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Tunable Syngas Production from Photocatalytic CO₂ Reduction with Mitigated Charge Recombination Driven by Spatially Separated Cocatalysts

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Photocatalytic CO₂ reduction represents a sustainable route to generate syngas (the mixture of CO and H₂), which is a key feedstock to produce liquid fuels in industry. Yet this reaction typically suffers from two limitations: unsuitable CO/H₂ ratio and serious charge recombination. This paper describes the production of syngas from photocatalytic CO₂ reduction with tunable CO/H₂ ratio via adjustment of component and surface structure of CuPt alloys and construction of a TiO₂ mesoporous hollow sphere with spatially separated cocatalysts to promote charge separation. Unlike previously reported cocatalysts-separated hollow structures, we firstly create a reductive outer surface that is suitable for CO₂ reduction reaction. A high evolution rate of 84.2 μmol h⁻¹ g⁻¹ for CO and a desirable CO/H₂ ratio of 1:2 are achieved. The overall solar energy conversion yield is 0.108%, which is higher than traditional oxide and sulfide based catalysts (generally about 0.006% ~ 0.042%). Finally, density functional theory calculations and kinetic experiments by replacing H₂O with D₂O reveal that the enhanced activity is mainly determined by the reduction energy of CO*, and can be affected by the stability of COOH*.

Introduction

Fossil fuels play a pivotal role in energy supply and production, while such sources are unsustainable because of the finite amounts and the massive emission of CO₂. Typically, CRR can produce various valuable chemical fuels, among which syngas (synthesis gas, the mixture of CO and H₂) is a critical feedstock to produce synthetic liquid fuels via established industrial process (e.g., Fischer-Tropsch synthesis). However, in industrial process, unsuitable CO/H₂ ratio often limit the practical applications of synthesis. Thus it is critical to precisely control the CO/H₂ ratio from photocatalytic CRR. To achieve this goal, proper catalysts with suitable chemical composition and surface properties are desired. Furthermore, fundamental understanding of reaction processes and energetic changes in every elementary step is also significant.

Another limitation for the photocatalytic CRR lies in the severe recombination of photo-induced charge carriers (electrons and holes). Many strategies have been developed to solve such an ineluctable problem in photocatalytic reactions. Typically, junctions between different materials, phases or crystallographic planes have been constructed to enhance charge separation. However, interfaces between different materials will create recombination centers, which greatly restricts the efficiency of charge separation. Alternatively, the loading of cocatalysts can serve as traps of charges to promote their separation. Typically, cocatalysts are particles of metals, metal oxides or sulfides deposited on semiconductors, which can be classified into reduction and oxidation cocatalysts. Metal particles (such as Pt, Ag, alloy) often act as the reduction cocatalysts as electron shuttles when their Fermi level lies below the CB of semiconductor and...
above the redox potential of target reaction. On the other hand, metal oxides or sulfides (MnO$_2$, PbO$_2$, and PbS etc.)$^{13,18,19}$ can trap holes, which are often used as the oxidation cocatalysts. Generally, the co-deposition of both reduction and oxidation cocatalysts can trap electrons and holes separately and improve the reduction and oxidation reactions simultaneously. Nevertheless, the simple addition of cocatalysts with a random distribution may increase the possibility of recombination and lead to severe back reactions.$^{15}$ One possible solution is to create catalyst with spatially separated oxidation (hole traps) and reduction cocatalysts (electron traps) based on hollow structures to facilitate charge separation.$^{14,17,20-23}$ For such structures with spatially separated cocatalysts, the overall photocatalytic activity is mainly determined by the property of outer surface, because active sites loaded inside will obstruct mass transportation and may cause severe cross reaction.$^{14,17}$ However, in most previously reported structures, the outer surface are loaded by oxidation cocatalysts,$^{14,17,20-23}$ creating oxidative outer surfaces only suitable for oxidation reactions.$^{14}$ This is because loading oxidation cocatalysts inside uniformly with a high dispersion is a great challenge due to the incompatibility between precursor and template.$^{14,17,20-23}$ Therefore, it is urgent to develop a structure with reductive outer surface suitable for reduction reactions including CRR.

