Photothermal \( \text{CO}_2 \) hydrogenation to hydrocarbons over trimetallic \( \text{Co–Cu–Mn} \) catalysts

Photocatalytic \( \text{CO}_2 \) reduction is a highly vital process for converting \( \text{CO}_2 \) into valuable chemicals. However, the reaction always proceeds less efficaciously at low temperature. The combination of photo and thermal conditions is one of feasible approaches to achieve the reaction with high efficiency and has gained much attention recently. In the present work, trimetallic \( \text{Co–Cu–Mn} \) catalysts were developed in photothermal \( \text{CO}_2 \) hydrogenation to \( \text{CH}_4 \) and \( \text{C}_2 \), hydrocarbons. The structural and photoelectric characteristics, as well as adsorption behaviors of these catalysts affected the catalytic performances remarkably.
Photocatalytic CO\textsubscript{2} reduction is a highly vital process for converting CO\textsubscript{2} into valuable chemicals. However, the reaction always proceeds less efficaciously at low temperature. A combination of optical and thermal conditions is one of the feasible approaches to achieve the reaction with high efficiency and has gained much attention recently. In the present work, we prepared several Co–Cu–Mn trimetallic catalysts via a simple co-precipitation method, which were used in catalyzing photocatalytic CO\textsubscript{2} reduction to hydrocarbons. The metal composition and reduction temperature of the catalysts had important effects on their structural and photoelectrical characteristics and adsorption behaviors, further resulting in diverse catalytic performances. Among the prepared trimetallic catalysts, Co\textsubscript{7}Cu\textsubscript{1}Mn\textsubscript{1}O\textsubscript{x}(200), with a Co/Cu/Mn molar ratio of 7/1/1 and reduced at 200 °C in H\textsubscript{2} for 2 h, could produce CH\textsubscript{4} with an activity of 14.5 mmol g\textsubscript{cat}\textsuperscript{−1} h\textsuperscript{−1} in 10% CO\textsubscript{2}/30% H\textsubscript{2}/60% N\textsubscript{2}, and CH\textsubscript{4} and C\textsubscript{2+} hydrocarbons with the activities of 15.9 and 7.5 mmol g\textsubscript{cat}\textsuperscript{−1} h\textsuperscript{−1} in 25% CO\textsubscript{2}/75% H\textsubscript{2}, respectively. The present strategy for constructing trimetal oxide catalysts for the photothermal reaction not only provides a highly active catalyst for CO\textsubscript{2} utilization, but also offers a potential possibility for reducing the high temperature of conventional thermal reactions.

### Introduction

CO\textsubscript{2} is the primary greenhouse gas, whose concentration in the atmosphere continues to rise.\textsuperscript{1} It is also an important C1 source and can be converted into many valuable chemicals such as CO\textsubscript{2}, hydrocarbons,\textsuperscript{3–5} olefins,\textsuperscript{6} acids,\textsuperscript{7–9} alcohols,\textsuperscript{10–12} etc. Although many efforts have been invested in this area, it is still very difficult to convert CO\textsubscript{2} into chemicals due to its thermodynamic stability and chemical inertness.\textsuperscript{1} CO\textsubscript{2} hydrogenation to hydrocarbons represents an essential and green way for its utilization.\textsuperscript{13} However, the conventional thermal process is always conducted under harsh conditions, leading to the formation of carbon deposit, the increase of energy consumption, etc. The photocatalytic method is an ideal way for the reaction, which could be carried out under mild conditions and using solar energy. However, this route suffers from low activity especially at room temperature, impeding its further applications. Recently, the photothermal catalytic method has gained increasing attention, especially in CO\textsubscript{2} reduction.\textsuperscript{14,15}

