



General strategy for enhanced CH₄ selectivity in photocatalytic CO₂ reduction reactions by surface oxophilicity engineering

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ABSTRACT

Rationally designing and controlling the interactions between reaction intermediates and the surface of photocatalysts is critical to obtain high product selectivity in photocatalysis. Herein, using CdS-based photocatalytic CO₂ reduction reaction (CO₂RR) as a model system, we demonstrate that CH₄ selectivity can be significantly enhanced through the introduction of La³⁺ ions with high oxophilicity on the surface of the photocatalysts. The high surface oxophilicity of the photocatalysts can increase CO* desorption energy and promote further hydrogenation to CH₄. In contrast, when Au³⁺ ions with low oxophilicity were doped in CdS, reduced CH₄ selectivity was observed in the CO₂RR. Significantly, enhanced CH₄ selectivity can be achieved by doping oxophilic La³⁺ ions into a broad range of alternative photocatalysts including ZnO, SnS₂, BiOBr, BiVO₄, TaON, and CsPbBr₃, which demonstrates the general strategy to enhance CH₄ selectivity of photocatalytic CO₂RR through increased surface oxophilicity of the photocatalysts by rare earth La³⁺ ion doping.

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1. Introduction

Photocatalytic CO₂RR for the generation of solar fuels represents one of the ideal sustainable technologies that can simultaneously overcome environmental issues and the energy crisis [1]. While photocatalytic activity and stability have been widely studied, the control of product selectivity of photocatalytic CO₂RR is challenging and less explored [2]. The photocatalytic CO₂RR process usually involves proton-coupled multi-electron transfers and reaction process with various intermediate products which can be produced due to their similar reduction potentials [3]. Therefore, it is crucial to enhance product selectivity through manipulating the reaction pathways on the photocatalysts to reduce unnecessary separation costs [4]. So far, there have been several successful strategies for obtaining highly selective products of photocatalytic CO₂RR such as loading appropriate co-catalysts [5], rational fabrication of dual metal active sites [6], the introduction of O₂ [7], doping [8], and defect engineering [9]. However, most of the reported methods are specific to a certain photocatalytic system and a gen-

eral method to refine product selectivity of photocatalytic CO₂RR is still lacking.

By tailoring the interactions of intermediates with active sites of a photocatalyst, high product selectivity can be achieved [10]. The oxophilicity of the catalyst surface is closely related to its binding affinity with oxygen [11]. Therefore, in principle, the product selectivity of catalytic reactions involving oxygen-containing intermediates can be adjusted through manipulating the oxophilicity of catalyst surface. Indeed, the importance of the surface oxophilicity of catalysts in organic synthetic chemistry has been reported back in the 1980s [12]. Recently, tailoring surface oxophilicity of a catalyst to obtain high product selectivity has received renewed interest. For example, the glycerol hydrodeoxygenation reaction selectivity can be tuned through modifying the surface cationic oxophilicity of Mo₂C with Cu [13].

Considering that most intermediates derived from photocatalytic CO₂RR are oxygen-containing species, we hypothesize that the corresponding product selectivity could be enhanced through controlling surface oxophilicity of photocatalysts. Usually, the main gaseous products of photocatalytic CO₂RR are CO and CH₄, which involves 2e⁻ + 2H⁺ and 8e⁻ + 8H⁺ processes, respectively. If the surface oxophilicity of a photocatalysts is enhanced, its binding

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ability to CO* will be increased, and therefore, boosted CH₄ selectivity could be achieved. To prove our hypothesis, we used CdS hierarchical microspheres (HMSs) for photocatalytic CO₂RR as a model system and doped strongly oxophilic La³⁺ ions on the CdS surface to enhance CH₄ selectivity. CdS is chosen mainly considering that it is a popular visible light-driven photocatalyst, which has been widely applied to photocatalytic CO₂RR [14]. So far, although various strategies have been developed to manipulate the product selectivity of CdS photocatalysts, the most commonly reported gaseous products are CO [15]. In addition, La³⁺ ion can be doped into CdS lattice [16], which provides a way to manipulate the oxophilicity of the CdS photocatalyst. As we expected, it was found that CH₄ selectivity was increased from 46 % to 74 % (product basis) and 77 % to 92 % (electron basis) after La³⁺ ions were introduced on the surface of CdS photocatalysts. More significantly, it was found that surface oxophilicity engineering by La³⁺ ion doping is a general strategy for enhanced CH₄ selectivity and can be applied to various photocatalysts including ZnO, SnS₂, BiOBr, BiVO₄, TaON, and CsPbBr₃. This work provides new insights on the surface engineering in tuning catalytic reaction selectivity for the design of highly selective photocatalysts for CO₂RR.

2. Experimental

2.1. Materials

Ethylenediamine (C₂H₈N₂) and nitric acid (HNO₃) were purchased from Zhejiang Zhongxing Chemical Co. Ltd. Hydrogen peroxide (H₂O₂) was supplied by Shanghai Union Chemical Co. Ltd. All other chemicals including cadmium acetate (Cd(Ac)₂·2H₂O), thiourea (CH₄N₂S), zinc acetate (Zn(CH₃COO)₂), tantalum pentoxide (Ta₂O₅), lanthanum nitrate hexahydrate (La(NO₃)₃·6H₂O), potassium bromide (KBr), bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O), sodium diethyldithiocarbamate trihydrate ((C₂H₅)₂NCSSNa·3H₂O), tin chloride pentahydrate (SnCl₄·5H₂O), titanium dioxide (TiO₂), sodium metavanadate (NaVO₃), ethylenediamine tetraacetic acid (EDTA, C₁₀H₁₆N₂O₈), sodium hydroxide (NaOH), cesium bromide (CsBr), lead bromide (PbBr₂), N,N-dimethylformamide (DMF, HCON(CH₃)₂), chloroauric acid (HAuCl₄), ethylene glycol ((CH₂OH)₂), triethanolamine (TEOA, C₆H₁₅NO₃), and ethanol (C₂H₅OH) were purchased from Aladdin Shanghai Co. Ltd.

2.2. Syntheses of CdSHMSs and CdS:La³⁺ HMSs

Typically, 2.0 mmol of Cd(OAc)₂·2H₂O and 6.0 mmol of thiourea were dissolved into 30 mL of ethylenediamine under stirring. Then the solution was transferred to a Teflon-lined stainless-steel autoclave (50 mL), heated at 100 °C for 8 h. After it was cooled to room temperature, the yellow CdS powders were washed several times with deionized water and ethanol successively, and dried in an oven at 60 °C. For the synthesis of high-crystallinity CdS HMSs, the as-obtained CdS powders were further annealed at 500 °C under Ar for 2 h. CdS:La³⁺ HMSs were synthesized through an impregnation method. In a typical process, 0.5 mmol of CdS powders were added into 6 mL of La(NO₃)₃·6H₂O aqueous solution (2.5 mM) under stirring. Then the solution was dried at 100 °C. The resultant solid powders were further annealed at 500 °C under Ar for 2 h.