This paper describes the design and fabrication of a structure with reductive outer surfaces, decorated by spatially separated cocatalysts, where oxidation cocatalysts are uniformly dispersed on inner surfaces, which is efficient for photocatalytic CRR. Besides, the CO$_2$/H$_2$O ratio can be adjusted in a large range including the desired 1:2 by changing the component and property of reduction cocatalysts.$^8,9,25$ Specifically, TiO$_2$ hollow spheres, MnO$_2$ and CuPt alloys act as main catalysts, oxidation and reduction cocatalysts, respectively, which is denoted as MnO$_2$@TiO$_2$@CuPt alloy mesoporous hollow spheres (MTCP-MSs, Fig. 1a). Driven by the spatially separated MnO$_2$ particles and CuPt alloys, holes and electrons will flow to opposite directions (Fig. 1b) to enhance the charge-separation efficiency. When these well-separated electrons reach the surfaces of reduction cocatalysts (CuPt alloy) with optimized Cu content, a high catalytic activity with desired CO/H$_2$O ratio will be achieved by adjusting the energy of CO$_2$ activation and CO* desorption during photocatalytic CRR, which can be explained by density functional theory (DFT) calculations and kinetic experiments.

Fig. 1 Schemes of (a) the MTCP-MSs structure and (b) the mechanism for photocatalytic CRR driven by MTCP-MSs. Electrons and holes are induced to opposite directions by spatially separated cocatalysts and the charge separation will be enhanced.

**Results and discussion**

Hard-templating method (using SiO$_2$ spheres as templates and divider to disperse small particles) was used to synthesize the MTCP-MSs.$^{14,17,20-23}$ Before the formation of final structure, the catalysts mainly went through five stages with different morphologies. 1) SiO$_2$-MnO$_2$ nanospheres (SM-NSs). A modified Stöber method was used to prepare the SiO$_2$ nanospheres loaded with MnO$_2$ particles.$^{15}$ In alkaline conditions, KMnO$_4$ was chosen as the precursor and it would be slowly reduced by ethanol to form MnO$_2$ (Fig. S2), ensuring the uniform distribution of MnO$_2$ particles (Fig. 2a, Fig. S3, Fig. S1a and b). The high resolution transmission electron microscopy (HRTEM) image further confirms the existence of MnO$_2$ particles (Fig. S3d). 2) SiO$_2$-MnO$_2$@TiO$_2$ core-shell nanospheres (SMTS-NSs). Subsequently, a layer of TiO$_2$ was uniformly coated on SM-NS by the hydrolysis of titanium tetra- butoxide (TBOT) (Fig. 2b and Fig. S4). 3) SiO$_2$-MnO$_2$@TiO$_2$@SiO$_2$ core-shell nanospheres (SMTS-NSs). Another SiO$_2$ layer was then coated on the outer surface of SMTS-NSs for protection. Without the protective layer, TiO$_2$ shells would be destroyed during the following calcination step (Fig. S1c).$^{26}$ The smooth surfaces shown in Fig. 2c and Fig. S5 suggest the successful coating of SiO$_2$ layer. Uniformly distributed MnO$_2$ particles can also be observed. 4) MnO$_2$@TiO$_2$ mesoporous hollow spheres (MT-MSs). SMT-NSs were then calcined to create mesoporous structure with highly crystallized anatase phase (a crystal type of TiO$_2$ suitable for photocatalysis).$^{26}$ Typically, the crystallization processes from amorphous to anatase and from anatase to rutile occur in the temperature ranges of 450–550 °C and 600–700 °C$^{26}$ respectively. Thus the temperature we adopted at 500 °C can ensure the formation of a pure anatase phase, which can be also evidenced by XRD patterns (Fig. S8). NaOH was used to etch all the SiO$_2$ layers to form MT-MSs (Fig. 2d and Fig. S6). Uniform MnO$_2$ particles are loaded on TiO$_2$ shells (Fig. 2e), which could be confirmed by HRTEM (Fig. S6c). 5) MnO$_2$@TiO$_2$@CuPt alloy mesoporous hollow spheres (MTCP-MSs). This final structure was formed after the loading of CuPt alloy (Fig. 2f). To selectively load CuPt particles uniformly on the outer surface without agglomeration (Fig. S1a), a photodeposition method (Fig. S7) was adopted$^{27}$ under the protection of N$_2$ atmosphere in methanolic solvent, using platinum acetylacetonate and copper acetylacetonate as precursors. Energy dispersive spectroscopy (EDS) mapping (Fig. 2g-i) and HRTEM (Fig. S8a) exhibit the relative position and components of every materials. It is obvious that MnO$_2$, and CuPt particles are selectively loaded on the inner and outer surface of TiO$_2$ hollow spheres. X-Ray Diffraction (XRD) patterns (Fig. S9) evidenced the formation of TiO$_2$ and CuPt alloy. For the low loading and small particle size, the single of MnO$_2$ is not obvious, while can be clearly seen in the HRTEM (Fig. S8a). The loading of CuPt alloy can also be evidenced by the result of X-ray photoelectron spectroscopy (XPS), which
show obviously peaks at the banding energy of 74 eV, 71 eV and 932 eV, representing the Pt4f_{5/2}, Pt4f_{7/2} and Cu2p_{3/2} of CuPt alloy (Fig. S10), matching well with references, indicating the successful loading of CuPt alloy on the outer surfaces. EDS analysis (Fig. S8b) focused on a single CuPt particle (within the dotted circle in Fig. S8a) quantitatively revealed the microscopic composition of CuPt alloy (Cu:Pt = 3.33), consistent with the result of inductively coupled plasma optical emission spectrometer (ICP-OES) (Cu:Pt = 3.17). Thus, the catalysts can be finally denoted as MTC_{3.17-P-MSs} according to the ICP-OES result. HRTEM of MTC_{3.17-P-MSs} with higher resolution are provided (Fig. S8) to show the composition and relative position of CuPt alloy and MnO. By changing the feed ratio of precursors, CuPt alloys with different component ratios were synthesized. The results of EDS at single point (Cu:Pt = 0.35, 1.48, 8.80) (Fig. S11) also consist with respective ICP-OES (Cu:Pt = 0.31, 1.13, 8.72), and corresponding catalysts can be denoted as MTC_{0.31-P-MSs}, MTC_{1.13-P-MSs} and MTC_{8.72-P-MSs}, respectively.