The photothermal routes always contain four types, including thermal-assisted photocatalysis, photo-assisted thermal catalysis, photothermal co-catalysis, and photo-driven thermal catalysis.\textsuperscript{16} Generally, these routes combine the advantages of both photocatalysis and thermal catalysis including high activity, proceeding under mild conditions, efficient energy utilization, etc. To date, many catalysts such as Ru/silicon nanowire,\textsuperscript{17} RuO\textsubscript{2}/SrTiO\textsubscript{3},\textsuperscript{18} RuO\textsubscript{2}/3D silicon photonic crystals,\textsuperscript{19} Ru@FL-LDHs (Ru/Mg-Al LDHs matrix),\textsuperscript{20} Ru/Al\textsubscript{2}O\textsubscript{3},\textsuperscript{21} Ru/TiO\textsubscript{2},\textsuperscript{22} Pd@NbO\textsubscript{2},\textsuperscript{23} CoFeAl-LDH nanosheet,\textsuperscript{11} Ni/SiO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3},\textsuperscript{14} Cu\textsubscript{2}O/Zn-MOF,\textsuperscript{24} Cu\textsubscript{2}O/graphene,\textsuperscript{25} etc. have been used for photothermal CO\textsubscript{2} hydrogenation, and their catalytic performances are given in Table S1.\textsuperscript{†} Significant advances have been made in recent years; however, most of the above catalysts suffer from drawbacks such as using expensive noble metals, working at high temperature, and exhibiting low activity. Besides, the obtained products mainly focused on C1 chemicals such as CO and CH\textsubscript{4}. The synthesis of C\textsubscript{2+} products via a photothermal route is a more difficult but significant issue, which is rarely involved in the above developed catalytic systems.\textsuperscript{26} Considering the above aspects, to develop a cost-efficient, highly active and reusable catalyst for photothermal
CO₂ reduction into CH₄ and C₂+ hydrocarbons is particularly important.

On the other hand, it has been well known that pure metals used in CO₂ hydrogenation always showed a low activity due to their low CO₂ binding capacity. Oxides could not only anchor metal atoms but also provide vacancies for the reaction, and in this way, they could participate in the reaction and enhance the catalytic performances. Trimetallic oxide catalysts show unique electronic and structural features different from their individual components. The complex composition of trimetallic catalysts could form multiple interfaces conducive to catalysis. In this aspect, trimetallic catalysts have been widely used in many reactions such as CO and CO₂ hydrogenation, ethanol steam reforming, ammonia oxidation, etc. with good performances. In particular, complicated metal-trimetallic oxides can provide many vacancies and active sites for catalysis, and have great potential for application in CO₂ reduction.

Herein, a series of Co–Cu–Mn trimetallic oxides were prepared and used for photothermal CO₂ reduction, and the screened Co₇Cu₁Mn₁Oₓ(200) catalyst, with a Co/Cu/Mn ratio of 7/1/1 and reduced at 200 °C in H₂, showed a high CH₄ formation activity (14.5 mmol g⁻¹ h⁻¹) even at low CO₂ (10%) and H₂ (30%) concentrations, which lies in the highest activity range in Table S1.† Interestingly, after increasing the CO₂ and H₂ concentrations to 25% and 75%, 15.9 and 7.5 mmol g⁻¹ h⁻¹ of CH₄ and C₂+ hydrocarbons were produced with selectivities of 65.4% and 30.8%, respectively. Moreover, the catalyst has a good temporal stability under continuous-flow conditions. The metal/oxides were confirmed to be very important for the catalytic performance, in which the Co⁰ species were the active sites, which together with the oxides acted as supports and semiconductors for providing a local heating environment via the photothermal effects. The Cu species could promote the reduction of Co and Mn oxides, and also promote the coupling of C–C bonds to produce C₂+ products especially at a high CO₂ concentration. The Mn species could on one hand enhance the adsorption of CO₂ and H₂, and also provide the photothermal effect to produce a local heating effect to promote the reaction. The present strategy for constructing trimetallic catalysts for the photothermal reaction does not only provide a simple but efficient way to convert CO₂ into valuable hydrocarbons, but also offer a general method for reducing the reaction temperature of conventional high-temperature reactions.

**Results and discussion**

**Preparation and characterization of catalysts**

Trimetallic Co–Cu–Mn catalysts were prepared by a simple co-precipitation method, and the details are given in the ESI.† The prepared catalysts were denoted as CoₐCuₐMnₐOₓ(T), in which a/b/c and T represent the Co/Cu/Mn molar ratio and the reduction temperature, respectively. CoₐCuₐMnₐOₓ means unreduced catalysts. The morphologies of the catalysts were examined by TEM tests. Initially, the Co₇Cu₁Mn₁Oₓ catalyst mainly showed the morphology of nanoparticles with the size range of 6–15 nm (Fig. 1a and b). The lattice spacings of 0.186, 0.246, 0.219, 0.152, 0.197, and 0.135 nm in the HRTEM image...
could be successively indexed to the (331) and (311) planes of CoO, the (411) and (611) planes of Mn2O3, and the (−112) and (−221) planes of CuO (Fig. 1c).

