

Bifunctional Co active site on dilute CoCu plasmonic alloy for light-driven H₂ production from methanol and water

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Abstract:

Catalytic H₂ production from CH₃OH and H₂O is acknowledged as a promising strategy in the growth of future hydrogen economy, yet its industrialization still faces significant challenges of substantial energy consumption. To overcome the high barrier of CH₃OH/H₂O activation, we report a low-cost plasmonic Co–Cu alloy catalyst for producing H₂ efficiently through a light-driven process, bringing an outstanding generation rate (6225.1 μmol g⁻¹ min⁻¹) without external thermal energy input. The bifunctional nature of Co active site on Cu favors the adsorption of CH₃OH and lowers the energy barrier for H₂O dissociation simultaneously. Moreover, the Co–Cu interface exploits the hot-carrier-induced reactant activation upon visible light irradiation, enormously decreasing the apparent activation energy from 100.8 to 68.2 kJ mol⁻¹. Our study unveils a novel method to harness renewable solar energy for H₂ production, and will provide numerous opportunities for constructing a robust and sustainable catalytic process.

Keywords: CoCu plasmonic alloy, Solar-driven reaction, Methanol activation, Water activation, Hydrogen Production

1. Introduction

Given the significant energy and environmental issues associated with conventional fossil fuels, it becomes an essential task for searching a clean and

renewable energy alternative, particularly in the current context of the appeal for carbon neutrality [1-3]. Hydrogen (H_2) stands out as a green energy carrier and exhibits the potential for sustainable utilization [4-7], but is somewhat limited by drawbacks of large-scale storage and transportation [8, 9]. In order to resolve these shortcomings, on-demand H_2 production from a stable and bio-renewable liquid was proposed, which utilizes methanol (CH_3OH) as an ideal liquid organic hydrogen carrier (LOHC) and releases H_2 with a high storage density in the process of reforming with H_2O vapor (methanol steam reforming, MSR) [10-12]. The state-of-the-art procedures for MSR using catalysts based on earth-abundant elements (e.g., copper-based and nickel-based materials) typically require relatively high reaction temperatures (250–350 °C) [13, 14]. Although some advances have been made in low temperature region, the noble-metal-catalysts and/or high reaction pressure are needed to break kinetic limitations (e.g., activating C–H and O–H bond of CH_3OH and H_2O , respectively) [10, 15, 16]. The development of an affordable and facile catalytic process for MSR holds paramount importance, which involves the construction of advanced non-noble-metal-based catalysts capable of using renewable stimulus.

The natural sunlight shows the prospect to mitigate the reliance on un-renewable fossil fuels [17-19]. Recent pioneering researches exemplified that the solar light can be harnessed by plasmonic metal-based materials (e.g., Au, Ag, and Cu) for driving surface catalytic reactions through the contribution of photo-induce local heating and/or energetic hot carriers [20-24]. A range of

energy-demanding reactions, which were originally driven by the thermal-energy, have been explored using plasmonic photocatalysis (e.g., N_2 fixation [25, 26], and CO_2 reduction [27-29]), delivering even superior performance compared to thermocatalytic counterparts [30]. In order to favor the hot carriers-induced bond activation process during plasmonic photocatalysis [31], “antenna-reactor” catalysts composing plasmonic nanocrystals (antenna) and surface deposited active site (reactor) has been proposed recently [20]. For instance, our previous work demonstrated the construction of Cu-Zn surface alloy for solar-driven methanol steam reforming [32]. Upon light excitation, surface Zn active sites could pump the hot electrons from Cu to surface H_2O molecules, leaving electron-deficient Cu for activating CH_3OH , thereby enabling a concerted and full activation of surface reactants. Similar geometry design concept can be found in other plasmonic nanostructures, such as Cu-Ru [20], Cu-Pt [33], Al-Pd [34] and Au-Pd [35]. Whilst their impressive catalytic performance, the use of noble metals as catalytically active site indispensably increases the capital cost, which encourages researchers to design non-noble-metal-based plasmonic nanostructures.

Co-based materials demonstrated unique capacity for adsorption and partial dissociation of carbon species, and therefore are generally considered to be active for synthesizing C_{2+} products through CO_2 hydrogenation or Fischer-Tropsch process [36-38]. Furthermore, recent research proved that atomic-dispersed Co site could also serve as co-catalyst that are highly active for H_2O

reduction [39]. These previous findings inspire us to introduce Co active site into Cu as a secondary metal, which could potentially influence the binding strength of some critical adsorbates as well as to facilitate the H₂O activation, enabling an efficient H₂ production [40, 41].

