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Article

Thermo-driven photocatalytic CO reduction and H₂ oxidation over ZnO *via* regulation of reactant gas adsorption electron transfer behavior

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ABSTRACT

Photothermal catalysis is a widely researched field in which the reaction mechanism is usually investigated based on the photochemical behavior of the catalytic material. Considering that the adsorption of reactants is essential for catalytic reactions to occur, in this study, the synergistic effect of photothermal catalysis is innovatively elucidated in terms of the electron transfer behavior of reactant adsorption. For the H₂ + O₂ or CO + H₂ reaction systems over a ZnO catalyst, UV irradiation at 25 °C or heat without UV irradiation did not cause H₂ oxidation or CO reduction; only photothermal conditions (100 or 150 °C + UV light) initiated the two reactions. This result is related to the electron transfer behavior associated with the adsorption of CO or H₂ on ZnO, in which H₂ or CO that lost an electron could be oxidized by O₂ or hydroxyls. However, the electron-accepting CO could be reduced by the electron-donating H₂ into CH₄ under photothermal conditions. Based on the *in-situ* characterization and theoretical calculation results, it was established that the synergistic effect of the photothermal conditions acted on the (002) crystal surface of ZnO to stimulate the growth of zinc vacancies, which resulted in the formation of defect energy levels, adsorption sites, and an adjusted Fermi level. As a result, the electron transfer behavior between adsorbed CO or H₂ and the crystal surface varied, which further affected the photocatalytic behavior. The results show that the effect of photothermal synergy may not only produce the expected kinetic energy, but more importantly, produce energy that can change the activation mode of the reactant gas. This study provides a new understanding of the CO catalytic oxidation and reduction processes over semiconductor materials.

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1. Introduction

In heterogeneous catalytic reactions, photocatalytic and

thermocatalytic conditions are usually regarded as two independent catalytic conditions, each with high expectations. However, over the past few decades, researchers have found

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that regardless of the type of catalytic system, there are technical shortcomings in the practical application of both systems [1–3]. Therefore, by combining thermocatalysis and photocatalysis, an effective and feasible new catalytic pathway, which maximizes the synergistic effects of both systems to overcome these limitations, has been designed. At present, this approach has been applied in several transformations, such as CO₂ reduction [4,5], methanation of CO₂ + H₂ [6,7], CO emission reduction [8], and VOC [9] degradation. With the development of photothermal catalysis, researchers have also considered the synergistic effects of photothermal catalysis. An *et al.* [10,11] suggested that photothermal catalytic synergism mainly stems from the photocatalytic acceleration of the Mars–van Krevelen redox cycle, enhanced light harvesting, improved charge separation, an increased capacity for reactive oxygen, or enhancement of the lattice oxygen activity of the material [12]. Furthermore, Yang *et al.* [13–15] showed that for the oxide-supported M-TiO₂ (M = Au/Ru/Pt) catalyst under photothermal conditions, photoinduced electrons are transferred to the M surface from TiO₂ to increase the surface electron density on the M sites. This enhanced the adsorption and activation of the CO/CO₂/NO molecules at the M sites, which promoted the reactivity of catalysts.

However, the above discussion regarding the synergistic photothermal effect is from the perspective of the material itself, considering the surface reaction, light absorption, or electron transfer behavior between the metal and support (i.e., the strong metal-support interaction effect [16]). As is well known, the surface reaction is only one of the steps in a heterogeneous photocatalytic reaction; the main reaction process of heterogeneous photocatalysis includes diffusion, adsorption, surface reaction, and desorption of the products [17,18]. Adsorption of the reactants is an essential part of heterogeneous photocatalysis because its changeable adsorption behavior plays an important role in the reaction. Photothermal synergism may regulate the selectivity and activity of the reaction by acting on the gas adsorption process; however, thus far, the underlying correlation between them is still not clear. As such, we believe that it is of great significance to investigate in-depth the synergistic effect associated with photothermal catalysis from the perspective of reactant gas adsorption behavior.

Recently, our group has attempted to study the relationship between reactant adsorption behavior and photocatalytic performance. We found that the gas adsorption behavior mainly includes the mode of adsorption, adsorption structure, and electron transfer behavior, which is associated with kinetic factors and are interrelated and unified and may ultimately affect the photocatalytic reaction process through the electron transfer behavior [19–22]. For instance, adsorbed CO (CO (ads)) can accept electrons from the catalyst, which is considered a pre-reduction process, which leads to a reduction reaction. In contrast, CO (ads) can donate electrons to the catalyst, which is considered a pre-oxidation process, leading to an oxidation reaction [23,24]. The electron transfer behavior of the reactant gas over the catalyst may be related to the Fermi level of the catalyst [19–22] and the gas adsorption mode [23]. Through in-depth analysis, the action of light and heat can be

determined so that the Fermi level of the catalyst can be regulated [19,25–27]. Some researchers have suggested that the electron transfer behavior of gas adsorption over metal oxide semiconductor materials is related to temperature, and that the electron transfer behavior may change with an increase in temperature [28,29]. As such, we believe that the photothermal synergistic effect may affect the selectivity of the reaction by regulating the electron transfer behavior of the gas adsorption kinetics.

The n-type zinc oxide semiconductor, with a bandgap of 3.4 eV [30], has attracted considerable attention [32–37] owing to its excellent optical and electrical properties [31]. As a research material, ZnO not only simplifies the research conditions and clarifies the analysis mechanism, but provides the possibility of investigating the mechanism of action caused by changes in the photothermal conditions. Specifically, the vacancy formation energy of ZnO is much lower than other metal oxides [37,38], which allows for the efficient formation of oxygen vacancy (V_{Os}) and zinc vacancy (V_{ZnS}) defects in ZnO. In previous experiments, it was established that the different vacancies on the surface of ZnO may act as different adsorption sites for H₂ in CO catalytic oxidation or reduction reactions and show different electron transfer behaviors [25]. CO catalytic oxidation or reduction, as an important base reaction in C1 chemistry [40–42], is applied in the deep purification of H₂ feed in proton exchange membrane fuel cells (PEMFCs) [43,44]. Investigations into control over CO oxidation or reduction behavior requires further attention.

Therefore, in this study, a photothermal catalytic system for CO oxidation and reduction (methanation) over ZnO was investigated to study the correlation between reactant gas behavior and reaction performance. Based on the photocatalytic reaction, it is expected that the thermo-driven effect could affect the electron transfer behavior of H₂/CO adsorption, and thus change the CO reaction performance. The hydrothermal synthesis of the ZnO sample with V_{Os} on the (100) crystal surface and the effects of the different photothermal conditions on the adsorption behavior of H₂/CO were investigated *via* various *in-situ* characterization methods. Moreover, the CO oxidation or reduction performance was also determined under the corresponding conditions. The thermo-driven effect could change the CO reaction behavior (from oxidation to reduction). After characterizing the ZnO sample through a variety of techniques, the adsorption kinetics of the CO oxidation or reduction reaction was proposed.