Brunauer-Emmett-Teller (BET) surface areas and pore structures of MTCP-MSs were measured by nitrogen adsorption at 77 K. A type IV (defined by IUPAC in 1984) isotherm along with two hysteresis loops at relative pressures (P/Po) of 0.40-0.66 and 0.86-0.99 were observed (Fig. 3a), indicating the presence of mesopores in this sample. BET surface area was calculated to be about 221.32 m² g⁻¹, which can provide abundant catalytically active sites for heterogeneous photocatalysis. The average pore size was determined to be 4.21 nm, which greatly improve the penetration and transportation of reactants and products.

Fig. 2 TEM images of (a) SM-NSs, (b) SMT-NSs, (c) SMTS-NSs, (d-e) MT-MSs and (f) MTCP-MSs. Inset in image f is a schematic model of MTCP-MSs. Image (g-l) show the EDS mapping of image f. Corresponding elements are labeled on the upper right corner of every image. Scale bar: 10 nm.

Fig. 3 (a) Nitrogen adsorption isotherms and pore size distribution (inset) of MTC_{1.17-P-MSs}. (b) TR-PL spectra of different MSs. (c) Gas-evolution rates of MSs with different form of cocatalysts loading. (d) Gas-evolution rates of different MTCP-MSs with different Cu contents. The samples of x=0 and 1 represent for pure Pt and Cu loading on the outer surface.

The light absorption for photocatalysts can be characterized by the ultraviolet-visible (UV-Vis) spectroscopy (Fig. S12). The UV-Vis of T-MSs consisted of pure TiO₂ show a strong absorption within the UV region (λ < 400 nm) while almost no absorption in visible region (λ > 400 nm). For MT-MSs, a slight absorption of visible light can be observed. Furthermore, after the loading of CuPt alloy to form MTCP-MSs, the absorption of visible light can be greatly enhanced, which may be attributed to the localized surface plasmon resonance of Cu and Pt. To further clarify the role of Cu, MT-MSs-Pt was synthesized by loading pure Pt on MT-MSs via photoreduction. Compared with MT-MSs-Pt, MTPC-MSs exhibit stronger absorption of visible light, indicating that the Cu particles could act as a sensitizer to expand the light response of TiO₂ to visible region.