In this work, a highly dilute CoCu plasmonic alloy (Co_{0.08}Cu_{99.92}) was reported, which delivered an outstanding catalytic activity for solar-driven MSR with a H₂ generation rate of 6225.1 μmol g⁻¹ min⁻¹ (without external thermal energy input). We found that with the concerted contribution of both photo-induced charge carriers and Co active sites, the apparent activation energy was decreased from 100.8 to 68.2 kJ mol⁻¹. *In-situ* investigations combined with finite difference time domain (FDTD) simulation and density functional theory (DFT) calculations revealed that the introduction of Co in Cu can promote CH₃OH adsorption and H₂O dissociation by the local polarization, and the hot carriers further stimulate the conversion of both CH₃OH and H₂O at Co–Cu interface. These findings expand the horizons of research focused on the development of cost-effective Cu-based catalyst systems, which can be utilized for the MSR and other energy-demanding reactions upon solar irradiance.

2. Experimental section

2.1 Synthesis of Cu and CoCu plasmonic catalysts

Wet chemistry method using NaBH₄ as reducing agent was employed to fabricate Cu and CoCu alloy nanoparticles (NPs). For the fabrication of Cu,

firstly, a mixture was prepared by combining 20 ml of ascorbic acid (0.1 M) with 100 ml $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.01 M) and PVP (molar ratio of Cu to PVP=50:1) solution. NaBH_4 aqueous solution (10 ml, 0.1 M), serving as reducing agent, was added into above mixture, followed by adding 500 mg of SiO_2 as inert support for NPs. The solution was stirred for 30 minutes and subsequently ultrasonicated for 10 minutes. After reaction completed, the precipitate was separated from the solution through centrifugation, washed by ultrapure water and dried overnight at 70 °C. Then, the catalysts were calcinated in air at 350 °C for 4 hours. The synthesis method of CoCu NPs is similar to that of Cu, but with the inclusion of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as the source of Co. Before activity measurement and characterization, the catalysts were subjected to a reduction process in a H_2 atmosphere at 350 °C, resulting in the formation of SiO_2 -supported metallic Cu or CoCu NPs (referred to as Cu or CoCu, hereafter). For comparison, impregnation method was employed to fabricate SiO_2 -supported noble-metal-based catalysts, including 1.0 wt.% of Pt, Pd and Au.

2.2 Photocatalytic activity measurement

The solar-driven MSR reaction was conducted using solar energy. AM 1.5 light was utilized as illuminant, and the diameter of irradiation was 10 mm. The surface temperature of catalysts upon light irradiation was recorded by thermocouple. Before measurement, the materials were reduced in a H_2 atmosphere. The gaseous reactants were bubbled into reaction chamber

through a CH₃OH/H₂O solution (volume ratio 1/1) with a flow rate of 50 ml min⁻¹.

Gas chromatography (GC) equipped with thermal conductivity detector (TCD) and flame ionization detector (FID) were employed to quantify the products. The solar energy conversion efficiency can be evaluated as below:

$$\eta = \frac{\alpha \text{ (mol}\cdot\text{s}^{-1}) \times \Delta H_{\text{MSR}}^0 \text{ (J}\cdot\text{mol}^{-1})}{\text{light power (J s}^{-1})} \times 100\% \quad (1)$$

where ΔH_{MSR}^0 is the standard reaction enthalpy changes of MSR (48.97 kJ mol⁻¹).

The photo-assisted thermocatalytic MSR was characterized by a self-made photo-assisted thermocatalytic reactor to probe the underlying mechanism of Co active sites and photo-induced hot carriers. LA-251 Xe lamp coupled with optical filters (HA30 and L42) was used to provide visible light irradiance, and the light was introduced into the reactor through a quartz window with irradiation diameter of 8.5 mm. The desired temperature of the catalyst was regulated by a resistive heater managed by a temperature controller. 5 mg catalyst was *in-situ* reduced in a H₂ atmosphere at 350 °C, afterwards, the Ar was injected into the reactor to remove the H₂ before reaction started. During reaction, the space velocity of gaseous reactants was 30 ml min⁻¹, and the measurement method of products was as same as in solar-driven catalysis.

2.3 Catalyst characterizations

The contents of Cu and Co in catalysts were analyzed by an inductively

coupled plasma optical emission spectrometer (ICP-OES, Agilent 5110). The ultraviolet-visible absorption spectra were obtained using a UV-vis spectrophotometer (UV-2600, Shimadzu). X-ray diffraction (XRD) patterns and surface electronic states were acquired by an X-ray powder diffractometer with Cu K α radiation (PANalytical) and X-ray photoelectron spectroscopy (XPS, Escalab 250 Xi, Thermo Scientific), respectively. Transmission electron microscopy (TEM) and high-resolution TEM images were conducted on a spherical aberration (Cs-corrected) TEM (JEOL JEM ARM 200F). Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) analysis was operated on a FT-IR-6300 system (JASCO Corp.), which is equipped with an *in-situ* cell and a liquid nitrogen-cooled mercury-cadmium-telluride (MCT) detector.