2. Materials and methods

2.1. Preparation of ZnO samples and sensors

The ZnO catalyst was prepared *via* a reported hydrothermal method [25]. Appropriate proportions and arrangements of Zn(CH₃COO)₂ and CH₃COONa were dissolved in deionized water under continuous stirring to obtain a homogeneous solution, and (NH₄)₂CO₃ (0.02 M) was added to the solution. Then, the reaction solution was heated at 180 °C for 16 h in a sealed Teflon-lined stainless-steel autoclave. Subsequently, the sample

was carefully washed with absolute ethanol and deionized water. The as-synthesized catalyst was dried in an oven at 80 °C for 6 h and calcinated at 550 °C for 3.5 h under air atmosphere to obtain the ZnO powder samples. The sensors were prepared using a drop-coating method and calcinated at 550 °C for 3.5 h under air atmosphere to obtain the ZnO sensors.

2.2. *In-situ* characterization

X-ray diffraction (XRD, Bruker, Germany) patterns were obtained using a D8 advanced X-ray diffractometer with Cu K_{α} radiation and a scattering range of 10° to 80° at a scan rate of 0.02°·s⁻¹. The accelerating voltage used was 40 kV and the current 40 mA. *In-situ* XRD was performed at different temperatures using a heating reactor chamber configured on the diffractometer, and N₂ was introduced as the background gas. The samples were purged with N₂ for 30 min at 25 °C, heated to 150 °C, and the spectrum recorded at four temperature points (25, 50, 100, and 150 °C) after holding at the selected temperature for 10 min.

In-situ UV-vis diffuse reflectance spectra (*in-situ* DRS) of the ZnO sample were recorded on a Varian Cary 500 UV-Vis-NIR spectrophotometer. An *in-situ* reactor cell (the same as the *in-situ* reactor cell used for *in-situ* DRIFTS, the main structure of which is shown in Fig. S1(A) equipped with two CaF₂ windows (200 nm–8 μm, Fig. S2(A)) was constructed on the DRS spectrometer. N₂ was introduced as the background circulating gas, and the temperature of the reactor was controlled by flowing water at 25 °C. The samples were purged with N₂ for 30 min at 25 °C, heated to 150 °C, and the spectrum collected at four temperature points (25, 50, 100, and 150 °C) after holding the sample at the selected temperature for 10 min. The experiments were conducted in parallel in two sets, under light and dark conditions. Four UV lamps (4 W, Philips TL/05) were used as the UV light source (Fig. S3).

The *in-situ* electron paramagnetic resonance (EPR) spectra were recorded on a Bruker A300 spectrometer operating at the X-band microwave frequency (9.84 GHz). The catalyst was added to an *in-situ* EPR reaction tube (its main structure is described in Fig. S1(B)) and the samples were pretreated at 25 °C for 20 min under vacuum (10⁻¹ Pa). The EPR spectra were recorded at 25 °C after UV irradiation for 1 h. The reaction tube was then heated to 50, 100, and 150 °C in an oil bath under UV irradiation and vacuum. The spectrum was recorded after holding at 50, 100, and 150 °C for 1 h.

In-situ DRIFTS was performed on a vacuum-holding Bruker vextor 80v FTIR spectrometer equipped with an MCT detector (cooled by liquid N₂ at 77 K) using a specially designed *in-situ* DRIFTS reactor cell (Fig. S1(A)). The spectra were recorded from 4000 to 800 cm⁻¹ at a spectral resolution of 4 cm⁻¹ (64 scans). Prior to each experiment, the samples were pretreated in a N₂ stream (80 mL · min⁻¹) at 200 °C for 1 h to eliminate any other impurities. After cooling to 25, 50, 100, and 150 °C, the real-time IR spectra were collected as background. Then, the samples were exposed to a controlled stream of 3% H₂ or 10% CO (80 mL · min⁻¹) in N₂ to explore the reaction process. For comparison, UV light irradiated the samples under identical

conditions through a ZnSe window (600 nm–15 μm, Fig. S2(B)) located on the dome of the DRIFTS cell.

In-situ ultraviolet photoelectron spectroscopy (UPS) was collected on a Thermo ESCALAB 250 electron spectrometer. The UPS measurements were conducted using the He I photon line of a He discharge lamp from a VSW dosed with 10⁻⁷ mbar of He. For the *in-situ* UPS tests conducted at different temperatures, a heating reactor chamber was configured on the spectrometer and the spectra recorded at 25–200 °C. Regrettably, the UPS profiles could not be studied under UV irradiation due to experimental conditions. The work functions (Φ) and Fermi level (E_{vm}) were calculated using the following equations [45,46]:

$$\Phi = h\nu - (E_{\text{cutoff}} - E_{\text{Fermi}}) \quad (1)$$

$$\Phi = E_{\text{vm}} - E_{\text{fm}} \quad (2)$$

where Φ , E_{fm} , E_{vm} , $h\nu$, E_{cutoff} , and E_{Fermi} are the work functions, Fermi level, vacuum level, excitation energy (21.22 eV), cutoff, and Fermi level edge, respectively.

2.3. Theoretical calculations

The adsorption model and crystal structure were constructed using density functional theory (DFT), as implemented in the Vienna Ab-initio Simulation Package (VASP) [47–50]. To model the ZnO (100) and ZnO (002) surfaces, a 4 × 4 supercell slab with three layers was employed. Oxygen vacancies (at 25 °C under UV irradiation) and zinc vacancies (at 150 °C under UV irradiation) exist on the ZnO (100) and ZnO (002) surfaces, respectively. The adsorption energy, E_{ads} , was defined as $E_{\text{ads}} = E_{\text{adsorbate/slab}} - E_{\text{adsorbate}} - E_{\text{slab}}$, where $E_{\text{adsorbate/slab}}$, $E_{\text{adsorbate}}$, and E_{slab} represent the total energies of the adsorbed system, adsorbate molecule in the gas phase, and the slab surface, respectively.

2.4. Electron transfer behavior of reactant adsorption

The electron transfer behavior of reactant adsorption was characterized using a gas sensing system (JF02F, GuiYanJin-Feng Tech. Corp. Ltd, Kunming, China, its main components are shown in Fig. 2(e)) that can register the impedance of ZnO sensors, by applying a fixed voltage of 5 V. The ZnO sensor tests were conducted in a stainless-steel climatic chamber (100 mL) with a quartz window, by maintaining the temperature constant at 25, 50, 100, 150, and 200 °C. During the tests, high-purity N₂ was introduced into the chamber as the background stream (the total flow rate was maintained at 250 mL·min⁻¹), and 3% H₂ (N₂) or 10% CO (N₂) as the probe gas. Prior to each experiment, the samples were pretreated in a N₂ stream at 200 °C for 1 h to eliminate any other impurities.

