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Article (Special Issue on Photocatalytic H₂ Production and CO₂ Reduction)Solar-heating boosted catalytic reduction of CO₂ under full-solar spectrumHongjia Wang^{a,b}, Yanjie Wang^a, Lingju Guo^a, Xuehua Zhang^a, Caue Ribeiro^{c,d}, Tao He^{a,b,*}^a CAS Laboratory of Nanosystem and Hierarchical Fabrication, CAS Center for Excellence in Nanoscience, National Center for Nanoscience and Technology, Beijing 100190, China^b University of Chinese Academy of Sciences, Beijing 100049, China^c National Nanotechnology Laboratory for Agribusiness, Embrapa Instrumentation, 13561-206, São Carlos – SP, Brazil^d Forschungszentrum Jülich GmbH – Institute of Energy and Climate Research – IEK-3/Electrochemical Process Engineering, Jülich 52425, Germany

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ABSTRACT

Catalytic converting CO₂ into fuels with the help of solar energy is regarded as ‘dream reaction’, as both energy crisis and environmental issue can be mitigated simultaneously. However, it is still suffering from low efficiency due to narrow solar-spectrum utilization and sluggish heterogeneous reaction kinetics. In this work, we demonstrate that catalytic reduction of CO₂ can be achieved over Au nanoparticles (NPs) deposited rutile under full solar-spectrum irradiation, boosted by solar-heating effect. We found that UV and visible light can initiate the reaction, and the heat from IR light and local surface-plasmon resonance relaxation of Au NPs can boost the reaction kinetically. The apparent activation energy is determined experimentally and is used to explain the superior catalytic activity of Au/rutile to rutile in a kinetic way. We also find the photo-thermal synergy in the Au/rutile system. We envision that this work may facilitate understanding the kinetics of CO₂ reduction and developing feasible catalytic systems with full solar spectrum utilization for practical artificial photosynthesis.

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1. Introduction

Artificial photosynthesis is the process that can convert carbon dioxide (CO₂) and water (H₂O) into high value-added chemicals (CO, CH₄, CH₃OH, etc.) and oxygen (O₂) with the aid of sunlight and catalysts like semiconductors [1–6]. Rising level of atmospheric CO₂ due to burning fossil fuels caused severe energy and environmental issues, while artificial photosynthesis may address both of them [7–9]. Many work have been done to improve the efficiency of artificial photosynthesis over semiconductors, including crystal facet engineering, element dop-

ing/deposition, hetero-structure fabrication, and molecular catalyst modification [10]. However, the low efficiency still impedes its practical applications because classic semiconductor-based solar-to-fuel (STF) processes are struggling in two major trade-offs: activity-stability and band edge-redox potential [7,11]. Since it is extremely hard to build the balance, new physics and chemistry are yearned for break-through. In addition, kinetics is usually far less considered than thermodynamics in this process, although the sluggish kinetics of electrochemical CO₂ reduction reaction (CO₂RR) and water oxidation reaction, and the reduction half reaction and oxidation half

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reaction of artificial photosynthesis, respectively, is a common sense [12,13].

Titanium dioxide (TiO₂) is the most frequently used photocatalyst since 1972, owing to its stability, earth-abundance and non-toxicity. It has been used in many important fields like water cleaning, dye bleaching and pollutant degradation [14–17]. However, TiO₂ still struggles in STF process because of its photoresponse only to UV light (< 400 nm), rapid carriers recombination and sluggish surface reaction kinetics [18,19]. Recently, coinage metal (Au, Ag and Cu) nanoparticles (NPs) with localized surface plasmon resonance (LSPR) have drawn great attention, as they can absorb wide range of light, especially visible light, by tuning the size, shape and component [20,21]. They can sensitize wide band gap semiconductors, especially TiO₂, and show considerable visible-light photocatalytic activity in hydrogen evolution reaction (HER), oxygen evolution reaction (OER), and CO₂RR through hot electrons and holes [22–24]. Compared to Ag and Cu, Au is more promising owing to its suitable LSPR peak position (~550 nm) and oxidation resistance. As a model catalyst, Au/TiO₂ shows promising in practical STF process due to its visible-light response, suitable band position and photo-corrosion resistance, which has been extensively studied and exhibits potential in overall water-splitting (OWS) and artificial photosynthesis [25–30]. The water oxidation reaction sites of Au/rutile plasmonic photocatalysts are studied recently [31]. The Au/rutile can also be used to drive the OWS [32]. Its ability to conduct artificial photosynthesis in continuous flow reactor has been demonstrated too [33], while the STF efficiency is still very low.