Details for *in-situ* DRIFTS measurement and theoretical calculations are available in the supplementary information.

3. Results and discussion

3.1 Catalyst characterization

Pristine Cu and a series of highly dilute CoCu plasmonic alloy NPs, with atomic ratios of Co (Table S1) ranging from 0.04% to 0.15% (named as Co_{0.04}Cu_{99.96}, Co_{0.08}Cu_{99.92}, and Co_{0.15}Cu_{99.85}, respectively), were deposited on inert SiO₂ supporter through wet chemistry method. TEM and STEM images show that Co_{0.08}Cu_{99.92} NPs were supported by SiO₂ with an average diameter of 3 nm (Fig. 1a and Fig. S1). Lattice fringe of 0.21 nm assigned to (111) plane of Cu

indicates that introducing a trace amount of Co did not change the lattice spacing enormously (Fig. 1b). No aggregation of Co species verifies the formation of a random CoCu alloy, which is further supported by a nearly homogeneous distribution of Co on a single $\text{Co}_{0.08}\text{Cu}_{99.92}$ nanoparticle from STEM energy dispersive X-ray spectrometry (STEM-EDS) mapping (Fig. 1c-f). The X-ray diffraction (XRD) patterns (Fig. 1g) further reveal that Cu and CoCu alloy all displayed similar diffraction peaks of metallic Cu. No peaks corresponding to Co were observed, which could be attributed to high dispersion and low concentration of Co in Cu.

Surface structures of Cu and $\text{Co}_{0.08}\text{Cu}_{99.92}$ NPs were analyzed by *in-situ* diffuse reflectance infrared spectroscopy using CO as probe molecules (*in-situ* CO DRIFTS). Upon CO adsorption on Cu, two peaks appeared at 2170 and 2128 cm^{-1} , which could be assigned to the R branches of gaseous CO and atop binding of CO on Cu NPs, respectively (Fig. 1h) [42]. Compared to pristine Cu, the CO DRIFTS of $\text{Co}_{0.08}\text{Cu}_{99.92}$ sample display an additional shoulder peak at 2088 cm^{-1} , indicating linearly coordinated CO to metallic Co center on the surface of the Cu catalyst (Fig. 1i) [43]. The high-resolution Cu 2p X-ray photoelectron spectroscopy (XPS) spectra of pristine Cu displays the binding energy of Cu 2p_{3/2} peak at 932.5 eV without noticeable satellite peaks, indicating the formation of metallic Cu (Fig. 1j) [44]. Compared to Cu, the Cu 2p_{3/2} peak of $\text{Co}_{0.08}\text{Cu}_{99.92}$ slightly shifts towards a lower value (0.1 eV, located at 932.4 eV), which might relate to electronic interaction between Cu and Co species. The

peak of Co $2p_{3/2}$ locating at 780.0 eV could be attributed to metallic Co (Fig. 1k) [45]. Above structural and chemical characterization results concertedly suggest the existence of Co atoms on the surface of Cu, forming CoCu alloy. Strong localized surface plasmon resonance (LSPR) absorption peak (approximately 570 nm) can be observed in both pristine Cu and CoCu alloys samples, suggesting that adding small amounts of Co on Cu did not affect the optical property significantly (Fig. 1l).