To confirm the enhancement of charge separation and CRR activity by spatially separated cocatalysts (MTC_{1.17-P-MSs}), reference catalysts including pure TiO₂ mesoporous hollow spheres (T-MSs, Fig. S13) and TiO₂/MnOₓ/CuₓPt mesoporous...
hollow spheres (T/M/C\textsubscript{3.21}P-MSs, Figs. 5a, 3d) were also synthesized. T/M/C\textsubscript{3.21}P-MSs stand for a T-MSs with MnO\textsubscript{x} and CuPt alloy (Cu:Pt ≈ 3.21, detected by ICP-OES) randomly distributed on both inner and outer surfaces, constructed by a direct immersion method.\textsuperscript{13} Catalysts with same components but oxidation outer surfaces constructed by loading CuPt inside while MnO\textsubscript{x} outside also synthesized, denoted as C\textsubscript{2.10}PTM-MSs. It should be noted that the Cu contents of CuPt alloy in MTC\textsubscript{3.17}P-MSs (with separated distributed cocatalysts), T/M/C\textsubscript{3.21}P-MSs (with randomly distributed cocatalysts) and C\textsubscript{2.10}PTM-MSs (with oxidation outer surface) are both around 76% (molar content). Thus, with similar compositions, the only differences between these catalysts is the distribution of cocatalysts, which should be responsible for the difference of activities.

The charge separation can be monitored by time-resolved photoluminescence (TR-PL) spectroscopy (Fig. 3b). Electrons and holes with long lifetimes would show slow PL decay, indicating efficient charge separation.\textsuperscript{14, 43-46} The decay curves are obtained by fitting the observed data (the dots in Fig. 3b) according to the extended exponential function

\[ I(t) = b + \sum_{i=1}^{n} a_i \exp(-t / \tau_i) \]

where \( \tau_i \) (excited-state luminescence decay times) and \( a_i \) (pre-exponential factors) are parameters to be fitted, and \( b \) is a baseline correction parameter. \( I \) and \( t \) refer to the instantaneous PL intensity and corresponding time, respectively. The fitting results of each decay component were shown in Fig. 3b. The average decay time, \( \langle \tau \rangle \), could be calculated from

\[ \langle \tau \rangle = \frac{\sum_{i=1}^{n} a_i \tau_i^2}{\sum_{i=1}^{n} a_i} \]

The fractional contribution \( f_i \) of each decay component was estimated by

\[ f_i = \frac{a_i \tau_i}{\sum_{j=1}^{n} a_j \tau_j} \]

Specially, in our research, to reflect the situation of charge recombination during reactions, catalysts are dispersed in water and the measurement was operation in air. The samples were excited at 355 nm, and the photoluminescence was monitored at 480 nm. Observed data points are indicated by dots, while the fits are shown as smooth curves in Fig. 3. The results of fitting parameters such as \( \alpha \) and \( \tau \) are summarized in Table 1.