Usually it is believed that infrared (IR) cannot be used directly in STF process because its photon energy is too low to drive reduction/oxidation half reactions simultaneously [11,34]. This can lead to a huge loss since IR makes up more than half of the solar spectrum (~54%), resulting in low STF efficiency. However, IR can bring significant thermal effect and temperature increase [35], which may boost chemical reactions and offer a new approach to take advantage of the full solar spectrum. There are some reports focusing on the heat-enhanced photo-(electro-)catalytic reaction, while the inherent mechanism is still under debate (i.e., how thermal effect influence the basic process of photo-(electro-)catalytic reaction, such as the generation/migration of charge carriers and surface reaction kinetics). It is reported that electrochemical OWS efficiency can be improved with the help of solar heating [36], and the photo-thermal catalysis can be realized over Cu₇S₄@ZIF-8 under 1450 nm laser [37]. However, external heat is usually required in previous work of thermal-enhanced artificial photosynthesis [38,39], which is counter to the actual goal. As a matter of fact, utilization of heating from solar illumination is environmentally friendly and energy saving.

In this work, we demonstrate the Au/rutile photocatalyst can achieve artificial photosynthesis by making utilization of full solar spectrum, among which UV and visible light initiate the reactions, and heat from IR and SPR relaxation boost the reactions. We envision that this may provide deep understanding in full solar spectrum utilization, activation energy of artificial photosynthesis and, specifically, overcoming this acti-

vation energy just simply with the help of solar heating.

2. Experimental

2.1. Catalysts preparation

Commercial rutile (Aladin) was used as the model catalyst. Au NPs were deposited onto the rutile (denoted as Au/rutile) using a similar protocol reported previously, in which the mechanism and active sites of water oxidation reaction driven by hot holes on Au/rutile were clearly elucidated [31], as well as the OWS [32]. Typically, 1.0 g of rutile was dispersed in 80 mL of deionized water, with the addition of 3.0 g of urea and 3.0 mL of 1% HAuCl₄ aqueous solution. The resultant suspension was then maintained at 80 °C for 2 h. The obtained product was washed with deionized water for three times and dried at 65 °C overnight. Au/rutile was finally obtained after being calcined at 400 °C for 3 h. Au/rutile is a suitable platform to study artificial photosynthesis because oxidation half reaction will not become the rate-limiting step in the over-all reaction.

2.2. Characterization

The crystal structure of as-prepared products was investigated by X-ray diffraction (XRD) using Bruker D8 focus diffractometer with Ni-filtered Cu-K_α radiation. The diffractograms were collected in the 2θ range of 10°–80° at a scan rate of 0.1°/min. UV-vis diffuse reflectance spectra (UV-vis DRS) were recorded with the wavelength ranging from 250 to 800 nm on Lambda 750 UV/visible/NIR spectrometer using BaSO₄ as the reference. Morphology and composition of the obtained samples were analyzed by using Hitachi S4800 field-emission scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectrometer (EDX) and Tecnai G2 F20 U-TWIN transmission electron microscopy (TEM). The Brunauer-Emmett-Teller (BET) specific surface area of the as-prepared samples was determined from N₂ adsorption isotherm obtained using an ASAP 2020 at –196 °C.

2.3. Photocatalytic evaluation

Catalytic reduction of CO₂ was carried out using the photo-reaction system described previously [40]. Typically, 20 mg of catalyst was used. High purity CO₂ gas (≥ 99.999%) was first bubbled before the reaction in a quartz reactor containing 15 mL of aqueous catalyst suspension. The wet CO₂ was flown through the whole system for ~40 min to ensure complete removal of air from the system and maximum adsorption of CO₂ molecules onto the active sites of the catalyst. A positive pressure of 25 kPa was maintained inside the system. A 300-W xenon lamp was placed 14–15 cm above the upper surface of the suspension. The system was constantly recycled with tap water (15 °C) during the entire reaction using water recycling pump. The reactor could be cooled down in the same system when necessary. The products were detected using helium as the carrier gas by 7890A GC/LC system (Agilent) equipped with two (front and back) flame ionization detectors (FID) and

one thermal conductivity detector (TCD) via an automated gas valve. Four control experiments were performed to study whether or not the observed products were from the CO₂ reduction, i.e., blank reactor with and without irradiation, dark experiment with the catalyst, and using Ar instead of CO₂ under the same experimental conditions.