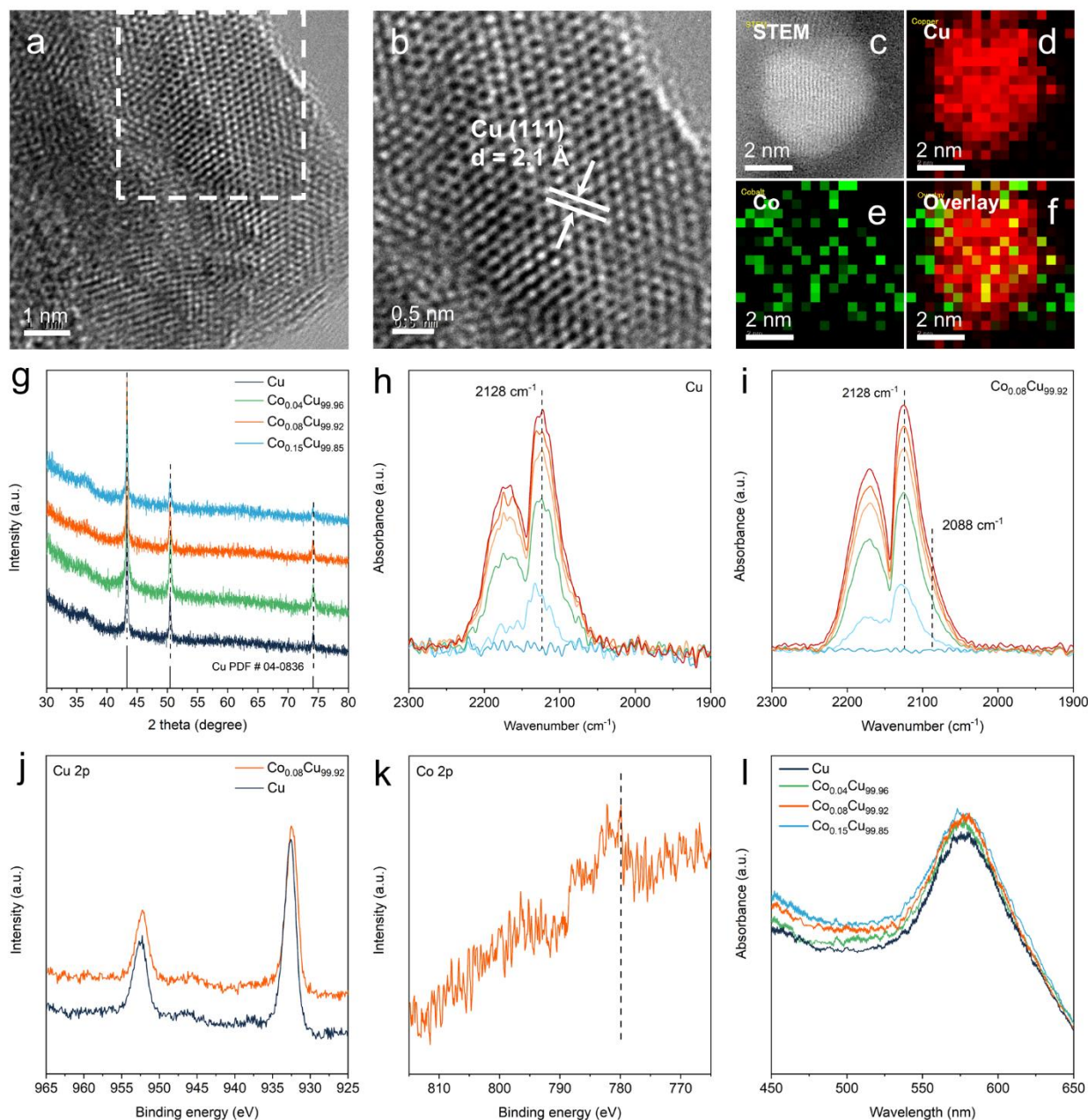


Fig. 1. Structural and chemical properties of Cu and CoCu plasmonic alloy catalysts. (a) TEM image of $\text{Co}_{0.08}\text{Cu}_{99.92}$. (b) HR-TEM image of $\text{Co}_{0.08}\text{Cu}_{99.92}$. (c-f) STEM-EDS mapping of $\text{Co}_{0.08}\text{Cu}_{99.92}$. (g) XRD patterns of Cu and CoCu catalysts. The catalysts were treated using sacrificial support method, followed by H_2 reduction. (h and i) CO-DRIFT spectrum of pristine Cu and $\text{Co}_{0.08}\text{Cu}_{99.92}$, respectively. (j) XPS Cu 2p spectra of Cu and $\text{Co}_{0.08}\text{Cu}_{99.92}$. (k) XPS Co 2p spectrum of $\text{Co}_{0.08}\text{Cu}_{99.92}$ catalyst. (l) UV-vis absorption spectra of Cu and CoCu

catalysts.

3.2 Solar-driven MSR over CoCu plasmonic catalysts

Solar-driven catalytic MSR was carried out on a solar-driven reactor (Fig. S2) to manifest the catalytic behavior of plasmonic Cu and CoCu alloy catalysts. A concentrated solar light simulated by AM 1.5G illuminant was used as the irradiance (Fig. S3). As shown in Figure 2a, the temperature and light intensity of pure Cu and CoCu alloy catalysts all display positive correlations under light irradiation. The highest surface temperature of 253 °C was detected at a maximum light intensity. Nevertheless, unlike surface temperature, the Cu and CoCu alloy catalysts deliver substantially distinct catalytic behavior under identical light irradiation condition (Fig. 2b). All CoCu alloy catalysts exhibit higher catalytic performances compared to pure Cu, especially for the alloy catalyst $\text{Co}_{0.08}\text{Cu}_{99.92}$, which displays the highest H_2 generation rate of $6225.1 \mu\text{mol g}^{-1} \text{min}^{-1}$ ($373.5 \text{ mmol g}^{-1} \text{h}^{-1}$). The addition of excessive Co in Cu did not further facilitate the reaction, which might suggest a cooperative contribution of Co/Cu dual active site in the optimized catalysts (Fig. 2b).