2.3. Characterization of materials

X-ray diffraction (XRD, D8 Advance) was used to characterize the crystal phases of the products. Field emission scanning electron microscopy (FE-SEM, Nova NanoSEM 200) and high-resolution

transmission electron microscopy (HRTEM, JEOL 2010) coupled with energy-dispersive X-ray (EDX) spectroscopy were used to study the morphology and composition of the samples. UV-Vis absorption spectra (Shimadzu 2450) obtained by a diffuse reflectance spectroscopy with BaSO₄ as the reference for studying the optical responsive range of the samples. The inductively coupled plasma (ICP) optical emission spectroscopy (ICP-OES, America Agilent 725) was used to detect the actual doping concentration of La in CdS:La³⁺ HMSs. X-ray photoelectron spectroscopy (XPS, Escalab 250Xi, Thermo Scientific) was used to analyze the composition and chemical states of the prepared samples, using Al K α radiation (h ν = 1486.6 eV) as excitation. The ultraviolet photoelectron spectrum (UPS) was attached to the same XPS system to determine energy band position of the sample. N₂ adsorption-desorption isotherms were recorded on a Micromeritics ASAP2020 instrument, which was further used to measure specific surface area of the samples. CO₂ adsorption isotherms were measured at room temperature using the same apparatus. Photoluminescence (PL) spectra were measured on a Fluoromax-4 spectrofluorometer (HORIBA JobinYvon Inc.) under an excitation wavelength of 365 nm at room temperature. The electrochemical impedance spectra (EIS) were carried out at 1 V versus reversible hydrogen electrode with an amplitude of 5 mV in a frequency range from 0.1 MHz to 0.1 Hz in 0.5 M Na₂SO₄ electrolyte in the dark and under light irradiation (AM1.5G, 100 mW cm⁻²). Photocurrent-time curves of the photoelectrodes were performed in 0.5 M Na₂SO₄ aqueous electrolyte under chopped light illumination (AM 1.5 G, 100 mW cm⁻²). CO₂-temperature programmed desorption (CO₂-TPD) and CO-TPD were performed on a Quantachrome Chem-BET Pulsar TPR/TPD automated chemisorption analyzer. In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was performed on a Nicolet iS50 FTIR spectrometer (Thermo Scientific, USA). Before DRIFTS testing, the samples were pretreated at 423 K for 4 h. Then, CO₂ and H₂O gases were introduced into the IR cell loading the sample. The baseline was obtained after adsorption equilibrium of CO₂ on the sample for 20 min. Subsequently, light source (Perfect Microsolar 300 W Xe lamp equipped with a 420 nm cutoff filter) was turned on and DRIFTS spectra of the samples at different time intervals were recorded. The gaseous and liquid products from the photocatalytic CO₂RR were analyzed by gas chromatograph (Fuli GC9790) and ¹H NMR spectroscopy (Bruker, 500 M), respectively.

2.4. Photocatalytic CO₂RR

The photocatalytic CO₂RR was carried out in a closed reactor containing a quartz container. Typically, 10 mg of photocatalysts were dispersed into the mixed solvents of H₂O and TEOA (V_{water}:V_{TEOA} = 10:1). Then the reaction setup was alternately vacuum-degassed and purged with highly pure CO₂ for three times. The pressure of CO₂ in the reactor was kept at one atmosphere. A 300 W Xenon lamp equipped with a high-pass filter (λ > 420 nm) was utilized as the visible light source. The intensity of light source is adjusted to 300 mW/cm² and irradiated area is 11.3 cm². The reaction temperature was controlled at 15 °C by circulating cooling water coupled with a heater. The gaseous products were analyzed by a gas chromatography (Fuli GC9790). To evaluate the stability of photocatalysts, the photocatalytic CO₂RR was performed for 6 h at first. After that, 1 mL of TEOA was added to the quartz container to replenish the consumed part of TEOA before next cycle test. The processes were repeated five additional times.

2.5. Computational details

All the spin-polarized theoretical simulations in our work were performed on the Vienna ab initio Simulation Package (VASP) with

the version 5.4.1 [17,18]. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional form was used to evaluate the electron–electron exchange and correlation interactions while the projector augmented-wave (PAW) methods were implanted to represent the core-electron (valence electron) interactions [19–21]. Plane-Wave basis function was set with a kinetic cut-off energy of 550 eV. The ground-state atomic geometries were optimized by relaxing the force below 0.02 eV/Å and the convergence criteria for energy was set with the value of 1.0×10^{-5} eV/cell. The Brillouin zone was sampled using a Monkhorst-Pack meshes with $5 \times 5 \times 1$. Gaussian method was employed for both electronic structures and total energy of our models and stress/force relaxations. To better describe the interactions between molecules, van der Waal (vdw) interactions are included describing by DFT-D3 method of Grimme [22]. Free Energy under standard conditions (298 K) was calculated. Gibbs free Energy (ΔG) was computed by the equation of $\Delta G = \Delta E + \Delta EZPE - T\Delta S$, where the ΔE is the difference energy between each reaction step, $\Delta EZPE$ is the difference of the zero-point energy between each reaction step, ΔS is the difference of vibrational entropy between each reaction step.

3. Results and discussion

3.1. Characterization of CdS HMSs and La^{3+} ions doped CdS HMSs ($\text{CdS}:\text{La}^{3+}$ HMSs)

The host CdS HMSs were synthesized through a solvothermal route and $\text{CdS}:\text{La}^{3+}$ HMSs were synthesized by an impregnation method, respectively (See details in Experimental section). To simplify descriptions of experimental results, the doped sample with the highest photocatalytic activity and selectivity was screened out and used for subsequent study. As a result, the optimal doping concentration of La^{3+} ion is ca. 3 % (Fig. S1). The FE-SEM image of the CdS HMSs obtained through the solvothermal route indicates that the HMSs consist of the assembled nanosheets (Fig. S2). The XRD pattern of the sample could be indexed to hexagonal phase CdS (JCPDS no. 41–1049), even though its crystalline degree is relatively low (Fig. 1a). To improve the crystallinity of the products and promote efficient La^{3+} doping into CdS lattice, the as-