2.4. Determination of apparent activation energy (E_a)

The reduction of CO₂ was also carried out at different temperatures so as to determine apparent activation energy (E_a). The reaction reactor was first put in a water bath for temperature control, which was kept at 20 °C during the CO₂ purging. When the Xenon lamp was switched on, the temperature was raised beforehand to 30 and 25 °C for Au/rutile and rutile, respectively. Here the IR light was blocked out using an IR cut-off filter so that the reaction temperature could be controlled precisely using the external water bath. The reactor was kept at each temperature for 2 h, and the sampling/detecting was performed every 1 h for two times. The temperature of water bath was raised by 10 °C after the 2nd sampling. The photocatalytic activity was studied using the data collected at 6 different temperatures, with the final value of 80 and 75 °C for Au/rutile and rutile, respectively. The activity determined at the 2nd sampling for each temperature interval was used to calculate the E_a , as the whole reaction system should be in steady state in this case. Accordingly, the resultant formation rate of CO and CH₄ ($\mu\text{mol}/(\text{g}\cdot\text{h})$) was denoted as the reaction rate constant k_{CH_4} and k_{CO} , respectively. So the $[\text{CO}] = -k_{\text{CO}}[\text{CO}_2][\text{H}_2\text{O}]^k$ and $[\text{CH}_4] = -k_{\text{CH}_4}[\text{CO}_2]^m[\text{H}_2\text{O}]^n$ can be achieved according to the classic kinetics.

The partial pressure of CO₂ as well as the amount of H₂O was almost unchanged during the reaction because of the excessive amount of CO₂ and H₂O present in the system, which can thus be regarded as a constant. In this regard, the k_{CO} and k_{CH_4} should be in proportion to the evolution amount of CO and CH₄ ($\mu\text{mol}/\text{g}$), which will have little impact on the calculation of E_a in terms of Arrhenius equation $\ln k = -E_a/RT + C$, where R represents the ideal gas constant, C is a constant related to the pre-exponential factor, and T is thermodynamic temperature scale (K). The relationship of $\ln k_{\text{CO}}$ versus T^{-1} (or $\ln k_{\text{CH}_4} \sim T^{-1}$) was plotted. The E_a can thus be determined according to the slope of the resultant fitting line.

3. Results and discussion

3.1. Structure and morphology characteristics

The Au/rutile samples are chosen as the platform to study the artificial photosynthesis mainly because oxidation half reaction will not become rate limiting step in over-all reaction, as reported previously [31,32]. The crystal structure of the obtained catalysts are studied by the XRD technique. The XRD patterns show that the TiO₂ in both samples are in rutile phase (Fig. 1), indicating that the Au deposition leads to no change in the crystal phase of TiO₂.

SEM images show that the obtained rutile are NPs with a

Fig. 1. XRD patterns of the rutile and Au/rutile samples.

size around 60 nm (Fig. 2(a) and (b)). The scattered bright spots in Fig. 2(a) are Au NPs, which is clearly confirmed by the TEM images (Fig. 2(c) and (d)). Specifically, the scattered black spots in Fig. 2(c) clearly indicate the presence of Au NPs in the Au/rutile sample since Au has a higher mass-thickness contrast than Ti and O, while no such black spots can be observed in the pure rutile sample (Fig. 2(d)). Both TEM and high resolution TEM (HRTEM, inset of Fig. 2(c)) images indicate the size of Au NPs is about 10 nm. The appearance of Au signal in the spectrum collected by EDX can further confirm its existence in Au/rutile (Fig. S1), as no Au signal can be observed in the EDX spectrum of rutile sample (Fig. S2). All these agree well with the XPS results too (Figs. S3–S5). Atomic ratio of Au to Ti in Au/rutile is very low, only about 6.8‰ according to the EDX results. Such a low content of Au in the composite catalyst explains why no diffraction peaks of Au can be observed in the XRD pattern of Au/rutile (Fig. 1). The respective crystal fringe is determined to be 0.25 and 0.35 nm for Au(111) and rutile(110) facets [41,42] (inset of Fig. 2(c)), further confirming

Fig. 2. SEM (a,b) and TEM (c,d) images of Au/rutile (a,c) and rutile (b,d) samples. Inset of (c) is the HRTEM image of Au/rutile with crystal fringes of the Au nanoparticle and rutile support, for which the scale bar is 5 nm.