As shown in Fig. 3b and Table 1, T-MSs exhibit the fastest PL decay (Fig. 3b, curve 1), indicating the most severe charge recombination.\textsuperscript{14, 43-46} The MT-MSs show a slower PL decay (Fig. 3b, curve 2), suggesting the enhancement of charge separation after the loading of MnO\textsubscript{x}. The decay time is further prolonged after the selective loading of CuPt alloy on outer surface (Fig. 3b, curve 4), indicating a better inhibition of charge recombination. In addition, T/M/C\textsubscript{3.21}P-MSs (Fig. 3b, curve 3) with randomly distributed cocatalysts show a faster PL decay than MTC\textsubscript{3.17}P-MSs, confirming the critical role of spatial separation of catalysts (Cu contents of T/M/C\textsubscript{3.21}P-MSs and MTC\textsubscript{3.17}P-MSs are very close, thus the difference between Cu contents is negligible). To further explore charge recombination, steady state fluorescence (PL) spectra was adopted with the wavelength from 280 to 750 nm. Excitation of catalysts with monochromatic light will lead to fluorescence as a result of the recombination of photogenerated charges. Thus, severer charge recombination will result in stronger fluorescence intensity. Results show that the fluorescence intensity is decreased following the sequence of T-MSs > MT-MSs > T/M/C\textsubscript{3.21}P-MSs > MTC\textsubscript{3.17}P-MSs (Fig. S15), supporting the conclusion that structures with separated cocatalysts will enhance the charge separation. The enhanced charge separation can be attribute to spatial separated MnO\textsubscript{x} and CuPt alloy, which act as hole and electron trap to drive different charge carriers to flow to different directions. The photocatalytic CRR activity of every catalyst was detected in the solvent of KHCO\textsubscript{3} (0.1 M, to enhance the solubility of CO\textsubscript{2}) and Na\textsubscript{2}SO\textsubscript{4} (0.1 M, acting as holes sacrifice agent) aqueous solution under AM 1.5G illumination. As holes sacrifice agent, Na\textsubscript{2}SO\textsubscript{4} can rapidly eliminate holes to ensure the smooth proceeding of CO\textsubscript{2} reduction reactions driven by electrons. In the contrastive experiment with the absence of Na\textsubscript{2}SO\textsubscript{4} over MTC\textsubscript{3.17}P-MSs, the generation of both CO and H\textsubscript{2} are obviously reduced by about 80% (Fig. S16), indicating the significant role of Na\textsubscript{2}SO\textsubscript{4}. The results of photocatalytic CRR show increase activities (Fig. 3c) follows the same trend of increasing charge separation (the trend of activity: MTC\textsubscript{3.17}P-MSs > T/M/C\textsubscript{3.21}P-MSs > MT-MSs > T-MSs). To reflect the conversion efficiency from solar to chemical energy, the overall conversion yields (\( \eta \)) was supplied based on the generation rate of product, irradiation intensity of light source and the change of Gibbs free energy during reaction (see section 5 of methods in supporting information). \( \eta \) of MTC\textsubscript{3.17}P-MSs, T/M/C\textsubscript{3.21}P-MSs, MT-MSs and T-MSs are calculated to be 0.108%, 0.065%, 0.036% and 0.018%, respectively, which also coincide with the

**Table 1.** Fitting results of the TR-PL spectra of catalysts.\textsuperscript{[a]}

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Pre-exponential factors</th>
<th>Decay life time / ns\textsuperscript{[b]}</th>
<th>Fractional contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \alpha_1 )</td>
<td>( \alpha_2 )</td>
<td>( \tau_1 )</td>
</tr>
<tr>
<td>T-MSs</td>
<td>0.54</td>
<td>0.46</td>
<td>0.42</td>
</tr>
<tr>
<td>MT-MSs</td>
<td>0.53</td>
<td>0.47</td>
<td>0.46</td>
</tr>
<tr>
<td>T/M/C\textsubscript{3.21}P-MSs</td>
<td>0.52</td>
<td>0.48</td>
<td>0.49</td>
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\[ \textsuperscript{[a]} \text{The double exponential fitting (n=2) was used according to the shape of decay curves.} \]

\[ \textsuperscript{[b]} \text{The contrastive experiment with the absence of Na\textsubscript{2}SO\textsubscript{4} over MTC\textsubscript{3.17}P-MSs, the generation of both CO and H\textsubscript{2} are obviously reduced by about 80% (Fig. S16), indicating the significant role of Na\textsubscript{2}SO\textsubscript{4}.} \]
trend of charge separation. The best η of 0.108% over MTC\textsubscript{3.17}P-MSs is higher than general oxides and sulfides based catalysts (generally about 0.006 % \(\sim 0.042\%\textsuperscript{50,51}\)). Given the similar Cu content (c.a. 76%) in both structures with separated and randomly loaded cocatalysts, the influence of surface reaction can be ruled out, thus the enhanced activity can be attributed to the improvement of charge separation. Additionally, compared with oxidation outer surface (C\textsubscript{1.17}P-MSs), reductive outer surface (MTC\textsubscript{3.17}P-MSs) show obviously advantages in photocatalytic CRR (Fig. 3c). During the reaction, influences of carbon contamination should be rule out. To clarify carbon in products comes from CO\textsubscript{2} instead of possible carbon containing contaminants, we design a contrastive experiment which operated without the injection of CO\textsubscript{2} with other situations unchanged over MTC\textsubscript{3.17}P-MSs. Results show that (Fig. S16) without CO\textsubscript{2} injection, negligible carbon containing products can be detected, indicating carbon in products originates from CO\textsubscript{2}.