synthesized CdS HMSs and $\text{CdS}:\text{La}^{3+}$ HMSs were further treated at 500 °C under Ar atmosphere for two hours. The as-obtained CdS HMSs and $\text{CdS}:\text{La}^{3+}$ HMSs after thermal annealing maintain their original morphology (Fig. 1b and Fig. 1c) but have higher crystallinity in hexagonal phase (Fig. 1a). As seen from their magnified XRD patterns (Fig. S3), FWHM (full width at half maximum) of the diffraction peaks for La^{3+} ions doped CdS HMSs are larger than those of undoped CdS HMSs, while diffraction peaks of $\text{CdS}:\text{La}^{3+}$ HMSs shift to lower degree. According to Scherrer's equation ($D = k \times \lambda / \beta \times \cos\theta$, where D , k , λ , β , θ represent crystallite size, shape factor, wavelength of X-ray used, FWHM, and diffraction angle, respectively), $\text{CdS}:\text{La}^{3+}$ HMSs have smaller crystallite size than CdS HMSs. The thickness of $\text{CdS}:\text{La}^{3+}$ nanosheet unit measured through FE-SEM is smaller than that of undoped CdS nanosheet one (Fig. S4), which also supports the result of XRD analyses. Therefore, La^{3+} ion dopants could slightly inhibit the growth of CdS crystals in the reaction. The XRD peaks shifting to lower diffraction angle after doping can be understood by the lattice expanding as the result of doping larger La^{3+} ions (106 pm) on the Cd^{2+} ion (97 pm) sites of the CdS crystal lattice based on the Bragg's equation ($2d\sin\theta = n\lambda$), which is consistent with previous dopant size-dependent XRD shift [23]. The HRTEM image of $\text{CdS}:\text{La}^{3+}$ HMSs shows the lattice spacings of 0.358 nm and 0.316 nm, which agree with interplanar separation of (100) and (101) planes of hexagonal phase CdS, respectively (Fig. 1d). The EDX elemental mapping shows that La^{3+} ions were doped into CdS lattices (Fig. 1e). The ICP measurements indicates 3 % molar concentration of La^{3+} ions doped in $\text{CdS}:\text{La}^{3+}$ HMSs, which implies that near all La^{3+} ions were doped into CdS HMSs.

XPS survey spectra indicate that the surface composition of CdS HMSs mainly consist of Cd and S elements, and Cd, S, La, C, and O elements for $\text{CdS}:\text{La}^{3+}$ HMSs (Fig. S5a), respectively. The small quantity of C and O present in $\text{CdS}:\text{La}^{3+}$ HMSs probably comes from adventitious carbon and chemisorbed oxygen [24]. Quantitative calculations of XPS data shows the molar percentage of La^{3+} ion in $\text{CdS}:\text{La}^{3+}$ HMSs is ca. 2.5 %, which indicates that while some La^{3+} ions are doped inside the CdS lattice, most of the dopants are located at the surface or near the surface of CdS HMSs considering a total 3 % La^{3+} doping concentration. The binding energies of Cd 3d (Fig. S5b) and S 2p (Fig. S5c) for CdS HMSs are consistent with

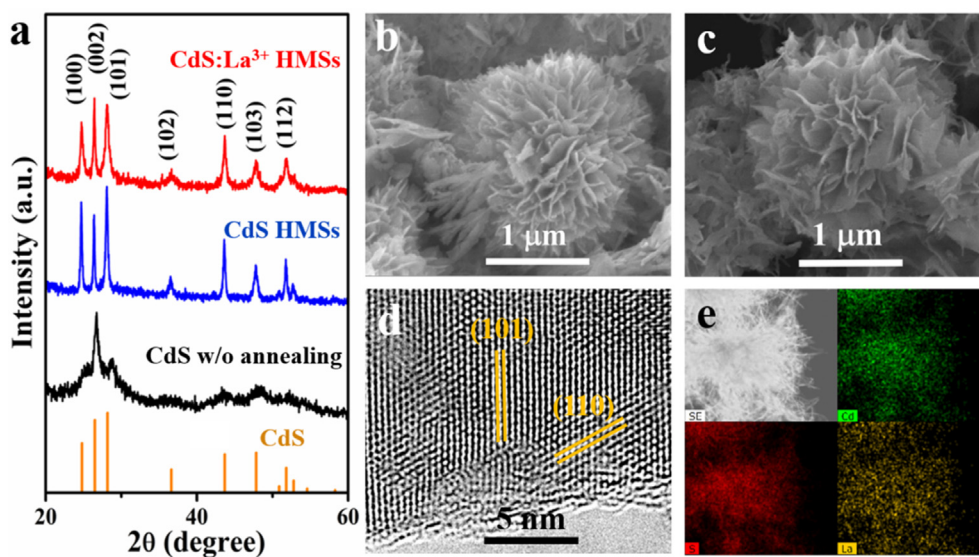


Fig. 1. XRD patterns of CdS synthesized through solvothermal route, CdS HMSs and $\text{CdS}:\text{La}^{3+}$ HMSs after thermal annealing (a). FE-SEM images of CdS HMSs (b) and $\text{CdS}:\text{La}^{3+}$ HMSs (c) after annealing. HRTEM image (d) and elemental mapping (e) of $\text{CdS}:\text{La}^{3+}$ HMSs. Green, red, and yellow represent Cd, S, and La elements, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

those of Cd and S in CdS [25]. The binding energies of Cd 3d3/2 and 3d5/2 are positively shifted by 0.09 eV after La³⁺ ions were doped into CdS, while those of S 2p are negatively shifted by 0.09 eV. This result shows that La³⁺ ions are doped into CdS crystal lattice and lead to charge redistribution of Cd and S. The binding energies of La 3d are located at 835.4 eV (La 3d5/2), 838.9 eV (La 3d5/2), 852.2 eV (La 3d3/2), and 855.7 eV (La 3d3/2) (Fig. S2d), which are closer to those of La 3d in CdLa₂S₄ rather than La₂S₃ [26,27]. The above XRD, EDX, and XPS results could confirm that La³⁺ ions were efficiently doped into CdS lattice.

UV–visible absorption spectra of pristine CdS HMSs and CdS:La³⁺ HMSs (Fig. 2a) indicate that the optical absorption edge of CdS was slightly blue shifted after La³⁺ ion doping. The band gap energy determined through $(\alpha h\nu)^2$ versus $h\nu$ curves increased from 2.25 eV to 2.34 eV after doping (inset in Fig. 2a). The slightly widened band gap mainly originates from the decreased crystal size of CdS:La³⁺ HMSs [16]. To ascertain the influence of La³⁺ ion doping on energy position of CdS HMSs, UPS of CdS and CdS:La³⁺ HMSs were measured (Fig. 2b and Fig. 2c). The work functions are 4.18 and 4.20 eV for CdS and CdS:La³⁺ HMSs, respectively, obtained through subtracting the secondary electron cut-off energy from the incident ultraviolet photon energy (He I excitation line, 21.22 eV). Therefore, their Fermi levels (E_F) are – 4.18 eV and – 4.20 eV versus vacuum energy level, respectively. The difference between E_F and valence band maximum (E_{VBM}) of CdS HMSs and CdS:La³⁺ HMSs are estimated to be 1.84 eV and 1.64 eV, respectively. Therefore, their E_{VBM} are – 6.02 eV and – 5.84 eV versus vacuum energy level. The calculated conduction band minimum (E_{CBM}) versus vacuum energy level of CdS and CdS:La³⁺

HMSs are – 3.77 eV and – 3.50 eV, respectively, using the equation $E_{CBM} = E_{VBM} + E_g$. To clearly show the positional relationship of their E_{CBM} and reduction potentials of CO₂ to CO and CH₄, energy band position changes of CdS HMSs before and after La³⁺ ion doping were further converted to normal hydrogen electrode potential (E_{NHE}) as shown in Fig. 2d. Obviously, both E_{CBM} and E_{VBM} of CdS HMSs were upshifted after the doping of La³⁺ ions. In theory, both CO and CH₄ can be thermodynamically produced on CdS HMSs and CdS:La³⁺ HMSs because of their more negative E_{CBM} than reductive potential of CO₂ toward CO and CH₄.