2.5. Photocatalytic performances

The photocatalytic activities for CO reduction and H₂ oxidation over the prepared samples were evaluated in a quartz reaction tube (30 mL). The samples (0.1 g) were spread over the reaction tube, and high-purity H₂ (5 mL) and O₂ (15 mL) (H₂ + O₂ system), or CO (5 mL) and H₂ (20 mL) (CO + H₂ sys-

tem) were added to the reaction tube. The gas was injected intermittently in an Agilent 7890A gas chromatograph (GC) equipped with TDX-01 packed and DB-Wax capillary columns, and two detectors (TCD and FID). The reaction activities under different experimental conditions were compared with the conversion of H_2 and the production of CH_4 .

3. Results and discussion

3.1. Photothermal catalytic activities of the ZnO samples

In order to study the essence of the photothermal synergistic effects, the H_2 oxidation and CO reduction activity under different photothermal conditions were tested. For the $H_2 + O_2$ reaction system, shown in Fig. 1, the conversion of H_2 at 25 °C (or 50 °C) under UV irradiation and dark conditions does not indicate a reaction (Fig. 1(a)) as the concentration of H_2 does not decrease but increases with an increase in the temperature or with the introduction of UV light (Fig. S4). H_2 (ads) may be desorbed because of an increase in the sample surface temperature induced by UV irradiation, suggesting physical adsorption [24,51]. As the reaction temperature increases to 100 °C, the conversion of H_2 significantly reduces under dark conditions; this may be due to the weakening of physical adsorption with an increase in temperature [51,52]. Upon further irradiation with UV light at 100 °C, the conversion of H_2 increases significantly. The conversion of H_2 is much higher than the concentration of physically adsorbed H_2 at 25 °C, indicating that the photocatalytic oxidation of H_2 with O_2 to produce H_2O occurred, and the H_2 (ads) is activated above 100 °C. Similarly, for the $CO + H_2$ reaction system (Fig. 1(b)), CO is effectively activated above 150 °C and methanation occurs. Thus, the direction of the photocatalytic reaction is regulated *via* photothermal synergy; H_2 can be oxidized from not oxidized, and CO can be reduced from not reduced. Subsequently, the electron transfer behavior of H_2/CO adsorption under different photothermal conditions was analyzed *via* a gas sensing system, and it was observed if the photothermal synergistic effects regulate the electron transfer behavior of gas adsorption.

3.2. Adsorption behavior of H_2/CO over ZnO under different

photothermal conditions

The gas sensing responses of H_2/CO on the surface of the ZnO samples under different photothermal conditions (from 25 to 200 °C) in N_2 atmosphere were studied. Regular variations in the electron transfer behavior of H_2/CO adsorption with increasing temperature were observed. Clearly, the temperature boundary is 50 °C, as below 50 °C under UV irradiation, the impedance of the ZnO sensors increases rapidly (Fig. 2(a)(1)) with the introduction of H_2 . This indicates that the electron density on the surface of the sample decreases and the H_2 (ads) accepts electrons from the ZnO sample during the adsorption process. Above 50 °C under UV irradiation, the impedance of the ZnO sensors decreases rapidly (Fig. 2(a)(3–5)), indicating that electrons are transferred from the H_2 (ads) (donator) to the ZnO sample. Simultaneously, similar experimental results are observed for the CO adsorption behavior. The temperature boundary is 100 °C, as below 100 °C under UV irradiation, the impedance of the ZnO sensors decreases rapidly (Fig. 2(b)(1,2)) with the introduction of CO, indicating that CO (ads) donates electrons to the ZnO sample. Similarly, above 100 °C under UV irradiation, the impedance of the ZnO sensors increases rapidly (Fig. 2(b)(4,5)), indicating that CO will accept electrons from the ZnO sample. The electron transfer behavior of H_2/CO adsorption at 150 °C under dark conditions is shown in Fig. 2(c) and 2(d). Compared with the results at 25 °C, the electron transfer behavior of reactant gas adsorption did not change, and the photocatalytic activity for the two reactions is poor. This suggests that the reactant gas is not activated under purely thermal conditions. As expected, the photothermal synergism changes the direction of electron transfer during H_2/CO adsorption. Combined with the reaction activity of the $H_2 + O_2$ and $CO + H_2$ systems under different photothermal conditions, it was considered that the photothermal synergism affects the entire heterogeneous photocatalytic reaction chain by regulating the electron transfer behavior of CO/H_2 adsorption over the sample. This further controls the direction and selectivity of the reaction, which is the nature of the photothermal synergistic effect.

Thus, the mechanism of the electron transfer behavior of CO/H_2 adsorption caused by photothermal synergism was fur-

Fig. 1. H_2 conversions in the photothermal catalytic H_2 oxidation reaction (a) and CH_4 yields in the CO reduction reaction (b) over the ZnO catalyst under different photothermal conditions.

Fig. 2. Gas sensitivity response of H₂ (a,c) and CO (b,d) adsorption on the surface of ZnO in N₂ atmosphere. (a) and (b) were measured at different temperatures under UV irradiation: (1) 25 °C, (2) 50 °C, (3) 100 °C, (4) 150 °C, and (5) 200 °C. (c) and (d) were measured under dark conditions at 150 °C. (e) Schematic diagram of the gas sensing test system.

ther studied from the perspective of the material structure and gas adsorption under photothermal conditions.

3.3. Changes in the material structure under different treatment conditions

3.3.1. Change in the crystal structure at different temperatures characterized via *in-situ* XRD

We previously [25] showed that the ZnO sample exhibits a pure wurtzite crystalline phase. The V₀s and V_{Zn}s formed on the (100) and (002) surfaces of the ZnO sample, respectively (the main data and analysis process is shown in Figs. S5–S13 and Table S1–S2), and we believe that the gas was mainly adsorbed on the (100) and (002) surfaces. Therefore, the changes in the characteristic diffraction peaks of the (100) and (002) surfaces at different temperatures were mainly investigated via *in-situ*

Fig. 3. *In-situ* XRD spectra of the ZnO samples at different temperatures. (1) at 25 °C; (2) 50 °C; (3) 100 °C; (4) 150 °C.

XRD analysis, as shown in Fig. 3. With an increase in temperature, the position of the (002) peak gradually shifts towards a lower 2θ value, which may be due to the lattice mismatch of the (002) surface or the *in-situ* growth of some defects [53]. In contrast, the (100) peak does not change, indicating that the increase in temperature has no effect on the (100) surface. Therefore, it is possible that the photothermal synergistic effect mainly occurs on the (002) surface.