The activity and composition of syngas production also be influenced by the Cu contents of CuPt alloy (Fig. 3d). With a low Cu content (MTC\textsubscript{3.17}P-MSs and MTC\textsubscript{3.17}P-MSs), H\textsubscript{2} is the main product, while the production of CO is low (12.42 \(\mu\)mol h\(^{-1}\)) and 23.93 \(\mu\)mol h\(^{-1}\), respectively).\(\eta\)\textsuperscript{54} for MTC\textsubscript{3.17}P-MSs and MTC\textsubscript{3.17}P-MSs are calculated to be 0.016% and 0.031%, respectively. With a high Cu content (MTC\textsubscript{2.72}P-MSs), catalyst also exhibits relatively low activity for CO (13.16 \(\mu\)mol h\(^{-1}\)) with a \(\eta\) of 0.017%. Higher CO activity was achieved with a moderate Cu content (MTC\textsubscript{3.17}P-MSs) (84.18 \(\mu\)mol h\(^{-1}\)) with a \(\eta\) of 0.108%. 0.08 g catalyst was used in the photocatalytic reaction, and the obtained production evolution rate without normalization by catalyst weight shows the same trend over various catalysts (Fig. S17 and Table S1). The desirable CO/H\textsubscript{2} ratio of 1:2\textsuperscript{8} is also obtained when using MTC\textsubscript{2.72}P-MSs, and it can be concluded that CO/H\textsubscript{2} ratio can be adjusted in a large range between 1:1.2 and 1:2 by changing Cu content. To investigate the stability of catalysts, photocatalytic reactions were repeated under similar conditions by 4 circles within 12 h. Results show that the generation of products decreases no more than 10% over every catalyst for either CO or H\textsubscript{2} (Fig. S18), indicating MTC\textsubscript{1.17}P-MSs maintain stable during photocatalytic reaction. The morphology of MTC\textsubscript{3.17}P-MSs can also be maintained after the photocatalytic reaction (Fig. S19). The enhancement of activity and control of CO/H\textsubscript{2} ratio are attribute to the balance of every elementary process. With different Cu content, the surface composition and properties of CuPt cocatalysts are changed, which directly affect the adsorption energy and reaction barrier for both reactant, intermediate and product.\textsuperscript{52} Only with appropriate ratio of Cu/Pt can we obtain the optimal reaction process and achieve the desirable product, which will be elaborately discussed with the help of DFT calculations (see section 7 of \textit{methods} in supporting information).

The DFT models of CuPt alloys are established based on similar Cu contents (Cu\textsubscript{1.3}, Cu\textsubscript{1.5}Pt, Cu\textsubscript{1}Pt and Cu\textsubscript{1}Pt, respectively) (Fig. S20 and Table S2). According to previous research\textsuperscript{50,51}, the formation of CO from photocatalytic CRR is mainly carry out along the carboxyl process, which can also be proved by the successful detection of adsorbed carboxyl groups (COOH\textsuperscript{*}) during reaction by in-suit infrared spectrometer (section 6 of \textit{methods} in supporting information and Fig. S21). The carboxyl process can be mainly divided into following three steps:\textsuperscript{49,53} 1) the activation of carbon dioxide (CO\textsubscript{2}+H\textsuperscript{+}+e\textsuperscript{-}→COOH\textsuperscript{*}) (Fig. 4a and b), 2) the removal of hydroxyl radical (COOH\textsuperscript{*}+H\textsuperscript{+}+e\textsuperscript{-}→CO\textsuperscript{*}+H\textsubscript{2}O, where CO\textsuperscript{*} stand for the adsorbed carbon monoxide) and 3) the desorption of carbon monoxide (CO\textsuperscript{*}→ CO), unlike step 2, step 1 and 3 are endothermic processes (Fig. 4b), which are thus dominant for the overall activity. Our previous study has shown that the local structure of Pt in PtCu alloy has strong effect over the CO\textsuperscript{*} binding strength.\textsuperscript{52} With the increase of surface Pt, the binding strength of CO\textsuperscript{*} is weakened, while subsurface Pt behaves oppositely. Additional calculations indicate similar trend for COOH\textsuperscript{*} adsorption. Genetic algorithm based global optimization indicates that a complete Pt skins exist over PtCu alloy (111) surface until the Pt/Cu ratio is lower than 1:1. Thus, the weakest adsorption of CO\textsuperscript{*} and COOH\textsuperscript{*} over Pt sites has been observed on CuPt(111) (a thermodynamically stable facet created by the final calcination during synthesis, which can be observed in Fig. S9a). Strong CO\textsuperscript{*} binding will inhibit its desorption (step 3)\textsuperscript{54} thus limits the CO formation rate, while too weak binding destabilized COOH\textsuperscript{*} thus suppress the first hydrogenation step (step 1). Therefore, suitable CO\textsuperscript{*} and COOH\textsuperscript{*} binding strength is needed to achieve the best performance for CO\textsubscript{2} reduction. In addition, DFT shows that the binding energy (defined in section 7 of \textit{methods} in supporting information) of CO on Pt, Pt\textsubscript{1.5}Cu, PtCu, PtCu\textsubscript{0.5} and PtCu\textsubscript{0.25} are 1.32, 1.05, 0.75, 1.18 and 1.02, respectively, indicating that the adsorption of CO on CuPt alloy is weakened. Thus, the poisoning of Pt can be weakened by the introduction of Cu. Results of photocatalysis (Fig. 3d) also indicate that increased Cu content will inhibit the competitive H\textsubscript{2} evolution reaction (HER). By investigating the interaction between Cu and Pt based on DFT and XPS, we found that the addition of Cu will enrich the electron density around Pt, which results in a greater energy barrier to inhibit HER (Fig. S23).\textsuperscript{55-59}