3.2. Visible-light-driven CO₂RR properties

To evaluate the influence of La³⁺ dopants on the photocatalytic properties of CdS HMSs, photocatalytic CO₂RR on CdS HMSs and CdS:La³⁺ HMSs were carried out under visible light irradiation ($\lambda > 420$ nm). It was found that both CdS HMSs and CdS:La³⁺ HMSs enable the photocatalytic reduction of CO₂ toward CO and CH₄ generation without any other liquid or gaseous CO₂ reduction products detected. Both the yields of CO and CH₄ were increased for CdS HMSs and CdS:La³⁺ HMSs with prolonging light irradiation time (Fig. 3a and 3b). However, La³⁺ ion doping significantly decreased the yield of CO but enhanced that of CH₄. Specifically, the mole percentage of CH₄ in the gaseous products increased from 46 % to 74 % within a 6-hour reaction time. The CH₄ selectivity (S_{CH_4}) was further calculated based on the photoelectrons participating the CO₂-RR through the following equation:

$$S_{CH_4} = 8R_{CH_4} / (2R_{CO} + 8R_{CH_4})$$

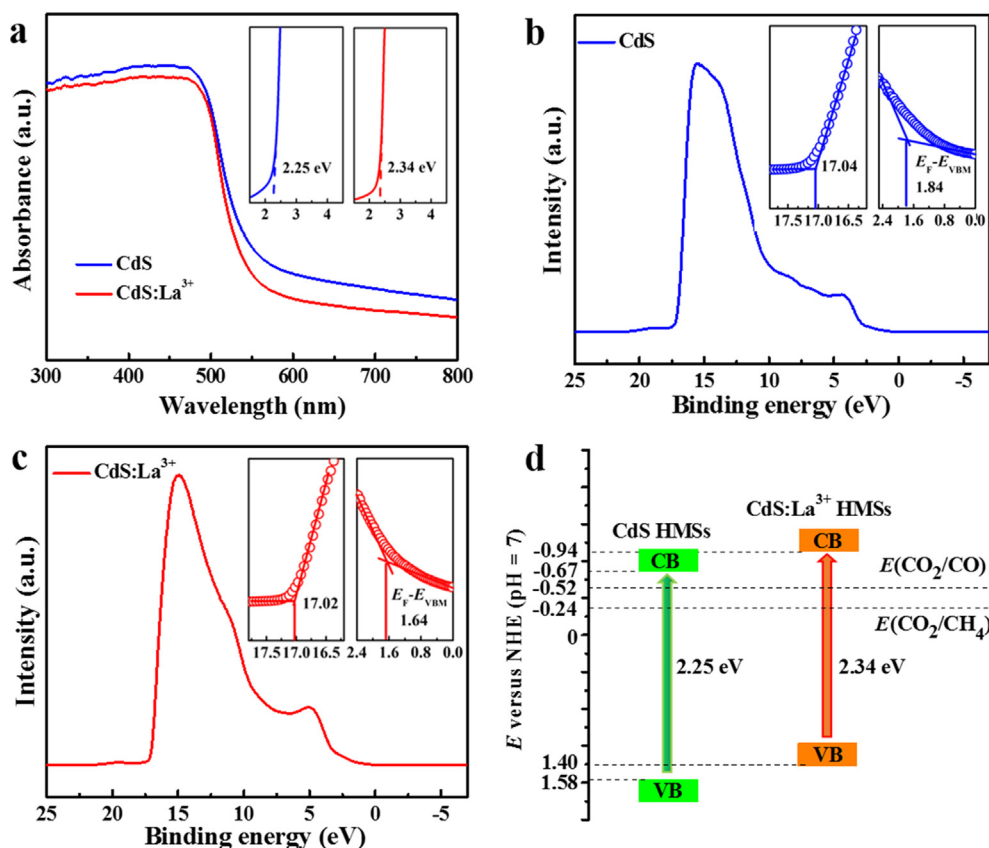


Fig. 2. UV–Vis absorption spectra (a) and corresponding curves of $(\alpha h\nu)^2$ versus $h\nu$ (the inset) of CdS HMSs and CdS:La³⁺ HMSs. UPS spectra and magnified views (the inset) for determining the secondary electron cut-off energy and E_{VBM} of CdS HMSs (b) and CdS:La³⁺ HMSs (c). Schematic illustration of energy band positions for CdS HMSs and CdS:La³⁺ HMSs, as well as reduction potentials of CO₂ to CO and CH₄ (d).

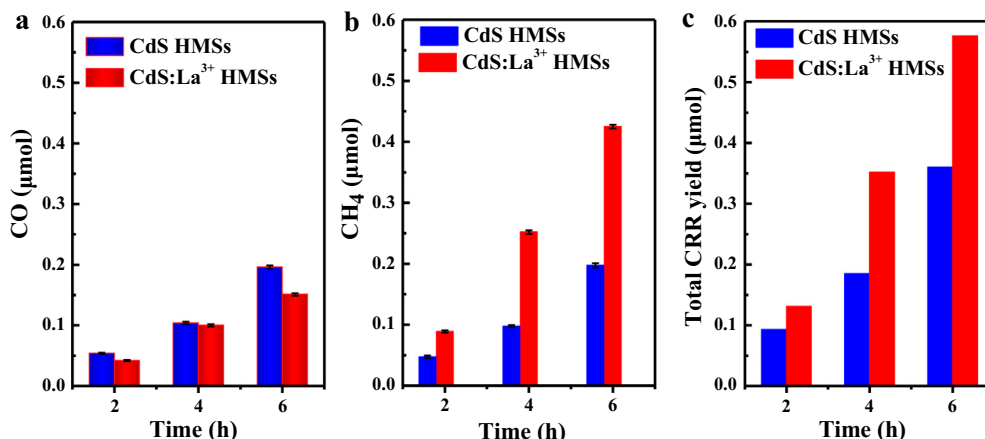


Fig. 3. CO (a), CH₄ (b), total CO and CH₄ (c) gases evolution amounts at different photocatalytic reaction times over CdS HMSs and CdS:La³⁺ HMSs. The error bars represent the standard deviation from three independent tests.