3.3.2. Energy level structure and light absorption properties under different photothermal conditions analyzed via *in-situ* DRS

Both UV irradiation and thermal conditions may affect the energy level structure of the semiconductor during the experiments; therefore, *in-situ* DRS spectra were collected under different photothermal conditions, as shown in Fig. 4. With longer UV irradiation times at 25 °C (Fig. 4(a)), the absorption spectrum of the sample is clearly blue-shifted. According to the formula for bandgap width and band edge wavelength ($E_g = 1240/\lambda$), the bandgap width is widened, which may be related to ZnO photocorrosion (the semiconductor structure was destroyed) [54]. On the contrary, with an increase in temperature under dark conditions (Fig. 4(b)), the DRS spectrum of the

sample is shifted to a longer wavelength (red shift) with approximately 10 nm when increasing the temperature from 25 to 150 °C; the band width (E_g) of the ZnO sample gradually narrows from 3.15 to 3.07 eV. Similarly, with an increase in temperature under UV irradiation (Fig. 4(b)), the absorption spectrum of the sample is also clearly red-shifted, and the degree of band gap narrowing is similar to that of the dark condition. Considering that the band gap of the sample will be narrowed *via* the introduction of an impurity defect level [55], this may be related to the formation of surface defects [56], which is in agreement with the *in-situ* XRD experimental data (Fig. 3). As such, *in-situ* EPR spectroscopy was further applied to investigate the surface vacancy defects of the sample under different photothermal conditions.

3.3.3. Surface defects under different photothermal conditions characterized via *in-situ* EPR

As illustrated in Fig. 5, there was no change in the surface defects of the ZnO sample under UV (Fig. 5(1)) and thermal (Fig. 5(2)) conditions; only V_{OS} exist on the surface (corresponding to $g = 1.960$) [57,58]. As expected, the signal at $g = 2.002$ can be attributed to V_{ZnS} [59–61] appearing on the surface of the sample with an increase in temperature to 100 °C (and 150 °C) under UV irradiation (Figs. 5(3) and (4)), clearly confirming that V_{ZnS} is formed *in-situ* under the synergistic action of the photothermal conditions. This result corresponds with the conclusions drawn from the DRS and XRD analyses. It can thus be concluded that the generated V_{ZnS} grows on the (002) crystal surface, which is consistent with that reported in literature [25]. Notably, new defect vacancies (V_{ZnS}) should be formed by enhancing the lattice vibration and providing the defect formation energy [62,63] under the synergistic effects of the photothermal conditions. Combined with the results of previous studies [24], we established that the photoinduced holes were enriched around V_{ZnS} under UV irradiation and H_2 adsorption formed Type II adsorption at the V_{ZnS} sites; thus, electrons would transfer from the adsorbed H_2 to ZnO. This corresponds to the adsorption behavior of H_2 (Fig. 2(a)); i.e., the photothermal synergistic effects (above 50 °C) may act on the (002) crystal surface to generate V_{ZnS} *in-situ*, providing a Type II adsorption site for H_2 , which causes the H_2 (ads) to donate electrons to the ZnO sample, thereby regulating the selec-

Fig. 4. *In-situ* DRS spectra of the ZnO sample under different photothermal conditions. (a) at 25 °C as a function of UV irradiation time. (1) dark conditions; (2) UV irradiation for 20 min; (3) UV irradiation for 40 min, and (4) UV irradiation for 60 min. (b) Under dark and (c) UV irradiation conditions as a function of temperature. (1) 25 °C; (2) 50 °C; (3) 100 °C; (4) 150 °C.

Fig. 5. *In-situ* EPR spectrum of the ZnO sample under UV irradiation at 25 °C (1), 50 °C (2), 100 °C (3), and 150 °C (4). The V_{Zn}^S were formed *in-situ* under the synergistic action of photothermal conditions.

tivity of the reaction.

In addition, the electron transfer behavior of the CO adsorption was not related to the surface defects. As shown in Fig. S14, the adsorption behavior of CO over the ZnO samples containing different vacancy defects was similar. Therefore, according to the boundary adsorption theory [64], for CO adsorption, the change in electron transfer behavior may be determined by its Fermi level.

3.3.4. Fermi level of ZnO at different temperatures determined by *in-situ* UPS

Considering the influence of the reaction temperature on the band structure and Fermi level of materials [65,66], *in-situ* UPS was applied to specifically analyze the work function (Φ) changes at different temperatures, according to Eqs. (1) and (2); the Fermi level with respect to the vacuum level was obtained [67–71]. As shown in Fig. 6, the Fermi edge of the UPS profile of the ZnO sample is calibrated to zero. The cut-off edges of the ZnO sample are from 13.96 to 17.60 eV with an increase in the reaction temperature (curve 1 to 4 in Fig. 6). This implies

Fig. 7. Diagram indicating the changes in the Fermi level at different temperatures under UV irradiation. The Fermi level change assumes an “S-shaped curve” trend.

that the work function gradually downshifts (from 7.26 to 3.62 eV) with an increase in temperature; a downshift in the work function causes an upshift in the Fermi level. A comparison between the spectra indicates that the Fermi level of the sample was upshifted with an increase in temperature within a certain range of values. However, the Fermi level downshifts slightly as the temperature increases above 200 °C. Overall, the Fermi level change assumed an “S-shaped curve” trend, as shown in Fig. 7. Additionally, UV irradiation could also cause the Fermi level to upshift [25]; therefore, the “S-shaped curve” trend is the comprehensive outcome of the UV and thermal conditions. According to the boundary adsorption theory, an increase in the Fermi level may provide a suitable energy level structure condition for the change in the electron transfer behavior of CO adsorption [23,24]. As expected, the CO adsorption electron transfer behavior was transitional at 100 °C under UV irradiation. At a temperature below 100 °C, the Fermi level is lower than that of the CO adsorption energy level, and ZnO accepts electrons from the adsorbed CO. At a temperature above 100 °C, the Fermi level is higher than that of the CO adsorption energy level, and the CO (ads) accepts electrons from ZnO. This corresponds with the adsorption behavior of CO (Fig. 2(b)); i.e., the photothermal synergistic effect on CO adsorption

Fig. 6. *In-situ* UPS profiles of the ZnO sample at 25 °C (1), 50 °C (2), 100 °C (3), 150 °C (4), and 200 °C (5). (b) An enlarged view of the cutoff edge region in (a).

can be attributed to the regulation of the Fermi level.

It is remarkable that there are two possible reasons for the temperature dependence of the Fermi level: (1) with an increase in the temperature, the carrier (electron) concentration and the electron energy increase, which leads to thermal excitation [27,28,72]; (2) the impurity concentration decreases, which leads to a more complete crystal form [19,25].

