7370.
- [43] X.X. Zhao, H. Yang, Z.M. Cui, Z. Yi, H. Yu, Synergistically enhanced photocatalytic performance of Bi₄Ti₃O₁₂ nanosheets by Au and Ag nanoparticles, J. Mater. Sci.-Mater. Electron. 30 (14) (2019) 13785–13796.
- [44] S.S. Lee, H.W. Bai, Z.Y. Liu, D.D. Sun, Novel-structured electrospun TiO₂/CuO composite nanofibers for high efficient photocatalytic cogeneration of clean water and energy from dye wastewater, Water Res. 47 (12) (2013) 4059–4073.
- [45] H.L. Zhao, X.Y. Zheng, X.H. Feng, Y. Li, CO₂ reduction by plasmonic Au nanoparticle-decorated TiO₂ photocatalyst with an ultrathin Al₂O₃ interlayer, J. Phys. Chem. C 122 (33) (2018) 18949–18956.
- [46] L.L. Sun, D.X. Zhao, Z.M. Song, C.X. Shan, Z.H. Zhang, B.H. Li, D.Z. Shen, Gold nanoparticles modified ZnO nanorods with improved photocatalytic activity, J. Colloid Interface Sci. 363 (1) (2011) 175–181.

W. Huang et al.

- [47] K.K. Haldar, T. Sen, S. Mandal, A. Patra, Photophysical properties of Au-CdTe hybrid nanostructures of varying sizes and shapes, Chemphyschem 13 (17) (2012) 3989–3996.
- [48] A. Primo, A. Corma, H. Garcia, Titania supported gold nanoparticles as photocatalyst, Phys. Chem. Chem. Phys. 13 (3) (2011) 886–910.
- [49] Q. An, T. Huang, F. Shi, Covalent layer-by-layer films: chemistry, design, and multidisciplinary applications, Chem. Soc. Rev. 47 (13) (2018) 5061–5098.
- [50] L.H. Nie, J.G. Yu, X.Y. Li, B. Cheng, G. Liu, M. Jaroniec, Enhanced performance of NaOH-modified Pt/TiO₂ toward room temperature selective oxidation of formaldehyde, Environ. Sci. Technol. 47 (6) (2013) 2777–2783.
- [51] W.C. Zhan, Q. He, X.F. Liu, Y.L. Guo, Y.Q. Wang, L. Wang, Y. Guo, A.Y. Borisevich, J.S. Zhang, G.Z. Lu, S. Dai, A sacrificial coating strategy toward enhancement of metal-support interaction for ultrastable au nanocatalysts, J. Am. Chem. Soc. 138 (49) (2016) 16130–16139.
- [52] C.Y. Xu, Y.W. Zhang, F.Q. Pan, W.H. Huang, B.W. Deng, J.Z. Liu, Z.H. Wang, M. J. Ni, K.F. Cen, Guiding effective nanostructure design for photo-thermochemical CO₂ conversion: from DFT calculations to experimental verifications, Nano Energy 41 (2017) 308–319.
- [53] X.Y. Zhang, J.Q. Qin, Y.N. Xue, P.F. Yu, B. Zhang, L.M. Wang, R.P. Liu, Effect of aspect ratio and surface defects on the photocatalytic activity of ZnO nanorods, Sci. Rep. 4 (2014) 8.
- [54] X.T. Cai, F. Wang, R.X. Wang, Y.M. Xi, A. Wang, J.W. Wang, B.T. Teng, S. Bai, Synergism of surface strain and interfacial polarization on Pd@Au core-shell cocatalysts for highly efficient photocatalytic CO2 reduction over TiO2, J. Mater. Chem. A 8 (15) (2020) 7350–7359.
- [55] H. Seyama, M. Soma, X-ray photoelectron spectroscopic study of montmorillonite containing exchangeable divalent cation, J. Chem. Soc. Faraday Trans. I 80 (1984) 237–248.
- [56] B. Laszlo, K. Baan, E. Varga, A. Oszko, A. Erdohelyi, Z. Konya, J. Kiss, Photoinduced reactions in the CO₂-methane system on titanate nanotubes modified with Au and Rh nanoparticles, Appl. Catal. B-Environ. 199 (2016) 473–484.

- [57] L.J. Liu, Y.Q. Jiang, H.L. Zhao, J.T. Chen, J.L. Cheng, K.S. Yang, Y. Li, Engineering coexposed {001} and {101} facets in oxygen-deficient TiO2 nanocrystals for enhanced CO2 photoreduction under visible light, ACS Catal. 6 (2) (2016) 1097–1108.
- [58] W.Q. Wu, K. Bhattacharyya, K. Gray, E. Weitz, Photoinduced reactions of surfacebound species on titania nanotubes and platinized titania nanotubes: an in situ FTIR study, J. Phys. Chem. C 117 (40) (2013) 20643–20655.
- [59] L.J. Liu, H.L. Zhao, J.M. Andino, Y. Li, Photocatalytic CO2 reduction with H₂O on TiO₂ nanocrystals: comparison of anatase, rutile, and brookite polymorphs and exploration of surface chemistry, ACS Catal. 2 (8) (2012) 1817–1828.
- [60] C.C. Yang, Y.H. Yu, B. van der Linden, J.C.S. Wu, G. Mul, Artificial photosynthesis over crystalline TiO2-based catalysts: fact or fiction? J. Am. Chem. Soc. 132 (24) (2010) 8398–8406.
- [61] L. Li, W.S. Li, C.Y. Zhu, L.F. Mao, DFT calculation about oxygen vacancy to promote adsorption of a CO molecule on single Au-supported titanium dioxide, Phys. Status Solidi B-Basic Solid State Phys. 256 (3) (2019) 7.
- [62] J. Wang, M. Lei, Z.X. Wang, Y.S. Liu, W.C. Zhuang, W.Y. Zhu, Methanol oxidation over rutile Au-1@TiO₂ catalyst: importance of facets and oxygen vacancy, Appl. Surf. Sci. 542 (2021) 5.
- [63] J.W. Zhao, B.Q. Liu, L.S. Meng, S. He, R.S. Yuan, Y.D. Hou, Z.X. Ding, H.X. Lin, Z. Z. Zhang, X.X. Wang, J.L. Long, Plasmonic control of solar-driven CO₂ conversion at the metal/ZnO interfaces, Appl. Catal. B-Environ. 256 (2019) 12.
- [64] J.Y. Li, P. Yan, K.L. Li, J.J. You, H. Wang, W. Cui, W.L. Cen, Y.H. Chu, F. Dong, Cu supported on polymeric carbon nitride for selective CO₂ reduction into CH₄: a combined kinetics and thermodynamics investigation, J. Mater. Chem. A 7 (28) (2019) 17014–17021.
- [65] S.J. Xie, Y. Wang, Q.H. Zhang, W.Q. Fan, W.P. Deng, Y. Wang, Photocatalytic reduction of CO₂ with H₂O: significant enhancement of the activity of Pt-TiO₂ in CH₄ formation by addition of MgO, Chem. Commun. 49 (24) (2013) 2451–2453.