Fig. 3. UV-Vis DRS of the rutile and Au/rutile samples.

the composition and crystallinity of the obtained Au/rutile catalyst. The BET specific surface area decreases from 48.2 to 37.2 m²/g after Au deposition, possibly owing to the high temperature annealing during the Au modification.

UV-Vis DRS shows the typical absorption characteristics of rutile in the UV range (Fig. 3), indicating its wide band gap nature with a value of about 3.0 eV derived from the Tauc plot (not shown here). The absorption peak at around 580 nm in the visible range for the Au/rutile sample is caused by the LSPR effect of Au NPs, which is consistent with the aforementioned particle size [43].

3.2. Catalytic reduction of CO₂

CO₂ reduction is used to evaluate the catalytic performance

of the obtained Au/rutile and rutile catalysts. No any products were observed in the four control experiments (i.e., blank with and without irradiation, with the catalyst but in dark, and using Ar instead of CO₂ under the same conditions), indicating the CO₂ is indeed the carbon source if a product can be observed. In order to study the solar-heating effect on catalytic performance without interrupting the experiments, the reactor is not cooled in the first 4 h and then is cooled down in the next 4 h. Fig. 4(a) shows catalytic results of CO₂ reduction over Au/rutile catalyst upon full-spectrum irradiation. No H₂ formation is observed for both cases, either because no H₂ is formed or the produced amount is beyond our GC detection limit. Furthermore, CO and CH₄ are the major products in both cases. Clearly, the formation rate (the ratio of yield over time, μmol/g/h) of both CO (r_{CO}) and CH₄ (r_{CH_4}) slows down once the reactor is cooled. The CO₂ reduction is also carried out with an IR cut-off filter (> 860 nm), whereas light intensity in the UV-visible range is kept nearly unchanged (Fig. 4(b)), so as to figure out the solar-heating effect on the catalytic reduction of CO₂. The catalytic performance becomes much lower compared to those under full-spectrum illumination, while the one without being cooled is still higher than that being cooled. That is to say, the Au/rutile catalyst exhibits enhanced activity for the reaction system without being cooled, no matter it is under UV-visible light or full-spectrum illumination. So such enhancement may not be specifically caused by the Au/rutile catalyst. Since the pressure is kept almost unchanged throughout the experiments, the temperature induced catalytic performance is further confirmed. It is noted that the oxidation product O₂ cannot be detected by the GC, possibly due to the low O₂ detection limit of the detector and column used in this work.

Fig. 4. Time vs catalytic production of CO and CH₄ over Au/rutile (a,b) and rutile (c,d) catalysts under illumination of full spectrum (a,c) and with IR cut-off filter (b,d). Blue curves mean that the reactor was cooled down by a circulating-water cooling system, and Red curves refer to that the reactor was not cooled.

Obviously, CO₂RR or OER cannot be initiated by IR-light irradiation over the Au/rutile catalyst, let alone the CO₂RR and OER be initiated simultaneously [11,34], as no light can be absorbed in this case. In other words, one cannot use the processes related to the classic photo-generated electron-hole pairs to explain the decrease in activity when the reaction system is cooled down [44]. Unlike some materials with up-conversion property [45], what is reported here is thus not a direct IR-induced STF process. It is noted that the final temperature of aqueous solution after illumination with full-spectrum light is the highest (~60 °C), followed by the one with IR cut-off filter (~30 °C), and the one being cooled is the lowest (~15 °C). Such an order is the same as that of the catalytic activity. Since the temperature increase caused by the solar heating is on a case by case basis, it is believed that the observed enhanced catalytic performance in this work are mainly temperature dependent.