3.4. Gas adsorption behavior under different photothermal conditions

3.4.1. Adsorption behavior of H_2 studied via *in-situ* DRIFTS

In-situ DRIFTS was performed to gain insight into the adsorption behavior of H_2 on the ZnO surface and to determine whether H_2 dissociation adsorption occurs. However, dissociated hydrogen is unstable in an oxygen atmosphere; therefore, the *in-situ* DRIFTS was performed on H_2 adsorbed in an N_2 atmosphere under different photothermal conditions. The peaks at 1600 cm^{-1} can be ascribed to surface-adsorbed water (OH groups) [73] formed after the adsorption of H_2 (Fig. 8(a)(2)). With an increase in temperature (Fig. 8(a)(3–5)), more surface-adsorbed water was generated after H_2 adsorption than at 25°C , and the peak was clearly blue-shifted (1620 cm^{-1}). This suggests that the adsorbed water binds more strongly to the surface of the sample at higher temperatures than at 25°C , which may be caused by the H_2 (ads) on the V_{ZnS} sites.

In addition, there is a sharp infrared peak at 870 cm^{-1} in the spectrum collected at 150°C (Fig. 8(a)(5)), which increases in intensity with an increased H_2 adsorption time (Fig. 8(b)). This peak corresponds to the O_{lat} -H species produced from H_2 dissociation from the ZnO surface [74,75]. Interestingly, Zn-H species are not observed, which could be owing to the dissociation of H_2 from the V_{ZnS} sites (H_2 (ads) + O - V_{Zn} - O -Zn $\rightarrow$ O - V_{Zn} (H_2)- O -Zn). This conjecture is consistent with the formation of V_{ZnS} under photothermal conditions (at 150°C) (Fig. 5(4)); molecular H_2 dissociates from the V_{ZnS} site where the produced H atoms spill over onto the lattice oxygen of ZnO (O - V_{Zn} (H_2)- O -Zn $\rightarrow$ H - O - V_{Zn} - O (H)-Zn). Based on the above results, it was established that under photothermal conditions the elec-

tron transfer behavior changes from accepting electrons (from ZnO) to H_2 (ads) donating electrons (to sample). As a result, the H_2 molecules were dissociated, and H_2 (ads) could be oxidized by O_2 .

3.4.2. H_2 adsorption model constructed via DFT calculations

The analysis results of various characterization methods suggested that the photothermal synergistic effects acted on the (002) crystal surface to form the V_{ZnS} , which acted as H_2 adsorption sites and induced H_2 dissociation. Subsequently, the structure information of the (100) and (002) crystal surfaces with V_{OS} and V_{ZnS} , respectively, were established and the H_2 dissociation and non-dissociation adsorption models were investigated via DFT, as shown in Fig. 9. Based on the DFT calculations, the adsorption energy of the H_2 non-dissociative adsorption (E_{ad}) at the lattice oxygen (O_{lat}), lattice zinc (Zn_{lat}), and V_{OS} sites of the (100) surface were compared. The calculated E_{ad} of H_2 at the O_{lat} and Zn_{lat} sites is -0.09 and -0.143 eV , respectively, which is notably lower than that at the V_{OS} site (-0.145 eV , Fig. 9(a)(1–3)). This indicates that the H_2 (ads) at the V_{OS} sites are more stable than at the O_{lat} and Zn_{lat} sites; i.e., the H_2 molecules are preferentially adsorbed at the V_{OS} sites. Similarly, for the (002) surface, the V_{ZnS} were formed *in-situ* under the photothermal conditions; therefore, O_{lat} , Zn_{lat} , and V_{ZnS} sites exist on the crystal surface. The E_{ad} of H_2 (ads) are -0.084 , -0.094 , and -0.153 eV , respectively (Fig. 9(b)(1–3)), indicating that the H_2 molecules are stable and preferentially adsorbed at the V_{ZnS} sites. In contrast, the dissociation energies of the H_2 dissociative adsorption (E_{dis}) at the V_{OS} sites on the (100) surface and V_{ZnS} sites on the (002) surface are also compared (Fig. 9(a)(4) and Fig. 9(b)(4)). The E_{dis} of H_2 (ads) are -0.140 eV and -2.60 eV for the V_{OS} and V_{ZnS} sites, respectively, indicating that the H_2 molecules can dissociate and form two O-H species at the V_{ZnS} site on the (002) surface. This is consistent with the *in-situ* DRIFTS results.

Furthermore, the adsorption of H_2 on the two surfaces were compared. It was established that under purely UV and thermal conditions, i.e., when the (002) surface was complete and the (100) surface contained V_{OS} , H_2 (ads) would preferentially

Fig. 8. *In-situ* DRIFT spectra of the ZnO sample after H_2 adsorption for 20 min under different conditions. (a): (1) fresh catalyst; (2) at 25°C under UV irradiation; (3) at 50°C under UV irradiation; (4) at 100°C under UV irradiation; (5) at 150°C under UV irradiation. (b) *In-situ* DRIFT spectra of the ZnO sample at 150°C under UV irradiation as a function of H_2 adsorption time. (1) for 5 min, (2) for 10 min, (3) for 15 min, and (4) for 20 min.

Fig. 9. H₂ chemisorption on the ZnO (100) (a) and (002) (b) surfaces at the different sites: (1) the H₂ non-dissociative adsorption at the O site; (2) the H₂ non-dissociative adsorption at the Zn site; (3) the H₂ non-dissociative adsorption at the V_Os or V_{Zn}s sites; (4) the H₂ dissociative adsorption at the V_Os or V_{Zn}s sites. Among them, the surface energies (E_{sur}) of the (100) and (002) surfaces are 0.86 and 3.13 J·m⁻², respectively.

adsorb at the V_Os sites on the (100) surface; this result confirmed the findings of our previous study [25]. In contrast, H₂ (ads) selectively adsorbed at the V_{Zn}s sites on the (002) surface under photothermal conditions, and adsorption transfer between the crystal surfaces (from (100) to (002) surface) was realized. In addition, the H₂ molecules dissociated to form dissociated hydrogen (O_{lat}-H). The correlation between the adsorption mode and electron transfer behavior can be obtained based on the electron transfer behavior of the H₂ adsorption: H₂ (ads) accepts electrons from ZnO in the non-dissociative mode and cannot undergo an oxidation reaction, while H₂ (ads) donates electrons to the sample in the dissociative mode and is oxidized by O₂.

Furthermore, the surface energies of the (100) and (002) surfaces are 0.86 and 3.13 J·m⁻², respectively, as shown in Fig. 9, indicating that the (002) surface is more unstable [76] and likely to adsorb the H₂/CO molecules [77,78]. This provides favorable conditions for the formation of V_{Zn}s and the adsorption of H₂/CO molecules on the (002) surface.