Where 8, 2, and R represent the consumed electron numbers of CO₂ reduction to CH₄ and CO and the formation rates of corresponding products, respectively. As a result, S_{CH_4} of CdS:La³⁺ HMSs was increased from 77 % to 92 % due to La³⁺ ion doping, while no significant change in S_{CH_4} was detected for both CdS HMSs and CdS:La³⁺ HMSs during photocatalytic CO₂RR processes (Fig. S6). Furthermore, the total amount of CO and CH₄ reaches 0.57 μmol for CdS:La³⁺ HMSs within 6 h under visible light irradiation, which is 1.7 times larger than that obtained over pristine CdS HMSs (0.33 μmol) (Fig. 3c). Therefore, La³⁺ ion doping can significantly enhance CH₄ production and selectivity, as well as boost the total photocatalytic CO₂RR activity. The apparent quantum yield of CH₄ could reach 1.4 % under monochromatic irradiation of 420 nm. In addition, the activity and CH₄ selectivity of photocatalytic CO₂RR for CdS:La³⁺ HMSs is the highest among the reported results to the best of our knowledge (Table S1).

It should be mentioned that no CO₂ reduction products were obtained in the absence of photocatalysts or in the dark, indicating that the CO₂RR was a light-driven photocatalytic process. Neither CH₄ nor CO were detected from control experiments in the absence of CO₂ with other reaction parameters unchanged. When CdS:La photocatalysts were dispersed into TEOA, CH₄ and CO were not detected under visible light irradiation, either. In addition, CH₄ and CO could also be produced in water without addition of TEOA. The above experimental results demonstrate that CH₄ and CO came from photocatalytic CO₂ reduction reaction over CdS:La.

To further evaluate stability of the CdS:La³⁺ HMSs for photocatalytic CO₂RR, cycle tests were operated. CdS:La³⁺ HMSs showed negligible drop in CO and CH₄ production yield after 6 consecutive cycles under visible-light irradiation, suggesting their good photocatalytic stability (Fig. S7). The crystal phase and morphology of CdS:La³⁺ HMSs can be maintained in the recycled photocatalysts, as shown in the XRD (Fig. S8) and FE-SEM analysis (Fig. S9). Furthermore, XPS spectra show almost no change in surface chemical states and compositions of the CdS:La³⁺ HMSs after six cycle tests (Fig. S10). The high stability of the doped CdS:La³⁺ HMSs is promising for large scale photocatalytic CO₂RR in industrial applications.

3.3. Mechanism of enhanced photocatalytic activity and selectivity

The introduction of La³⁺ ion could promote the separation of photogenerated carriers (electrons and holes) of CdS HMSs, as confirmed by their photocurrent and PL spectra. Compared with CdS HMSs, CdS:La³⁺ HMSs showed 1.5 times larger photocurrent under the same measurement conditions (Fig. 4a), which shows photo-

generated electrons and holes were more efficiently separated over CdS:La³⁺ HMSs. Consistent with larger photocurrent, PL intensity of CdS:La³⁺ HMSs is significantly lower than that of CdS HMSs (Fig. 4b), which suggests more efficient separation of photogenerated charge carriers and less exciton recombination in CdS:La³⁺ HMSs. The EIS of CdS:La³⁺ HMSs show a smaller semicircular diameter than the undoped CdS HMSs (Fig. 4c), indicating smaller charge transfer resistance in the doped CdS:La³⁺ HMSs than the undoped CdS HMSs. The enhanced separation and transfer efficiency of charge carriers for CdS:La³⁺ HMSs can be attributed to the role of La³⁺ ions as a trapping center for photoexcited electrons [28].

To achieve highly efficient photocatalytic CO₂RR, the fixation and activation of CO₂ is a prerequisite. As seen from Fig. 4d, the amount of adsorbed CO₂ on the CdS:La³⁺ HMSs is higher than that of CdS HMSs despite similar Brunauer – Emmett – Tellr (BET) specific area of the two HMSs (Fig. S11). This result shows that the introduction of La³⁺ ions can activate the surface of CdS HMSs and facilitate the adsorption of CO₂, which is attributed to the stronger oxophilicity of La³⁺ ions than Cd²⁺ ions [29]. To further confirm the role of the oxophilic dopants on CO₂ adsorption, CO₂ temperature programmed desorption (TPD) measurements were conducted. CO₂ TPD profiles (Fig. S12) show a higher number of basic sites, corresponding with the La³⁺ dopant locations, and therefore higher adsorption capacity toward CO₂ from CdS:La³⁺ HMSs than CdS HMSs. Taken together, the enhanced photocatalytic CO₂RR activity of CdS:La³⁺ HMSs are mainly attributed to: 1) enhanced CO₂ adsorption from the oxophilic La³⁺ dopant ions; 2) increased charge separation and transfer after introducing La³⁺ ions into CdS crystal lattice.

The reduction potentials of CO₂ toward CO and CH₄ are – 0.52 and – 0.24 V versus normal hydrogen electrode, respectively. Because the doping of La³⁺ ions upshifted conduction band position of CdS HMSs, the CO formation would become more thermodynamically favored. In theory, CO₂ reduction toward CH₄ involves 8e[–] + 8H⁺ process, which is less favored than the 2e[–] + 2H⁺ reduction of CO₂ to CO in kinetics. Interestingly, it was found that the yield of CO decreased and correspondingly the yield of CH₄ increased for doped CdS:La³⁺ HMSs (Fig. 3b). The enhanced CH₄ selectivity observed in the doped CdS:La³⁺ HMSs is intriguing and could indicate that La³⁺ ion doping modulates the surface environment of the CdS HMSs photocatalysts and may change energy barriers associated with the CO and CH₄ formation pathways.

To elucidate the enhanced CH₄ selectivity of CdS:La³⁺ HMSs, density functional theory (DFT) calculations on Gibbs free energy