After reduction, the Co3Cu1Mn1O4(200) catalyst maintained the nanosheet morphology in the size range of 6–12 nm (Fig. 1d and e). CoO, Mn, and Mn2O3 were also detected, as shown in Fig. 1f. The HAADF-STEM and EDX elemental mappings of the Co3Cu1Mn1O4(200) catalyst showed that Co, Cu, Mn, and O elements are homogeneously dispersed over the whole grain (Fig. 1g to k).

For comparison, the TEM images of catalysts with different Co/Cu/Mn ratios were also studied, and the results are shown in Fig. S1.† With the increasing Co content, the morphology changed from nanosheets to nanoparticles. For example, the Co3Cu1Mn1O4(200) and Co3Cu1Mn1O4(200) catalysts were nanosheets, while the Co3Cu1Mn1O4(200) and Co3Cu1Mn1O4(200) catalysts were mainly nanoparticles, which were beneficial for exposing more active sites.

The molar ratios of the bimetallic and trimetallic catalysts were tested by ICP-OES, and the results are given in Table S2.† The molar ratios of metals were consistent with the feed amounts.

XRD examinations showed that all the tested unreduced catalysts such as Co3Cu1Mn1O4, Co3Mn1O4, and Co3Cu1O2 showed the XRD patterns of Co3O4 (JCPDS file no. 73-1701). No obvious CuO or MnO2 peaks were found, implying that they were easily incorporated into the Co3O4 crystals and were well dispersed (Fig. 2a). The Co3Cu1Mn1O4(200) catalyst showed the same peaks as that of the Co3Cu1Mn1O4 catalyst, but with lower intensities, indicating the crystallinity decrease of the Co3O4 component after reduction.

The XRD pattern of the Co3Cu1Mn1O4(200) catalyst was almost the same as that of the unreduced catalyst, and it is mainly attributed to the Co3O4 phase (Fig. 2b). However, two small peaks at 43.0° and 61.8° were carefully detected, which could be assigned to the CoO (200) and (220) planes (JCPDS file no. 70-2855). No CoO, CuO, Cu2O, or Mn2O3 species were detected due to their low amounts. The Co3Mn1O4(200) catalyst showed three peaks at 36.8°, 42.7°, and 61.8°, which could be assigned to the CoO (111), (200), and (220) planes (JCPDS file no. 78-0431), respectively. Two phases of CoO fcc and hcp were identified in the Co3Cu1O2(200) catalyst, and the formation of two phases is commonly observed in the synthesis of cobalt nanostructures.35 The peaks at 41.5°, 44.4°, 47.4°, and 75.9° could be indexed to CoO hcp (100), (002), (101), and (110) facets (JCPDS file no. 01-071-4239), respectively. The peaks at 44.4° and 51.5° could be contributed to the CoO fcc (111) and (200) planes (JCPDS file no. 01-071-4651).† The results indicated that Co3O4 could be reduced to Co0 by the promotion of Cu species, and this will be further verified by the following H2-TPR tests. No MnO2 or CuO species were detected due to their good dispersion. It is worth noting that although Cu could promote the reduction of Co3O4 to Co0, no Co0 was detected in the bulk phase of the Co3Cu1Mn1O4(200) catalyst.

The XRD patterns of the catalysts with different Co/Cu/Mn ratios also showed the main peaks of Co3O4 and CoO (Fig. S2†); however, the Co3Cu1Mn1O4(200) and Co3Cu1Mn1O4(200) catalysts showed a wide peak at around 20°, indicating that they possess amorphous structures.

The results of the N2 adsorption/desorption tests are shown in Fig. S3 and Table S3.† The reduction temperature affects the catalyst structure remarkably, and the BET surface areas of the tested trimetallic catalysts declined gradually with the increase of the reduction temperature, which is probably because the high reduction temperature leads to catalyst sintering. The bimetallic Co–Cu catalyst shows the lowest BET surface area, while the Co–Mn catalyst presents the highest. Indeed, the surface areas of the Co3O4 and Co3Cu1Mn1O4(100, 200, and 300) catalysts did not differ greatly from one another, thus their diverse performances did not stem from the difference in their surface areas.