Compared to conventional photocatalytic or thermocatalytic processes under even higher reaction temperatures, $\text{Co}_{0.08}\text{Cu}_{99.92}$ demonstrated an outstanding catalytic performance (Table S2). The solar-to-energy conversion efficiency exhibits a progressive enhancement with the increasing light intensity, reaching a maximum value of 1.4% for $\text{Co}_{0.08}\text{Cu}_{99.92}$, which is approximately

three times of that pristine Cu (Fig. 2c). Furthermore, the catalytic performance of $\text{Co}_{0.08}\text{Cu}_{99.92}$ alloy catalyst presents an order of magnitude higher than that of noble-metal-based materials, which are typically regarded as representative materials for MSR (Fig. 2d). Only a trace amount of undesirable CO was observed on $\text{Co}_{0.08}\text{Cu}_{99.92}$ plasmonic alloy, whereas the Pd/SiO₂ displayed higher selectivity of 53.8% towards CO (Table S3).

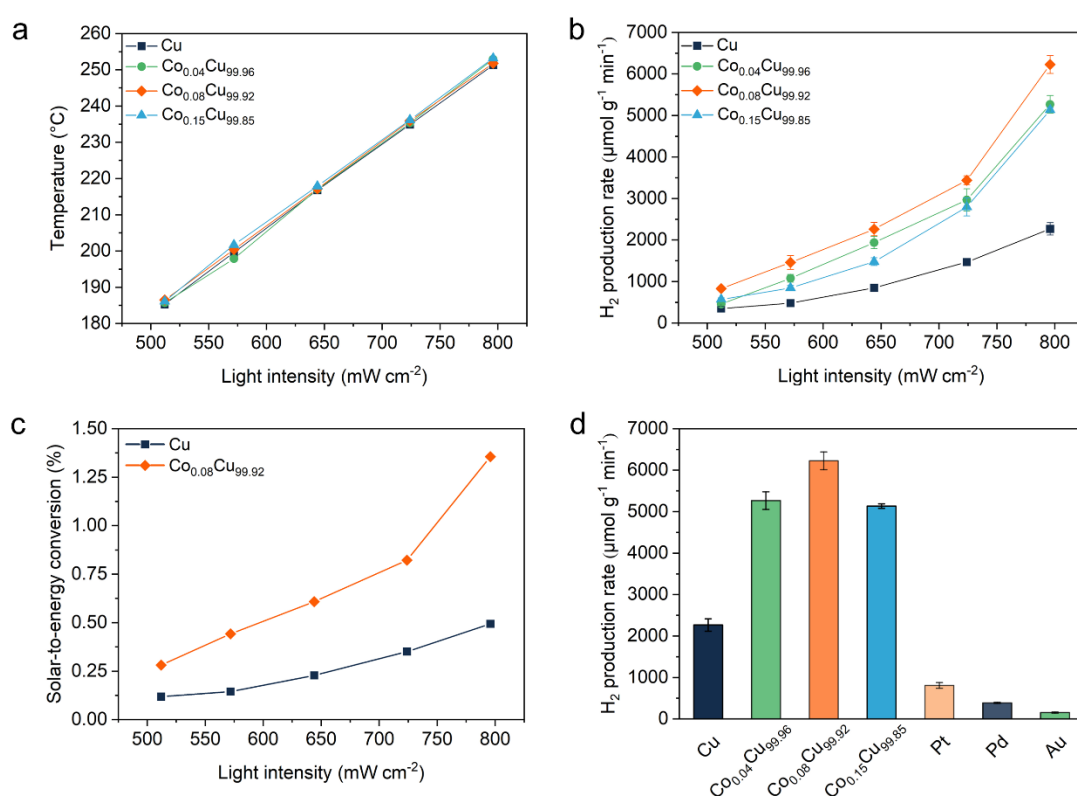


Fig. 2. Catalytic behavior for light-driven MSR. (a) Surface temperature of Cu and CoCu alloy catalysts upon light irradiation. (b) Catalytic performance for solar-driven MSR of Cu and CoCu plasmonic catalysts. (c) Solar-to-energy conversion efficiency of Cu and Co_{0.08}Cu_{99.92}. (d) Catalytic performance of pristine Cu, CoCu alloy, and noble-metal-based catalysts.