3.4.3. Adsorption behavior of CO and CO + H₂ analyzed via

in-situ DRIFTS

Similarly, *in-situ* DRIFTS was applied to understand the adsorption behavior of CO on the ZnO samples under different photothermal conditions. The adsorption behavior of pure CO on the sample surface under UV irradiation at 25, 50, 100, and 150 °C was compared and is displayed in Fig. 10. As shown in Fig. 10(a), upon the introduction of CO into the system, the adsorption peaks of gaseous CO appear at 2173 and 2116 cm⁻¹ [79] (physisorbed CO), and then two gaseous CO₂ peaks are formed at 2362 and 2332 cm⁻¹ [80]. This indicates that the CO (ads) will further react with surface active species (the surface adsorbed H₂O or hydroxyl groups) and be converted to CO₂.

Significantly, the CO adsorption mode does not change, and the chemisorbed CO does not appear [81] with an increase in the temperature (Fig. 10(b)). This suggests that the adsorption sites and modes of CO are not regulated by the photothermal synergistic effect, and the change in electron transfer behavior may be affected by the Fermi level of the ZnO sample itself. Moreover, multiple intermediates formed during CO adsorption (Fig. 10(c)); the infrared peaks corresponding to these species are listed in Table 1 [82–88]. The results clearly show that

Fig. 10. *In-situ* DRIFT spectra of the ZnO sample under different conditions (a–c). (1) ZnO prior to CO adsorption at 25 °C under UV irradiation; (2) CO adsorption for 20 min at 25 °C under UV irradiation; (3) CO adsorption for 20 min at 50 °C under UV irradiation; (4) CO adsorption for 20 min at 100 °C under UV irradiation; (5) CO adsorption for 20 min at 150 °C under UV irradiation.

Table 1

Assignment of the infrared peaks observed after adsorption of pure CO and CO + H₂ on the ZnO surface.

Species	Pure CO (cm ⁻¹)	CO + H ₂ (cm ⁻¹)
$\nu(\text{CO}_3^{2-})$	1662, 1510, 1374, 1310	1376
$\nu_{\text{as}}(\text{COO})$	1606	1597
$\nu_{\text{s}}(\text{COO})$	1547	1339
$\delta(\text{CH}_3, \text{CH}_2)$	1427, 1458	1475
$\nu_{\text{as}}(\text{CH}_3, \text{CH}_2)$	3000, 2946	2970
$\nu_{\text{s}}(\text{CH}_3, \text{CH}_2)$	2904	2900
$\nu(\text{HCO}_3^-)$	—	1249
$\nu(\text{C-O})-\text{CH}_3\text{O}-$	1076, 1012	1058

Note: ν , ν_{s} , ν_{as} , and δ represent the stretching, symmetric stretching, asymmetric stretching, and bending vibrations, respectively.

with an increase in temperature, the surface intermediates gradually change from carbonate (CO_3^{2-}) species (corresponding to the peaks at 1662, 1510, 1374, and 1314 cm⁻¹) to COO (1606 and 1547 cm⁻¹), $\text{CH}_3\text{O}-$ (1076 and 1012 cm⁻¹), and CH_2 species (1458 and 1427 cm⁻¹). Furthermore, the negative peaks at 3000–2900 cm⁻¹ can be ascribed to the consumption of the CH species, which remained on the sample surface after the preparation process.

In addition, the *in-situ* DRIFTS of the ZnO sample was performed at different temperatures in N₂ atmosphere. As expected, the hydroxyl groups (1633 cm⁻¹) on the surface decreased gradually with increasing temperature (Fig. 11); i.e., some impurity defects related to the hydroxyl groups (such as Zn–OH in the shallow trapped level [20]) also decreased, which improved the surface structure and shifted the Fermi level upwards. This is consistent with the *in-situ* UPS profile results of ZnO at different temperatures, as shown in Fig. 6.

Subsequently, *in-situ* DRIFTS of the CO + H₂ reaction gas adsorption was performed at 150 °C under dark and UV irradiation conditions, as shown in Fig. 12. As in the case of pure CO adsorption, some of the CO (ads) can also be converted into CO₂ by the surface-active species through an oxidation reaction, and

Fig. 11. *In-situ* DRIFT spectra of the ZnO sample in N₂ atmosphere at 25 °C (1), 50 °C (2), 100 °C (3), and 150 °C (4). The surface hydroxyl groups decreased gradually with an increase in the temperature.

the CO (ads) is only adsorbed in the gas phase without chemical adsorption. The difference is that the infrared peaks of the CH_2 (CH_3) species at 2970 and 2900 cm⁻¹ are positive peaks under UV irradiation, and their intensity increases with longer UV irradiation times. This indicates that the CO (ads) could be converted into CH_4 via a reduction reaction with H₂. Similarly, it was also found that the amount of CH_4 (2970 and 2900 cm⁻¹) increases with an increase in the amount of COO (1597 and 1339 cm⁻¹), CH_2 (1475 cm⁻¹), and $\text{CH}_3\text{O}-$ (1058 cm⁻¹) species. In addition, a $\text{HCOO}-$ stretching vibration peak appears at 1249 cm⁻¹, which may be owing to the hydrogenation of the COO species. These species were identified as methanation reaction intermediates. Simultaneously, some of the CO (ads) also undergoes an oxidation reaction, and a small amount of CO_3^{2-} (1376 cm⁻¹) species are formed on the surface; that is, the intermediates of the oxidation reaction. However, the above intermediates and methane are not formed under dark conditions, indicating that the CO reduction reaction does not occur, which is consistent with the activity test results (Fig. 1). Combined with the electron transfer behavior of CO adsorption, the preliminary results show that the CO (ads) donates electrons to the ZnO sample, mainly forming CO_3^{2-} intermediates, which tend to produce CO₂ by oxidation. The CO (ads) accepts the electrons from ZnO, mainly forming COO, HCO_3 , and CH_3O intermediates [89–91], which tend to produce CH_4 via a reduction reaction.

The infrared background absorption spectrum can reflect the concentration of the conduction band electrons [92,93], as shown in Fig. 12(a). There was no artificial translation of the curve in this figure. The electron transition from the valence band (VB) to the conduction band (CB) under UV irradiation increases the electron density in the CB and then causes the background absorption spectrum to be raised (curves (2) to (3) in Fig. 12(a)). Similarly, two opposite changes in the background spectra are observed in the presence and absence of UV irradiation after CO + H₂ adsorption (Fig. 12). The background spectra of the ZnO sample were raised after CO + H₂ adsorption in the dark (curves (1) to (2) in Fig. 12(a)), indicating that electrons accumulated in the CB [20], while the background spectrum decreased gradually after CO + H₂ adsorption under UV irradiation (curves (3) to (5) in Fig. 12(a)). This indicates that the electrons (CB) would be transferred during CO + H₂ adsorption, which is in accordance with the adsorption behavior of CO (Fig. 2(b)).