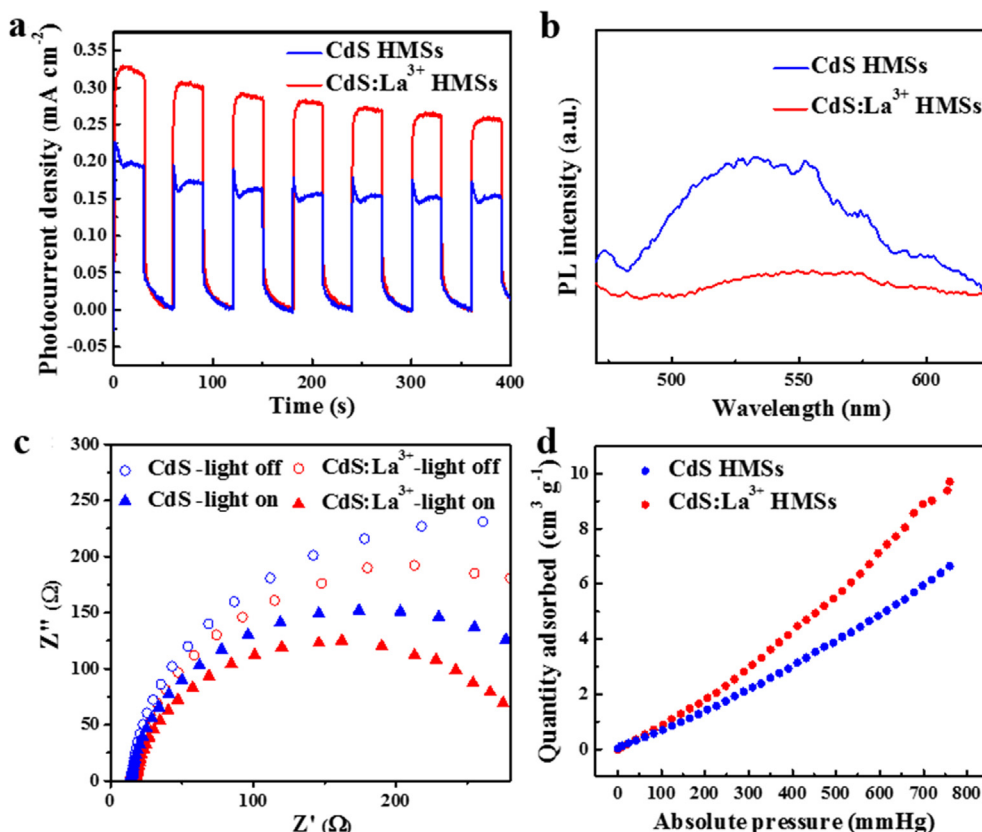


Fig. 4. Photocurrent spectra (a), PL spectra (b), EIS spectra in the dark and under visible light irradiation (c), and CO₂ adsorption isotherm curves (d) of CdS HMSs and CdS:La³⁺ HMSs.

of reaction pathways for CO and CH₄ formation from CO₂ reduction were carried out. As shown in Fig. 5a, the free energy of CO₂* for doped CdS:La³⁺ is significantly lower than that of pristine CdS. This result suggests that the doping of La³⁺ ions can boost the CO₂ adsorption capacity of CdS HMSs, which is in good agreement with the results of CO₂ adsorption measurements (Fig. 4d). According to the calculations, the formation of CO* intermediate is the rate-limiting step for both photocatalytic CO₂RR toward CO over CdS HMSs and toward CH₄ over CdS:La³⁺ HMSs. The subsequent CO* conversion determines the products of the reaction, i.e., CO* direct desorption results in the production of CO, while further hydrogenation produces CH₄. Although the formation of CH₄ is an exothermic and spontaneous process for both photocatalysts, there is a significant difference in their reaction energy barriers for CO formation. The desorption energy barrier for CdS HMSs is 0.11 eV while CdS:La³⁺ HMSs have a much greater desorption energy barrier of 2.36 eV. The CO-TPD measurements (Fig. 5b) show that the CO desorption temperature for CdS:La³⁺ HMSs (202 °C) is higher than that of CdS HMSs (178 °C), which also supports the calculated results of CO desorption energy. The further hydrogenation of adsorbed CO* molecules into CHO* is much easier for CdS:La³⁺ HMSs than CdS HMSs due to the lower formation energy for the former than the latter. The result of CO-TPD measurements suggests that the doping of La³⁺ ion can activate adsorbed CO molecules, which can be supported by Bader charge analyses on CO adsorption structure. As shown in Fig. 5c, 0.15 e and 0.43 e were transferred from individual Cd sites in CdS HMSs and dual La and Cd sites in CdS:La³⁺ HMSs to the adsorbed CO molecules, respectively, indicating that adsorbed CO molecules can be easily activated on La sites. The stronger CO* adsorption and activation ability of La³⁺ ion than those of Cd²⁺ ions (Fig. 5a and 5b) is due

to higher oxophilicity of the former than the latter. In addition, the desorption energy of CH₄ molecules on CdS:La³⁺ HMSs (−0.57 eV) is more negative than that on pristine CdS HMSs (−0.53 eV), which suggests that the CH₄ desorption from the surface of the former is also easier than that from the latter. This is possibly attributed to the strong adsorption of O in CH₃O* on La³⁺ ions, which can weaken the C–O bands in CH₃O radical. As a result, the breakage of C–O bands and subsequent CH₄ desorption become more feasible. Considering all the above results, enhanced CH₄ selectivity for CdS:La³⁺ HMSs could be ascribed to the introduction of highly oxophilicity of La³⁺ ions on the surface of the CdS HMSs. Unreacted O* can be removed through TEOA acting as sacrificial agent freeing active sites for next catalytic cycle, which is supported by the fact that there is little change in surface oxygen content of CdS:La³⁺ HMSs after six cycle tests (Fig. S10).

In order to further confirm that La³⁺ ion doping could facilitate CO* hydrogenation to CH₄, in-situ DRIFT measurements over CdS and CdS:La³⁺ HMSs were carried out. To reduce the interference of organic TEOA molecules, only H₂O vapor and CO₂ gas were added into the sample cell. After 20 min adsorption of CO₂ gas and H₂O vapor over pristine CdS HMSs, as seen from Fig. 6A, some absorption bands assigned to bidentate carbonate species (b-CO₃²⁻, located at 1650 and 1512 cm⁻¹), HCO₃⁻ (located at 1427 and 1215 cm⁻¹), and monodentate carbonate species (m-CO₃²⁻, located at 1535, 1459, 1120, and 1088 cm⁻¹) are detected [30]. Under visible light irradiation, new vibration peaks corresponding to COO⁻ species (1337 cm⁻¹) and CH₃O⁻ groups (located at 1744 and 1706 cm⁻¹) appeared [31]. In contrast, after doping of La³⁺ ions, a new band appears at 1031 cm⁻¹ (Fig. 6B) under visible light irradiation, which can be assigned to HCO* [32]. According to previous reports [33,34], HCOO⁻ and COO⁻ species, HCO* and CH₃O⁻ groups