3.3 Contribution of hot carriers during MSR

To probe the contribution of hot-carriers during reaction, photo-assisted thermal catalytic MSR was executed. In order to alleviate the influence of photothermal heating, only visible light ($420 < \lambda < 720$ nm, 423.6 mw cm^{-2}) was irradiated on the catalysts (Fig. S4). Under dark condition, reaction rate of pure Cu increases with the rising reaction temperature, reaching a maximum value of $460.1 \mu\text{mol g}^{-1} \text{ min}^{-1}$ at $220 \text{ }^\circ\text{C}$ (Fig. 3a). Adding a small amount of Co can promote the reaction effectively (Fig. 3a), and a H_2 generation rate of $715.9 \mu\text{mol g}^{-1} \text{ min}^{-1}$ is observed at $220 \text{ }^\circ\text{C}$, indicating that Co could serve as an additional active site to activate CH_3OH or H_2O towards MSR. Under visible light irradiation, the catalytic performances of both Cu and $\text{Co}_{0.08}\text{Cu}_{99.92}$ plasmonic alloys are enormously enhanced, with a much higher yield of H_2 ($2532.9 \mu\text{mol g}^{-1} \text{ min}^{-1}$) for $\text{Co}_{0.08}\text{Cu}_{99.92}$ (Fig. 3a). The rate enhancement under light irradiation demonstrates its superiority at lower temperatures, as evidenced by the decline in the enhancement of reaction rate for $\text{Co}_{0.08}\text{Cu}_{99.92}$ from 5.1 to 3.5 times as the temperature rose from 180 to $220 \text{ }^\circ\text{C}$ (Fig. S5), whereas the disparity in H_2 production rates increases with the rise in temperature (Fig. S6). We propose that the observed visible-light-enhanced activity might be attributed to the hot carriers from plasmonic Cu, and this assumption is further verified by the linear dependence between reaction rate and light intensity (Fig. 3b and Fig. S7 for the output irradiance of visible light in different intensities) [46].

To unravel the intrinsic reaction mechanism of both Co active sites and

photo-induced charge carriers, the reaction kinetics of MSR under different reaction conditions were investigated. Through fitting of conversion rates using the Arrhenius plot ($\ln r = -E_a/RT + \ln A$), we calculated the apparent activation energy (E_a) (Fig. 3c). The E_a of pristine Cu in the absence of light is $100.8 \text{ kJ mol}^{-1}$, and decreases to 86.6 kJ mol^{-1} after introduction of Co, verifying that Co active site could facilitate the rate determining step of MSR (Fig. 3c). Adding visible light leads to an enormous decrease of E_a (68.2 kJ mol^{-1}), further illustrating a distinctive role of visible-light-induced hot carriers beyond simple photothermal heating (Fig. 3c). The contribution of hot carriers during reaction is further supported by the irradiation of monochromatic light (Fig. S8) at $220 \text{ }^\circ\text{C}$. As shown in Fig. 3d, the tendency of the apparent quantum efficiency (AQE) matches well with the light absorption spectra of $\text{Co}_{0.08}\text{Cu}_{99.92}$ plasmonic alloy, indicating the enhanced catalytic performance under visible light irradiation can be attributed to the excitation of LSPR [47]. In addition, no obvious loss in catalytic performance under both dark and light condition was observed after 5 h reaction (Fig. S9), and nearly unchanged structure of spent catalysts confirms a good stability of the $\text{Co}_{0.08}\text{Cu}_{99.92}$ alloy catalysts (Fig. S10).