To further confirm that the catalytic activity is temperature dependent, the catalytic performance was investigated using pure rutile catalyst under the same experimental conditions (Fig. 4(c) and (d)). As reported previously [26], pure rutile shows inferior r_{CO} and r_{CH_4} to Au/rutile due to the hot electron reduction, lower charge separation and/or less active sites. Albeit a higher temperature is observed for the Au/rutile system (~60 °C) than the rutile one (~55 °C) due to the relaxation of Au LSPR, the order of catalytic activity is still consistent with that of the temperature, i.e., full spectrum > IR filter (~25 °C) > being cooled (~15 °C). Since the CO₂ photoreduction can be realized over both rutile under UV-light illumination [46] and Au/rutile under either UV or visible light irradiation [47], it is believed that the CO₂ reduction can indeed be boosted by solar thermal effect.

In addition, considering the relative amount of Au NPs in the Au/rutile system is very low (0.2 mg of Au, 20 mg of rutile and 15 g of H₂O), the relative small increase amplitude in the temperature (~5 °C) due to the presence of Au NPs cannot be ignored, mainly because it can still influence the catalytic activity greatly. As indicated in Fig. 4, the Au/rutile system exhibits a much larger r_{CO} and r_{CH_4} than pure rutile in almost all the experiments carried out in this work, with the exception of r_{CO} using an IR cut-off filter, for which the Au/rutile shows a slightly larger r_{CO} than rutile. This means that the thermal effect induced by Au LSPR is considerably significant for the catalytic reduction of CO₂. As a matter of fact, a giant temperature increase (over 227 °C) on nanosized Au upon illumination has been reported both experimentally and theoretically [48].

Furthermore, an interesting phenomenon is observed when a specific temperature is acquired by an external heating source instead of the IR light. That is to say, the catalytic reduction of CO₂ in 4 h boosted by solar heating under full-spectrum irradiation without being cooled is compared to that by water-bath heating at the same temperature but with IR cut-off filter (Fig. 5). It is found that at the same temperature the catalytic activity using solar heating is much higher than that using water-bath heating for the CO production over both rutile and Au/rutile catalysts as well as for the CH₄ evolution over rutile; whereas the CH₄ evolution shows an opposite rule over

Fig. 5. Comparing the catalytic activity performance in 4 h boosted by solar heating to that by water-bath heating.

Au/rutile. This is ascribed to the photo-thermal synergy, as reported previously [49]. In addition, owing to the presence of Au NPs, the observed temperature may not be the ‘real’ one adjacent to the catalysts due to the local heating effect of plasmonic metal NPs [48]. Such a high local temperature cannot be totally mimicked by water-bath heating. These two factors may also lead to the aforementioned difference in the catalytic activity of CO₂ reduction.

3.3. Apparent activation energy and kinetic concern

Apparent activation energy (E_a) of CO and CH₄ formation reaction is determined using Arrhenius equation to study the related kinetics. Thus, the catalytic reduction of CO₂ over Au/rutile and rutile catalysts is done with IR cut-off filter at different temperatures so as to mimic the real catalytic conditions (Fig. 6). Clearly, both the r_{CO} and r_{CH_4} increase with elevating temperature. The E_a of CH₄ formation reaction ($E_{a(\text{CH}_4)}$) is about 17.3 kJ/mol using Au/rutile (Fig. S6), higher than 5.5 kJ/mol of $E_{a(\text{CO})}$ (Fig. S7). This explains well kinetically the inferior r_{CH_4} to r_{CO} , as reported in many CO₂ photoreduction systems [10,11], though the formation of CH₄ is more thermodynamically favorable than that of CO. Albeit the sluggish kinetics of CO₂RR is a common sense for a long time [7,10,11], only recently few work has related the reaction kinetics to the catalytic performance [50,51] and in most cases the thermodynamics (CB position or flat-band potential vs. standard redox potential) is still the major concern [52]. The difference between $E_{a(\text{CH}_4)}$ and $E_{a(\text{CO})}$ may be closely related to the multiple proton-coupled-electron-transfer (PCET) processes involved in the CO₂ reduction [53]. More electrons and protons are involved in the CH₄ formation than those for CO production. As predicted by the classic collision theory [54], such proton-involved process can be enhanced greatly with increasing temperature. Moreover, the kinetic resistance of multiple PCET process at room temperature has been reported [55].