To distinguish the valences of the Co, Cu, and Mn species on the surface of the catalysts, the XPS of Co 2p, Cu 2p, Mn 2p and 3s, and AES of Cu L1M1/2were analyzed (Fig. 3).5,36,37 In the XPS of the Co3Cu1Mn1O4 catalyst, the Co element was composed of Co3+ and Co2+ species, which was confirmed by the peaks at 779.5 eV and 780.9 eV, which can be attributed to the Co3+ and Co2+ 2p3/2 peaks (Fig. 3a).38 The Cu2+ 2p XPS showed two peaks at 934.5 eV and 954.2 eV, which could be assigned to Cu2+ 2p3/2 and 2p1/2, respectively (Fig. 3b and c). The XPS peaks of Co species in the Co3Cu1Mn1O4(200) catalyst were the same as those in the unreduced catalyst; however, the Cu species was found to be Cu+. The Mn XPS indicated that the catalyst contains Mn3+ oxidation state (Fig. 3d and e). The XPS results indicated that the surface of the Co3Cu1Mn1O4(200) catalyst mainly contained Co2+, Co3+, Cu+, a small amount of Cu2+, and Mn3+, respectively, but no Co0 or Cu0 species were detected for air oxidation.

For comparison, the XPS spectra of the catalysts reduced at different temperatures were also tested. The Co element in these catalysts was mainly composed of Co2+ and Co3+ species.
but with different contents. The Co$^{2+}$ component increased with the increase of the reduction temperature. No obvious Co$^0$ species was found until the reduction temperature reached 500 °C. As for the Cu XPS, the area of the satellite peak around 942 eV decreased with increasing reduction temperature, indicating that Cu$^0$/+ 2p$^{3/2}$ increased. Besides, all the reduced catalysts possess the dominant Cu$^+$ component. The Mn 3s XPS showed that the Co$_7$Cu$_1$Mn$_1$O$_x$(500) catalyst is composed of Mn$^{2+}$ species, i.e., MnO, while the others showed Mn$^{3+}$ species.

The XPS spectra of the Co–Cu–Mn trimetallic catalysts with different molar ratios were also investigated, and the results are given in Fig. S4.† All the elements had the same valences but contained different contents, such as Co$^{3+}$, Co$^{2+}$, Mn$^{3+}$, Cu$^+$, and a small amount of Cu$^{2+}$, which are similar to the Co$_7$Cu$_1$Mn$_1$O$_x$(200) catalyst, indicating that they are probably active in the reaction. This was confirmed by the following catalytic activity studies (Table 1).

The Raman spectrum of the Co$_7$Cu$_1$Mn$_1$O$_x$(200) catalyst showed a peak at 680 cm$^{-1}$, which could be assigned to the A1$^g$ mode of Co$O_x$ [Fig. S5†]. This profile is similar to those of the Co$_7$Cu$_1$Mn$_1$O$_x$, and Co$_7$Cu$_1$Mn$_1$O$_x$ (100, 300, and 400) catalysts, indicating that Co$O_x$ exists in these catalysts. Interestingly, the Co$_7$Cu$_1$Mn$_1$O$_x$(500) catalyst showed a wide peak at 540 cm$^{-1}$, assigned to the one-phonon LO mode of Co$O_x$, which was formed by the partial oxidation of Co$^0$ by local laser heating. No obvious Cu or Mn species were detected, indicating that they have permeated into the Co$O_x$ crystal lattice.

The above characterization studies showed that the Co$_7$Cu$_1$Mn$_1$O$_x$(200) catalyst mainly possesses Co$O_x$ in the bulk phase, while the surface of the catalyst was composed of Co$^{3+}$, Co$^{2+}$, Mn$^{3+}$, Cu$^+$, and a small amount of Cu$^{2+}$ species, which are in the forms of Co$_3$O$_4$, Mn$_2$O$_3$, Cu$_2$O, and CuO. The catalysts reduced at 100, 200, and 300 °C, and the catalysts with different Co/Cu/Mn molar ratios contained similar components but of different concentrations, indicating that they possess similar structures and properties.