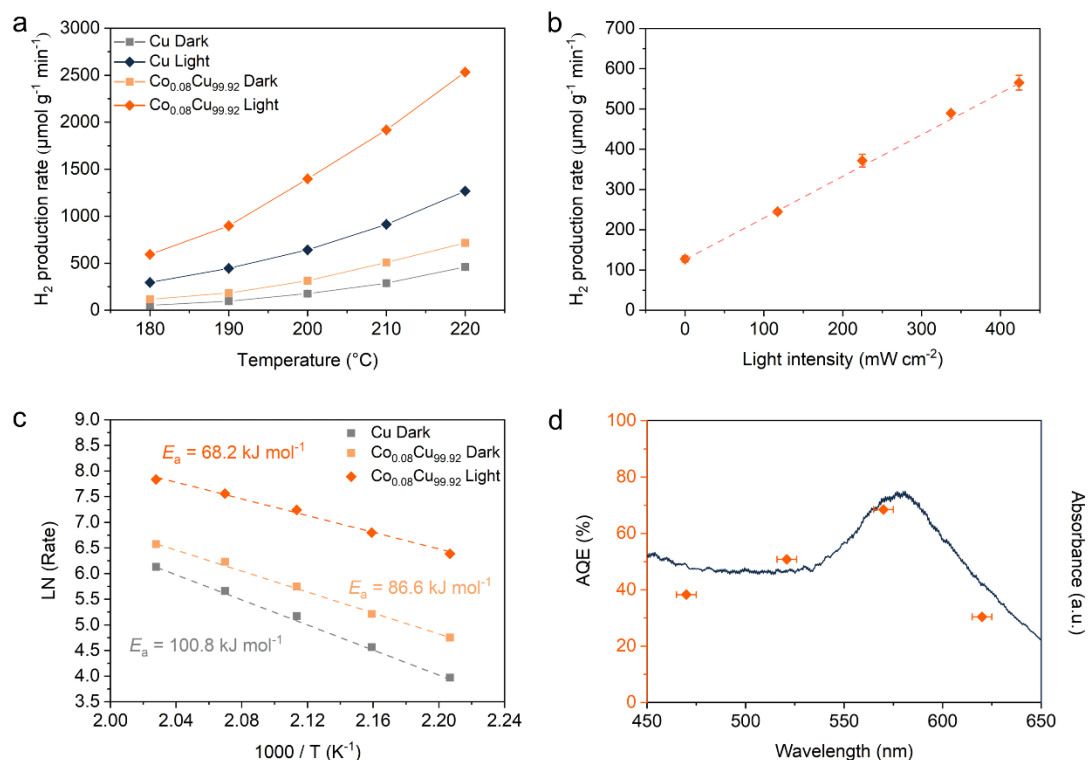


Fig. 3. Contribution of hot carriers during photo-assisted MSR. (a) Catalytic behavior of Cu and Co_{0.08}Cu_{99.92} under the dark and light condition at different temperatures. (b) Dependence of H₂ generation rate of Co_{0.08}Cu_{99.92} on light intensity at 180 °C. (c) Arrhenius plots for reaction rate under different conditions. (d) Light absorption spectrum of Co_{0.08}Cu_{99.92} and corresponding AQE value measured at 220 °C with monochromatic light irradiation.

3.4 Reaction mechanism of MSR over CoCu plasmonic alloy

To provide a deeper insight into the LSPR effect of plasmonic Cu and Co_{0.08}Cu_{99.92}, finite-difference-time-domain (FDTD) simulations were conducted. As demonstrated in Fig. 4a, under the irradiation of visible light, spatially non-homogeneous distribution of local electric field emerges around the Cu NPs, and these electric field is further intensified in the interstitial position between

each plasmonic NPs, forming “hot spots” that could yield higher rates of energetic charge-carrier formation [48]. As the wavelength of monochromatic light increased from 470 to 670 nm, the electric field enhancement firstly maximizes at 570 nm, followed by a decrease in the higher wavelength region. This tendency matches well with light absorption spectrum and corresponding AQE values (Fig. 3d), indicating that the light excitation at 570 nm might play a significant role in facilitating the reactant conversion. The addition of a small amount of Co did not modify the tendency of electric field enhancement on Cu enormously (Fig. 4a). We propose that hot carriers are generated through the decay of LSPR of Cu, and these charge carriers have the potential to participate in the surface reaction through the surface dispersed Co active sites.

The influence of hot carriers on the MSR intermediates was studied using *in-situ* DRIFTS measurements on $\text{Co}_{0.08}\text{Cu}_{99.92}$ under purely thermocatalytic condition or with visible light irradiation at 200 °C (Fig. 4b). Characteristic rotational vibration of gaseous CO_2 can be observed at around 2360 cm^{-1} [32]. The C–H vibrations of Si– OCH_3 species appear at 2856 cm^{-1} [49]. As the reaction proceeded, two sets of peaks gradually emerge, which can be assigned to HCOO^* (2970 , 1595 , and 1371 cm^{-1}) [50] and HCHO^* (1720 and 1410 cm^{-1}) [32], respectively. The existences of these intermediates indicates that the MSR mainly proceeded through formate pathway. Upon light irradiation, the peak increment of CO_2 (2360 cm^{-1}) became more evident (Fig. 4b), in accordance with the observed rate enhancement under light condition. The absence of

external absorption peaks following light exposure indicates that the photo-induced charge carriers mainly serve to accelerate the conversion of surfactants.

On the basis of the aforementioned *in-situ* spectroscopic investigations, density functional theory (DFT) calculations were subjected to construct a comprehensive Gibbs free energy diagram. Two surface models, namely Cu (111) and Co–Cu (111) surfaces, were firstly constructed, and their energy barriers of each elementary step for MSR were depicted in Fig. 4c. Building upon the references over Cu-based catalysts [51], the sequential steps of the MSR can be elucidated as follows: initially, the adsorbed CH₃OH species undergo dissociation, forming CH₃O* species, which is subsequently dehydrogenated into CH₂O* via C–H bond activation. The CH₂O* species interacting with OH* which is generated from H₂O dissociation produces CH₂OOH*. Further dehydrogenation of CH₂OOH* leads to the formation of HCOOH*, which could finally decompose into CO₂ and H₂. Notably, on the CoCu surface, the dissociative adsorption of CH₃OH is highly exothermic, indicating the introduction of Co active sites favors the CH₃OH adsorption and subsequent dissociation (Fig. 4c). The strong endothermic nature in the processes of CH₃O* → CH₂O* + H* (C–H bond activation) and H₂O* → OH* + H* (H₂O dissociation) suggests the critical role in activating both CH₃OH and H₂O molecules for improving the catalytic performance. Interestingly, adding Co active sites slightly reduces the C–H bond activation energy of Cu (1.39 vs 1.56 eV), indicating that the C–H bond activation of CH₃O* species might be

favorable with the assistance of surface Co, whilst such a process is dominantly controlled by Cu active site. Furthermore, it is worthy of note that, for the water dissociation, the reaction energy for activating O–H bond on pristine Cu (0.91 eV) is much higher than that of CoCu surface (0.07 eV), revealing a decisive role of Co active site in activating H₂O molecules.