3.5. Nature of the photothermal synergistic effect: regulation of the electron transfer behavior of H₂/CO adsorption

The photothermal synergistic effect is different for H₂ and CO adsorption. Thus, we compared the clear changes in adsorption behavior and catalytic performances at 25 and 150 °C. First, the mechanism by which the H₂ adsorption behavior is regulated was analyzed (Fig. 13). On the one hand, the photothermal conditions (at 150 °C under UV irradiation) provide more energy than pure light and heat and act on the unstable (002) crystal surface to overcome the V_{ZnS} formation energy [94] or to enhance the lattice vibration [62]. As a result, the V_{ZnS}

Fig. 12 *In-situ* DRIFT spectra of the ZnO sample at 150 °C under dark and UV irradiation conditions (a–c). (1) CO + H₂ adsorption for 10 min in the dark; (2) CO + H₂ adsorption for 20 min in the dark; (3) CO + H₂ adsorption for 10 min under UV irradiation; (4) CO + H₂ adsorption for 15 min under UV irradiation; (5) CO + H₂ adsorption for 20 min under UV irradiation.

will selectively grow *in-situ* on the (002) surface. On the other hand, it also acts on the H₂ adsorption process and provides enough energy to overcome the H₂ dissociation energy [95,96], as shown in Fig. 13(a). In other words, the V_{OS} could be preferentially grown on the (100) surface [24] under pure light (at 25 °C under UV irradiation) and heat (at 150 °C in dark) conditions; the V_{OS} will capture photoinduced electrons from the VB under UV irradiation. Further, type I H₂ (ads) adsorbed at the V_{OS} site and H₂ (ads) that accepts electrons from ZnO cannot be oxidized by O₂. However, the photothermal conditions synergistically act on the material itself to form V_{ZnS} on the (002) surface, providing Type II adsorption sites for H₂, and the photoinduced holes (VB) will be captured by V_{ZnS} under UV irradiation. Through *in-situ* DRIFTS and DFT calculations, it was shown that H₂ (ads) will selectively adsorb at the V_{ZnS} sites on the (002) surface under photothermal conditions, and the adsorption of H₂ transferred from the (100) to (002) surface. Furthermore, the H₂ molecules dissociate to form dissociated hydrogen (O_{lat}-H). The H₂ (ads), adsorbed through Type II adsorption sites, and H₂ (ads) which donates electrons to the ZnO in the adsorption kinetics, could be oxidized by O₂, as shown in Fig. 13(c). In addition, it has been proposed that the adsorption kinetic behavior required for hydrogen oxidation is that the H₂ (ads) donates electrons to the ZnO sample (pre-oxidation).

Moreover, H₂ is only adsorbed on the designated V_{ZnS} sites on the (002) surface rather than on the entire surface. As such, it is no longer the Fermi level (E_F) that affects the electron transfer behavior, but rather the energy level difference between the V_{ZnS} defect level and the adsorption level of H₂ (E_{H_2}). As shown in Fig. 13(b), the V_{ZnS} defect levels (near the top of the VB) are much lower than that of E_{H_2} , which provides energy-level structure conditions for the transition of H₂ adsorption behavior. Therefore, as H₂ is adsorbed, electrons transfer from H₂ to V_{ZnS}.

Second, for CO adsorption, as indicated in the *in-situ* DRIFTS of the CO adsorption, CO molecules adsorb on the pure ZnO surface; the adsorption mode of CO does not change because of the lack of CO chemical adsorption sites under photothermal conditions, which suggests mainly physical adsorption. Moreover, the CO molecules tend to be adsorbed on the (002) surface because of their large surface energy and strong adsorption capacity. As such, the change in CO adsorption behavior may be

mainly dependent on the Fermi level of the sample itself. As shown in Fig. 13(b), the Fermi level (E_{F1}) is lower than the adsorption level of CO (E_{CO}) under pure light and heat conditions, resulting in CO (ads) donating electrons to ZnO in the adsorption kinetics through a facile oxidation reaction. CO₃²⁻ species are identified on the surface as oxidation reaction intermediates; however, the reduction reaction cannot occur.

Subsequently, the Fermi level of ZnO will shift upwards from E_{F1} to E_{F3} under photothermal conditions, and evidently the upshift-effect of the Fermi level is a result of the comprehensive effects of light and thermal irradiation. Among them, E_{F1} is upshifted to E_{F2} by thermal energy. However, the E_F is still lower than E_{CO} at this point. This may also explain why the adsorption behavior of CO does not change (Fig. 2(d)). Based on this, the introduction of UV light will result in a further upward shift from E_{F2} to E_{F3} , resulting in the E_F being higher than the E_{CO} . As a result, CO (ads) accepts electrons from ZnO, which is favorable for the CO reduction reaction (Fig. 13(b)) [23]. Fur-

Fig. 13 Photothermal synergistic effect on the (002) surface of the ZnO sample: (a) provides energy to overcome the energy barrier and enhances the lattice vibration; (b) raises the Fermi level and forms a zinc vacancy adsorption level; (c) and (d) regulates the electron transfer behavior of H₂ and CO adsorption, and the further photocatalytic oxidation and reduction reactions.

thermore, for the methanation reaction of $\text{CO} + \text{H}_2$, the two gases are adsorbed on the (002) crystal surface, resulting in CO (ads) accepting electrons from ZnO (pre-reduction) and H_2 (ads) donating electrons to ZnO (pre-oxidation) in the adsorption kinetics. Then, H_2 (ads) dissociates to form O–H species, which react with CO (ads) to form COO, HCOO^- , and CH_3O^- intermediates, which finally produce methane. As such, it is also suggested that the adsorption kinetic behaviors required for the hydrogenation of CO is that the CO (ads) accepts electrons from ZnO (pre-reduction) and the H_2 (ads) donates electrons to ZnO (pre-oxidation), as shown in Fig. 13(d).