Similarly, the $E_{a(\text{CH}_4)}$ and $E_{a(\text{CO})}$ using pure rutile catalyst are calculated to be 77.5 and 35.6 kJ/mol, respectively (Figs. S8 and S9). Like that using Au/rutile, the $E_{a(\text{CH}_4)}$ using the rutile is still higher than $E_{a(\text{CO})}$. Interestingly, both of them are much larger

Fig. 6. Time vs CO and CH₄ production yield at different temperatures for Au/rutile (a) and rutile (b).

than those using Au/rutile. Besides the commonly suggested mechanisms of visible-light harvesting, charge separation and/or hot-electron injection [56], this provides the kinetic explanation about the superior catalytic performance of Au/rutile to pure rutile. It is noted that direct experimental evidence that the co-catalyst can lower the activation energy of catalytic CO₂RR is rarely provided, although it is reported that the reaction pathways of electro-CO₂RR can be altered by a co-catalyst like Au [57]. Thus, besides the traditional thermodynamic based mechanism, herein we correlate the enhanced catalytic activity of CO₂ reduction for the first time to the kinetics based on the calculated E_a results when plasmonic Au NPs are introduced into the catalytic system. Furthermore, the apparent activation energy experiments also indicate considerable stability of both Au/rutile and rutile systems at a relatively high temperature (80 °C for Au/rutile and 75 °C for rutile), as in a 12-h experiment neither the catalytic performance loss is observed, nor the Arrhenius-type relationship between catalytic performance and increasing temperature is obtained.

To further verify the above conclusions that the PCET process in CO₂ reduction is kinetics related, the catalytic experiments are conducted by changing CO₂ partial pressure (P_{CO_2}). The catalytic activity over Au/rutile under full-spectrum illumination at ‘unit’ pressure of ~ 108 kPa is compared to that under half-‘unit’ pressure of ~ 54 kPa (balanced by Ar). Fig. 7 shows the 4-h catalytic yield of CO and CH₄. The r_{CO} over Au/rutile is slowed down greatly when reducing P_{CO_2} , while the r_{CH_4} is just slightly changed (Fig. 7(a)). This means that r_{CO} is more sensitive to P_{CO_2} than r_{CH_4} , possibly implying that the r_{CH_4}

is more restricted by the post-transfer steps like PCET, instead of by the reactants-involved steps like adsorption and/or photochemical transformation, and vice versa for CO. However, such sensitivity becomes less evident for the rutile catalyst (Fig. 7(b)). Moreover, the r_{CO} over rutile slightly increases when reducing P_{CO_2} . This may be because the whole reaction over rutile is limited by the OER, instead of CO₂RR-related steps, due to its poor photo water oxidation capability [31].

Therefore, it is suggested that the kinetics can play a crucial role in the activity and selectivity of CO₂ reduction. In all cases, the r_{CO} is higher than r_{CH_4} owing to its low E_a . Due to the same reason, as manifested in Fig. 4, the production yield of CO increases more greatly with elevating temperature than that of CH₄, no matter the catalyst is rutile or Au/rutile. In addition, a higher r_{CH_4} at elevated temperature is ascribed to the acceleration of post-transfer steps (i.e., PCET), like the classic temperature-dependent chemical reactions; while the enhanced r_{CO} is related to both the E_a and CO desorption. Although CO exhibits a strong binding energy to Au NPs [58], elevating the temperature can promote its desorption and, thereby, improving the catalytic activity.

It is known that the photocatalysis is commonly carried out at ambient temperature. The E_a is the core concept of reaction kinetics and catalysis, specifically in traditional thermal catalysis [49], which indicates the dependence of reaction rate on the temperature. However, in most cases the E_a and reaction kinetics are usually overlooked in photocatalysis, which may lead to incomplete, or even wrong, elucidation of the reaction mechanism. Only recently E_a is attracting concern to study the tem-

Fig. 7. P_{CO_2} related photocatalytic activity over Au/rutile and rutile catalysts after 4-h reaction with the reactor not being cooled (a) and being cooled (b).