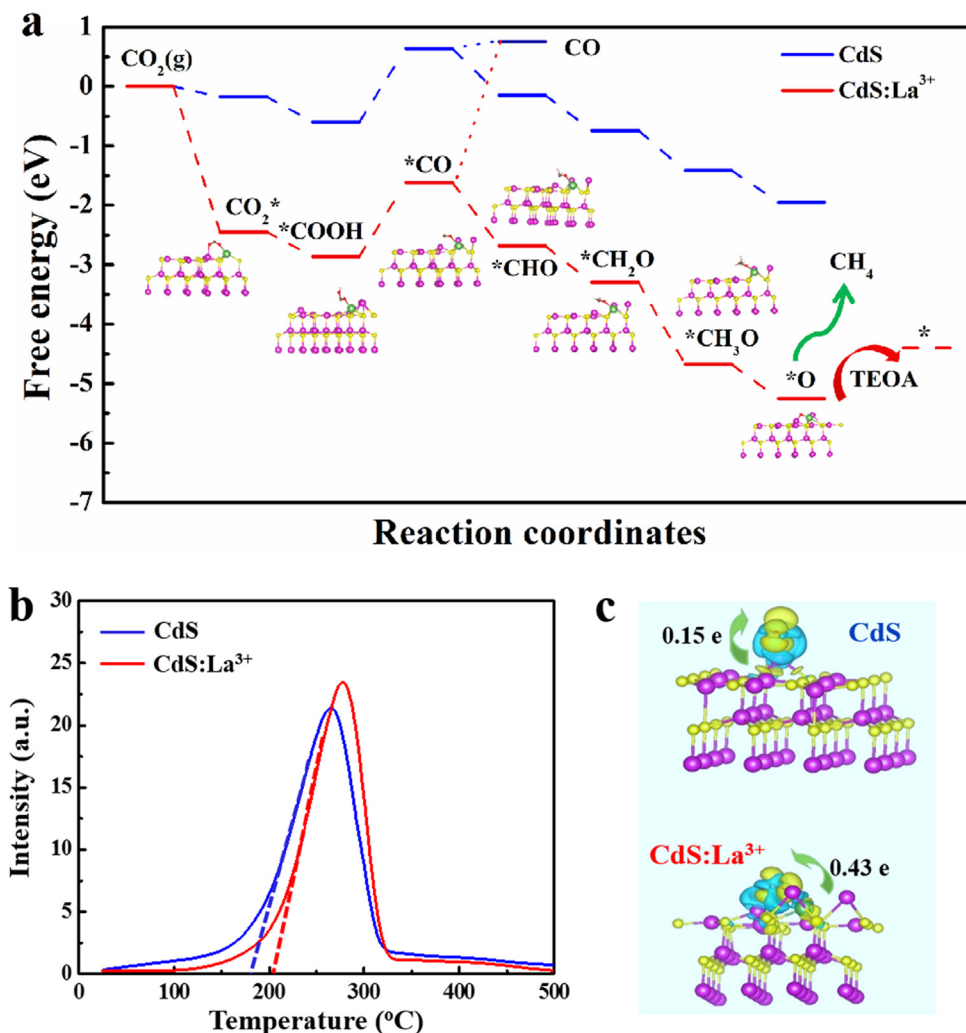


Fig. 5. Calculated Gibbs free energy diagrams for CO₂ reduction to CO and CH₄ over CdS and CdS:La³⁺ (a). CO-TPD profiles of CdS HMSs and CdS:La³⁺ HMSs (b). Charge density difference and net Bader charge transfer of CO adsorbed on Cd sites in CdS HMSs and dual Cd and La sites in CdS:La³⁺ HMSs (c).

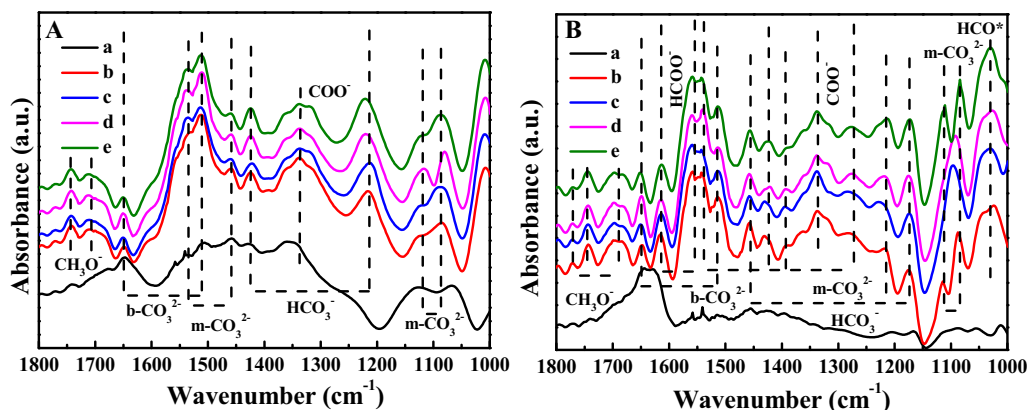


Fig. 6. In-situ DRIFT spectra of CdS HMSs (A) and CdS:La³⁺ HMSs (B) under different conditions: a) after flowing CO₂/H₂O gas for 20 min in darkness, b) visible light irradiation for 5 min, c) visible light irradiation for 10 min, d) visible light irradiation for 15 min, and e) visible light irradiation for 20 min.

are related to the important intermediate species in CO and CH₄ generation, respectively. The presence of strong HCO* signals from the doped HMSs indicates that the reaction paths of photocatalytic CO₂RR over CdS HMSs changed after La³⁺ ion doping. HCOO⁻ and COO⁻ species were preferentially converted to HCO*, which is

one of the intermediates for CH₄. Strong HCO* signal implies that more CH₄ will be produced on CdS:La³⁺ HMSs. In addition, the enhanced peak intensity ratio of CH₃O⁻ groups to COO⁻ species also indicates more CH₄ produced over CdS:La³⁺ than CdS. Therefore, in-situ DRIFTS data further approves that La³⁺ doping can change

reaction pathways of photocatalytic CO₂RR and enhance CH₄ product selectivity of CdS HMSs.

To further confirm the role of the oxophilic surface of photocatalysts on the product selectivity in CO₂RR, we modulated the surface oxophilicity of a broad range of photocatalysts by introducing different dopants with different oxophilicity. To address the potential influence of doping concentration on CH₄ selectivity, we prepared the samples with different doping concentrations and the samples with optimal doping concentration were used for comparison. According to DFT calculations on a quantitative scale of oxophilicities $\theta(M)$ proposed by Kepp [29], θ values for La, Cd, and Au are 1.0, 0.2, and 0, respectively. As seen from the above photocatalytic CO₂RR results, CH₄ selectivity was enhanced after Cd²⁺ ions of CdS HMSs were partly replaced by La³⁺ ions with higher oxophilicity. On the contrary, when Au³⁺ ions with low oxophilicity were doped in CdS HMSs (Fig. S13–17), the yield of CO significantly increased and reduced CH₄ production was observed (Fig. 7a). Specifically, CH₄ selectivity was decreased from 77 % to 59 % at the optimal doping concentration. This result is also consistent with reported single Au atom modified CdS and Ni²⁺ ion doped

CdS that mainly produced CO during photocatalytic CO₂RR process [34,35].