In summary, the reaction kinetics of H_2/CO oxidation or CO reduction mainly depend on the adsorption kinetics. Here, the photothermal synergism affects the selectivity of the photocatalytic reaction by regulating and optimizing the adsorption kinetic factors (i.e., adsorption mode and electron transfer behavior). Moreover, considering that the bimolecular reaction may occur *via* one of two mechanisms, the Eley-Rideal (E-R) [97,98] and Langmuir-Hinshelwood (L-H) mechanisms [99,100], the abovementioned CO/H_2 photocatalytic oxidation or CO reduction could also be attributed to different reaction mechanisms. For the oxidation of H_2 ($\text{H}_2 + \text{O}_2$) or CO ($\text{CO} + \text{O}_2$), only the oriented adsorption of H_2/CO needs to be satisfied, i.e., H_2 (ads)/CO (ads) donates electrons to ZnO ($\text{CO}^* + \text{O}_2 \rightarrow \text{CO}_2$ or $\text{H}_2^* + \text{O}_2 \rightarrow \text{H}_2\text{O}$), which could suggest the E-R mechanism. In contrast, for the hydrogenation of CO ($\text{CO} + \text{H}_2$), it is necessary to satisfy the oriented adsorption of CO and H_2 , i.e., CO (ads) accepts electrons from ZnO and H_2 (ads) donates electrons to ZnO ($\text{CO}^* + \text{H}_2^* \rightarrow \text{CH}_4$), which may be attributed to the L-H mechanism. This may also be why the CO oxidation reaction occurs more easily than the CO reduction reaction. This work shows that temperature (thermal energy) may induce the CO photocatalytic oxidation reaction to switch into its reduction behavior. This also provides in-depth insight into the understanding of the synergistic photothermal mechanism and the kinetic behaviors associated with Langmuir-Hinshelwood and Rideal surface reactions. This strategy could provide an approach to design a highly effective photothermal catalytic system for CO or CO_2 reduction and other reactions.

4. Conclusions

Photocatalytic CO/H_2 oxidation and CO reduction is dependent on the oriented adsorption (activation) of CO and H_2 gases, in which the electron-donated CO or H_2 can be oxidized, but only the electron-accepted CO can be reduced. At 25 °C under UV irradiation, H_2 (ads) accepts electrons from ZnO and cannot be oxidized, while the CO (ads) donates electrons to ZnO (oriented activation) and can be oxidized but not reduced. With an increase in temperature (approximately 100 °C), both the photo and thermal energy may act on the (002) crystal surface to generate V_{ZnS} *in-situ*, which further provides adsorption sites for H_2 molecules. These H_2 (ads) adsorption sites can be transferred from V_{OS} to V_{ZnS} on the (100) crystal surface, resulting in the H_2 (ads) transforming from accepting electrons into donating electrons (forming the oriented adsorption for H_2 oxidation); H_2 can then be oxidized. Moreover, the electron transfer

behavior of H_2 (ads) can be regulated by the defect level of V_{ZnS} controlled by temperature. For adsorbed CO on the (002) crystal surface of ZnO, the high temperature can also result in a change in its electron transfer behavior by raising the Fermi level. Here, the CO (ads) could receive electrons from ZnO and further be reduced by the electron-donated H_2 (ads) under UV irradiation. However, the electron-accepting CO (ads) cannot be reduced in the dark at 150 °C because the H_2 (ads) accepts electrons in this case.

CO or H_2 photocatalytic oxidation is dependent on the CO- or H_2 -oriented activation (not considering the O_2 adsorption and activation), indicating that its oxidation may be attributed to the E–R reaction. CO photocatalytic reduction is dependent on both CO- (ads) and H_2 - (ads) oriented activation, exhibiting a possible L–H reaction process.

The essential role of photothermal synergism in this work is to regulate the kinetic electron transfer behavior of reactant adsorption by changing the ZnO material structure *in-situ*. This causes the orientation activation of the reactants and subsequently the corresponding reaction behavior (oxidation or reduction reaction).

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Graphical Abstract

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Thermo-driven photocatalytic CO reduction and H₂ oxidation over ZnO via regulation of reactant gas adsorption electron transfer behavior

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CO (ads) donates electrons to ZnO under only light or heat energy in a facile oxidation reaction, while CO (ads) accepts electrons from ZnO under photothermal conditions, which is favorable for the CO reduction reaction.

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通过调节反应物气体吸附电子转移行为实现热驱动ZnO光催化CO还原和H₂氧化反应

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摘要:传统催化和低温光催化体系在实际应用中都存在技术缺陷。近些年, 人们通过将光和热耦合, 克服它们各自的局限性, 开创了光热协同催化新领域。目前已在CO减排、CO甲烷化和VOCs降解等诸多应用领域得到应用。当然, 随着光热催化的发展, 研究者也一直在思考光热协同的内在作用机理。目前大多数的机理分析都是从材料本身出发, 通过研究表面反应、光吸收或金属与载体之间的电子转移行为来探讨光热协同效应。然而, 表面反应只是多相光催化反应的其中一个步骤, 此外还包括反应物的扩散和吸附及产物的脱附和扩散, 其中反应物的吸附过程因其多变的吸附行为可能在整个反应过程中起着重要的作用。光热协同可能通过作用于气体吸附过程来调节反应的选择性和活性, 但到目前为止, 两者之间的内在联系尚不清楚。所以, 从反应物气体吸附行为(尤其是吸附电子转移行为)的角度深入研究光热协同效应具有重要意义。

本文在光催化CO还原和H₂氧化体系中引入一定的热条件, 希望通过热驱动效应影响H₂/CO吸附时的电子转移行为, 进而改变反应行为。为简化实验附加条件, 选用常见的具有合适带隙宽度以及良好光吸收的ZnO作为研究材料, 通过水热法合成了在(100)晶面具有氧空位(V_{Os})的ZnO样品, 引入气敏传感系统检测不同光热条件下的H₂/CO气体吸附电子转移行为,

并结合多种原位手段从物质结构和气体吸附两个角度出发,分析光热条件下气体吸附行为变化的机理。与我们预测一致,在紫外光照下随着温度的升高,光热协同作用于(002)晶面,原位生长了锌空位(V_{Zn} s),为 H_2 分子提供吸附位点。 H_2 从Vos位点吸附转移到 V_{Zn} s上,并导致 H_2 (ads)从得电子转变为失电子行为(形成有利于 H_2 氧化的定向吸附),从而发生 H_2 氧化反应。对于同样吸附在高表面能(002)晶面上的CO分子来说,光热协同效应通过抬升材料费米能级来改变其电子转移行为,CO(ads)由失电子转变为得电子行为(形成有利于CO还原的定向吸附),并进一步被失去电子的 H_2 (ads)还原。此外,还发现CO或 H_2 的光催化氧化反应的发生只依赖于CO或 H_2 单分子的定向活化(不考虑 O_2 的吸附和活化),表明其归属于E-R反应过程。而CO的光催化还原反应需要同时满足CO和 H_2 双分子的定向活化,可能归属于L-H反应过程。综上,本文研究结果表明,光热协同内在作用可能是通过改变ZnO材料结构,调节反应物吸附动力学中的电子转移行为,从而引起反应物的定向活化,进而改变反应选择性。

关键词: 光热协同; 电子转移行为; 吸附动力学控制; 原位表征; 费米能级

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