perature-dependent reaction rate, especially in the SPR-based photocatalysis since the thermal effect induced by the SPR relaxation cannot be ignored [59,60]; while most of them are about the ‘down-hill’ reactions rather than the ‘up-hill’ ones. Like many other chemical reactions, the catalytic reduction of CO₂ also follows the classic Arrhenius temperature-dependent reaction rate. So a high collision frequency between the molecules and catalysts is expected [54]. With this regard, solar heating can be used to overcome the reaction activation energy, providing a simple approach compared to the others like prolonging the lifetime of key intermediates via surface-engineering [61]. Accordingly, there may be no need to cool down the reactor during photocatalytic reduction of CO₂, as demonstrated above. Meanwhile, the utilization of plasmonic metal NPs can lead to strong photo-thermal synergetic effect, which further improves the catalytic performance. It is also noted that the different E_a comes not only from CO₂RR on Au/rutile, but also from easier OER kinetics brought by the metal-oxide interface [31]. The sluggish kinetics can thus be speeded up, and the traditional trade-off in semiconductor-based photocatalytic reactions may be resolved [11]. Furthermore, full solar spectrum (UV, visible and IR light) can be simultaneously utilized in such a catalytic system. All these can be in favor of future real applications, not only for the cost concern, but also the STF efficiency.

4. Conclusions

In summary, we have demonstrated that Au NPs deposited rutile can realize catalytic reduction of CO₂ via utilizing full solar spectrum. The UV and visible light can initiate the reaction (i.e., thermodynamically), and the heat from IR light as well as photo-thermal effect from SPR can boost the reaction (i.e., kinetically). This is in favor of the full utilization of solar energy, especially the IR light with low photon energy. Moreover, the mechanism of enhanced production yield of CO and CH₄ over

Au/rutile catalyst has been investigated from the kinetic point of view based on the study of apparent activation energy experimentally, which plays a critical role in the STF process. So the plasmonic system can be a promising catalyst in practical artificial photosynthesis, specifically for full-solar spectrum utilization, in case SPR utilization efficiency is high enough in future.

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Graphical Abstract

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Solar-heating boosted catalytic reduction of CO₂ under full-solar spectrum

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Au deposited rutile exhibits high artificial photosynthesis performance via utilizing full-solar spectrum, for which UV and visible light are used to initiate reaction and IR light is used to boost reaction kinetically through solar heating.

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光致热效应促进的全光谱光催化CO₂还原

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摘要: 以半导体等为催化剂, 在太阳能作用下将CO₂和H₂O转化为可再生燃料与氧气的“人工光合作用”有望同时解决目前面临的严峻能源和环境问题, 因而备受关注。但半导体催化剂光谱响应范围较窄、表面反应动力学缓慢, 从而导致目前仍无法获得可观的太阳能-燃料转换效率。已有很多研究采用了晶面调控、元素掺杂和异质结构建等方法, 以提高半导体光催化剂的太阳能-燃料转换效率, 但效果仍不令人满意, 主要原因是半导体光催化剂很难在吸收带边-氧化还原能力和活性-稳定性这两种关系中取得较好的平衡。此外, 光催化反应中的动力学也是主要问题之一, 尤其在人工光合作用反应中, CO₂还

原半反应和 H_2O 氧化半反应的动力学均较困难,这已成为共识,而解决这个问题,将有助于我们从一新的角度理解光催化过程,从而提升光催化反应性能。

本文以Au NP/金红石为模型催化剂,纯金红石为参照,证明了存在太阳光中的红外光致热和可见光诱导的等离激元热效应等两类光致热效应,它们均可以促进人工光合作用反应。研究发现,人工光合作用反应与其他许多化学反应一样,表观活化能为正,从而表明动力学因素在该反应中起着重要作用。此外,根据不同反应温度下的结果,通过计算Au NP/金红石和纯金红石上生成CO和 CH_4 的表观活化能,发现在这二种样品上 CH_4 的表观活化能均高于CO,这就从动力学上解释了热力学上更容易得到的 CH_4 在绝大多光催化 CO_2 还原反应中的产率均低于CO。此外,无论是对于CO还是 CH_4 ,Au NP/金红石的催化表观活化能均低于纯金红石的。因此,本文从实验上提供了贵金属纳米粒子改善人工光合作用动力学的实验证据,并从动力学角度解释了人工光合作用反应中的活性和选择性。本研究证明了动力学因素在光催化反应,尤其是人工光合作用反应中的重要性,并提出了从动力学角度提升人工光合作用反应的新方法,即利用太阳光的光致热效应加速反应,这不仅有助于提升太阳能转化效率,也有望减少反应设备成本,从而促进其大规模应用。

关键词: CO_2 还原;表观反应活化能;反应动力学;光致热效应;光-热协同效应

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