\textsuperscript{49} DFT, \textsuperscript{50}Cu, PtCu\textsubscript{0.5}, \textsubscript{1}PtCu, \textsubscript{0.25}PtCu, \textsuperscript{51}\textsubscript{1}PtCu, \textsuperscript{52}\textsuperscript{55-59}
Fig. 4. (a) The main processes and intermediate species for CO₂ reduction to CO. (b) The calculated free energy of the main intermediate species in every step. Models of every steps over each catalyst are shown in Fig. S22. (c) The calculated binding energy of CO* and the overall activity for CO generation over each catalyst. (d) CO evolution rates of each catalyst in H₂O and D₂O. The rate ratios of r(H₂O)/r(D₂O) over MTC₃₋₂P-MSs, MTC₁₋₂P-MSs, MTC₁₋₂P-MSs and MTC₂₋₂P-MSs are 1.20, 1.16, 1.67 and 1.26, respectively, suggesting that MTC₂₋₂P-MSs are greatly affected by D₂O.

Specifically, with the increasing Cu content in our catalysts, the volcano curve of activity is well consistent with the volcano curve of CO* binding energy in Fig. 4c, suggesting that the enhanced activity over optimal CuPt alloy is mainly caused by the weakening of CO* binding energy. It should be noted that there is a shift of peak position between the two volcano curves. The shift is mainly caused by the un-uniform distribution of Pt/Cu ratio in the synthesized nanoparticles, and the influence of COOH* formation. To be more elaborate, the kinetic isotope experiment was performed to investigate the shifted peak position. Interestingly, only MTC₁₋₂P-MSs shows notable kinetic isotope effect after replacing H₂O by D₂O (Fig. 4d), indicating that the COOH* formation step influences the whole conversion only over MTC₁₋₂P-MSs because hydrogen element only take part in step 1 instead of step 3, thus the isotope of hydrogen can only affect step 1. Less stable COOH* accompanied with weaker binding of CO* (Fig. 4b), consisting with the trend analysis shown in Fig. 4c. Therefore, the different activity is mainly determined by the energy of CO*, which is affected by the stability of COOH*.

Conclusions

In summary, to overcome the main limitations of syngas production by photocatalytic CRR (unsuitable CO/H₂ ratio and serious charge recombination), we construct a structure with spatially separated cocatalysts and firstly introduced a reduction outer surface to avoid back and cross reaction. The CO/H₂ ratio can be adjusted in a wide range including the desirable 1:2 by changing the component of reduction cocatalysts. Furthermore, with the help of DFT calculations and kinetic experiments, we disclose the diversity in activity mainly determined by the energy of CO* desorption and CO₂ activation. Under optimal conditions, the evolution rate of CO reaches 84.2 μmol h⁻¹ g⁻¹ and the overall conversion yield reaches 0.108%, which is higher than traditional oxide and sulfide based catalysts (generally about 0.006% ~ 0.042%). This work opens up opportunities to develop sustainable and carbon neutral syngas production from the reduction of CO₂ and H₂O using solar energy with rationally designed heterostructures.

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Notes and references

Journal Name

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