Above DFT calculation suggests that the activation of both CH₃OH and H₂O molecules is of pivotal importance for MSR with positively high Gibbs free energies, and the surface Co active sites greatly facilitate dissociative adsorption of CH₃OH and the H₂O activation. In order to disclose the reason for the reduced energy barrier of the key elementary step of H₂O dissociation over Cu–Co dual active sites, charge density difference was simulated using Bader charge analysis. Fig. 4d compares the charge density difference as well as bond length of O–H in H₂O* adsorbed on pristine Cu and CoCu substrate, respectively. Theoretically, the prolonged bond length weakens the corresponding bond strength, leading to bond activation [52]. Indeed, in comparison to H₂O* on Cu (average O–H bond length of 0.950 Å), the O–H bonds are greatly elongated on CoCu surface with an average bond length of 0.982 Å, suggesting the interactions between H₂O* and surface Co sites facilitates the activation of O–H bond for water dissociation. From the perspective of atomic charges, the adsorption of H₂O on CoCu surface significantly redistributes the charges of H₂O, and the substantial difference of atomic charges in H1 and H2 could lead to the local polarization, thereby facilitating the dissociation of H₂O molecules.

irradiation with different wavelengths. (b) *In-situ* DRIFTS spectra of $\text{Co}_{0.08}\text{Cu}_{99.92}$ under dark and light conditions at 200 °C. (c) Calculated Gibbs free energy diagram for MSR over Cu (111) and Co-atoms-substituted Cu (111) surfaces. (d) Bader charge analysis of optimized structure during H_2O adsorption on surface of Cu and Co-atoms-substituted Cu surface, respectively. H_2O molecule is adsorbed on Co atom on CoCu surface.

Our mechanistic investigations sculpture a comprehensive picture of Co–Cu bimetallic active site, elucidating how it functions as an efficient catalyst for MSR under light irradiation. The Co active site exhibits a superior capacity in adsorbing CH_3OH , enabling a smooth production of $^*\text{CH}_2\text{O}$ species through C–H bond activation at the interface between Cu and Co. Moreover, considering the distinctive role of Co towards H_2O activation, the produced $^*\text{CH}_2\text{O}$ intermediates could be subsequently converted through the interaction with $^*\text{OH}$ (product of H_2O activation), rendering a more rapid surface catalytic transformation. Visible light irradiation can further amplify the reaction by exciting hot electrons from plasmonic Cu to Co active sites to activate corresponding $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ molecules. The cooperative bond activation processes, together with charge transfer and photothermal heating, concertedly contribute to an outstanding performance of solar-driven photocatalysis over CoCu alloy catalyst.

4. Conclusion

In conclusion, a CoCu bimetallic alloy catalyst with a high dispersion of Co active site on plasmonic Cu was successfully synthesized. The CoCu catalyst exhibited an outstanding activity for solar-driven methanol steam reforming, delivering a H₂ production rate of 6225.1 μmol g⁻¹ min⁻¹. Detailed experimental and theoretical investigations, including *in-situ* DRIFTS studies and various DFT simulations, suggested that surface Co active site favored the CH₃OH adsorption and H₂O activation simultaneously. Hot electrons produced by LSPR of Cu could further promote the CH₃OH/H₂O activation on dual Co–Cu active sites, thereby enhancing the kinetics of H₂ production at Co–Cu interface. Our study unveils a novel and highly effective method for harnessing renewable solar energy to produce H₂ from CH₃OH and H₂O, thus expanding the horizons of research focused on developing alloy materials for sustainable H₂ production from various biomass-derived hydrogen carriers.

CRedit authorship contribution statement

Wen-Ning Lu: Investigation, Formal analysis, Validation, Writing – original draft, Writing – review & editing, Funding acquisition. **Shunqin Luo:** Conceptualization, Supervision, Formal analysis, Writing – review & editing. **Yibo Zhao:** Formal analysis, **Jianbing Xu:** Formal analysis. **Emmanuel Picheau:** Formal analysis, Writing – review & editing. **Minmin Han:** Formal analysis. **Qi Wang:** Methodology, Software, Writing – original draft. **Sijie Li:**

Formal analysis. **Ming-Xing Ling**: Supervision, Writing – review & editing. **Tetsuya Kako**: Resources. **Jinhua Ye**: Project administration, Supervision, Resources, Funding acquisition, Writing – review & editing.

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. Supporting information

Supplementary data related to this article can be found, in the online version, at doi:

Reference

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