Significantly, it was found that oxophilic La³⁺ ion doping is a general strategy to enhance activity and selectivity of photocatalytic CO₂RR toward CH₄ for various common photocatalysts such as ZnO nanoparticles (Fig. S18–20), SnS₂ nanosheets (Fig. S21–23), BiVO₄ hollow nanoplates (Fig. S24–26), BiOBr nanoplates (Fig. S27–29), TaON (Fig. S30–32), and CsPbBr₃ (Fig. S33–35) (Table S2). Furthermore, as seen from Fig. 8, the larger the positive oxophilicity difference between the dopant ion and the host metal element in the photocatalysts, the more significant enhancement in CH₄ selectivity was obtained (Table S3). It should be pointed out that enhanced CH₄ selective as the function of oxophilicity can also be abided by the samples with the same dopant concentration (Table S4–5, Fig. S39). If the metal ion in the host semiconductor photocatalyst has similar oxophilicity to that of La³⁺ ion, the La³⁺ ion doping only has a small effect on product selectivity. For example, La³⁺ doped TiO₂ (Fig. S36–38) showed similar product selectivity to that of pristine TiO₂ (Fig. 7b) due to the similar oxophilicity between La³⁺ and Ti⁴⁺. However, for La³⁺ ion doped

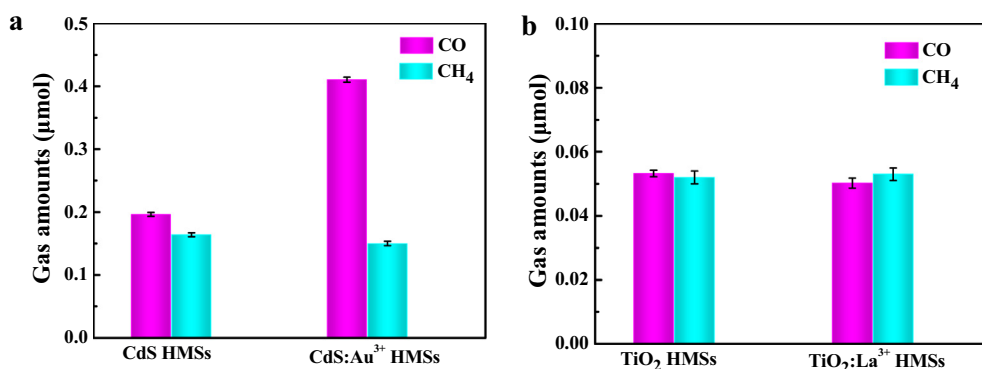


Fig. 7. CO and CH₄ gases evolution amounts over photocatalysts with different oxophilicity difference between the dopant ion and the host metal element under the optimal doping concentrations: CdS HMSs and CdS:La³⁺ HMSs (a), TiO₂ and TiO₂:La³⁺ nanoparticles (b).

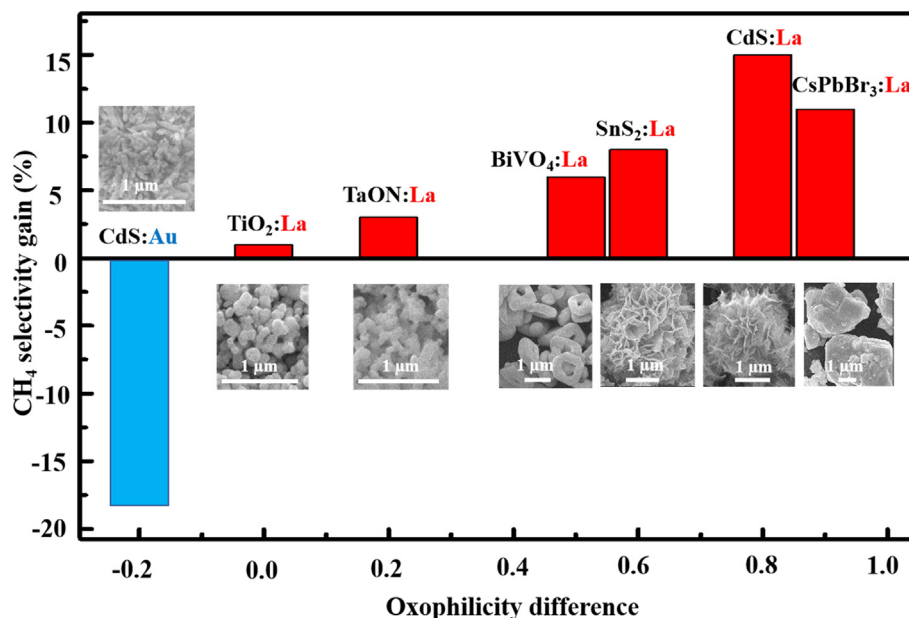


Fig. 8. The influence of oxophilicity difference between host metal elements and dopants in photocatalysts on CH₄ selectivity of CdS:La, TiO₂:La, TaON:La, BiVO₄:La, SnS₂:La, CdS:La, and CsPbBr₃:La (from left to right). The insets show the SEM images of corresponding doped photocatalysts with the same order from left to right side.

CdS and CsPbBr₃ with larger oxophilicity differences between original metal sites and dopants (a difference of 0.9 between Pb and La and 0.8 between Cd and La), greater CH₄ selectivity was achieved (15 % for CdS:La³⁺ and 11 % for CsPbBr₃). The lower CH₄ selectivity gained for La³⁺ ions doped into CsPbBr₃ than that of CdS:La³⁺ might be due to the different bonding environments within the host lattice; especially considering the soft ionic nature of CsPbBr₃ (tested in pure organic phase, see Table S1 for details) [36], while CdS is largely covalent (tested in aqueous/organic phase). Further in-depth studies of the mechanism including the bonding, bandgap, size, and shape-dependent CH₄ selectivity are underway. However, the current results indicate that oxophilic doping is a general strategy to enhance CH₄ selectivity of photocatalytic CO₂RR. It is expected that more efficient photocatalysts with higher selectivity during CO₂RR could be developed through more elaborately designed oxophilic surfaces of the photocatalysts.

4. Conclusions

In summary, we have demonstrated that doping oxophilic La³⁺ ions increase both photocatalytic CO₂RR activity and CH₄ selectivity of the CdS HMSs photocatalysts. The enhanced photocatalytic CO₂RR activity of CdS:La³⁺ HMSs is attributed to improved photo-generated charge separation and transfer efficiency, as well as greater CO₂ adsorption capacity. Theoretical calculations indicate that the oxophilic La³⁺ ion dopants can 1) increase the energy barrier of CO* desorption and thus facilitate subsequent hydrogenation process, and 2) promote the breakage of C–O bonds and the desorption of CH₄. As a result, higher CH₄ selectivity was achieved by the introduction of oxophilic La³⁺ ions to the CdS:La³⁺ HMSs. Furthermore, enhanced CH₄ selectivity can be achieved by doping oxophilic La³⁺ ions into various known photocatalysts such as ZnO, SnS₂, BiOBr, BiVO₄, TaON, and CsPbBr₃, demonstrating the general strategy to enhance CH₄ selectivity of photocatalytic CO₂RR through increased surface oxophilicity of the photocatalysts. The present study not only provides a new strategy for enhancing activity and selectivity of photocatalytic CO₂RR but also sheds light on the importance of surface oxophilicity engineering of the photocatalysts.

Data availability

No data was used for the research described in the article.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jcat.2022.10.004>.

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