**Catalytic performances**

Photothermal CO$_2$ hydrogenation was carried out in a tubular reactor [Fig. S6],† and the procedure details are given in the ESI.† The products of photothermal CO$_2$ reduction include CO, CH$_4$, and C$_2$+ hydrocarbons (mainly C$_2$ to C$_6$) in the present work. Initially, the catalytic performances over different catalysts are given in Table 1. No products were detected in the absence of a catalyst, and the sole metal catalysts or the bimetallic catalysts showed a very low activity in the reaction. The Co$_7$Cu$_1$Mn$_1$O$_x$(200) catalyst showed the best catalytic performances with a CH$_4$ formation activity of 14.5 mmol g$_{cat}^{-1}$ h$^{-1}$ and a selectivity of 85.3% (entries 1–7 vs. 8). These activities were achieved under the irradiation of a 300 W Xe lamp (234 mW cm$^{-2}$, 300–1100 nm) and heat generated by an additional electric heater [Fig. S6†]. Unlike the CuO$_x$(200) and MnO$_x$(200) catalysts, the CoO$_x$(200) catalyst could show a very low CH$_4$ formation activity (only 3.1 mmol g$_{cat}^{-1}$ h$^{-1}$) (entries 2–4), demonstrating that the Co species is probably the active species, while the CuO$_x$ and MnO$_x$ species are the promoters for the Co species. Indeed, the Cu and Mn species are always used as promoters or active sites for the Co-catalyzed CO$_2$ reduction.† The activities of the bimetallic Cu$_1$Mn$_1$O$_x$ or Co$_2$Mn$_1$O$_x$ catalysts confirmed that Cu or Mn are not the active sites (entries 5–7). Interestingly, the Co-CuO$_x$(200) catalyst showed higher activities for the formation of CH$_4$ and C$_2$+.

![Fig. 3 XPS spectra of the unreduced Co$_7$Cu$_1$Mn$_1$O$_x$ catalyst and the Co$_7$Cu$_1$Mn$_1$O$_x$(100, 200, 300, and 500) catalysts. (a) Co 2p XPS, (b) Cu 2p XPS, (c) Cu L$_3$M$_4,5$M$_4,5$ AES spectra, (d) Mn 2p XPS, and (e) Mn 3s XPS, respectively.](image-url)
Photothermal CO₂ hydrogenation over diverse catalysts

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<th>C₂⁺</th>
<th>CO</th>
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a Reaction conditions: catalyst 50 mg, CO₂/H₂/N₂ 10%/30%/60%, full irradiation, 200 °C, 3 h. b Detected by GC and obtained from three successive runs. 1 N₂ was replaced by Ar.

hydrocarbons than those of the pure CoO₂(200) and CuO₂(200) catalysts, indicating that the Cu species could not only enhance the activity of the Co-based catalyst in CO₂ reduction to CH₄, but also promote the formation of C₂⁺ products. For comparison, other trimetallic catalysts with different ratios were also assessed; however, all of them possessed lower activities than that of the Co₇Cu₁Mn₁Oₓ(200) catalyst (entries 8 vs. 9–13).

The activities achieved in CO₂/H₂/N₂ and CO₂/H₂/Ar were very similar (entries 8 vs. 14), indicating that the catalytic performances were not affected by the type of diluent gas. In addition, the C₂⁺ activities of the Co₆Cu₂Mn₁Oₓ(200), Co₇Cu₁Mn₁Oₓ(200), Co₅Cu₁Mn₁Oₓ(200), and Co₇Cu₁Mn₁Oₓ(200) catalysts were only 0.9, 1.4, 0.8, and 0.5 mmol g⁻¹ h⁻¹, respectively, and inconsistent with the change rule of the catalyst composition. Because the formation of C₂⁺ products is closely related to the Cu species, the uneven distribution of Cu species on the catalyst surface is probably the reason for the discrepancy between the C₂⁺ activity and the Co/Cu/Mn molar ratio of the catalyst.

The Co species are the active sites; however, the promoters of Cu and Mn species are also very important for the reaction. To confirm this, the catalysts with the same component of Co element were investigated, and the results indicated that the Cu and Mn concentrations affected the catalytic performances remarkably (entries 15–18). The Co₆Cu₁Mn₁₂₅Oₓ(200) and Co₅Cu₁₂₅Mn₆₇₅Oₓ(200) catalysts showed high CH₄ formation activities, while the Co₅Cu₁₂₅Mn₁₇₅Oₓ(200) and Co₅Cu₁₂₅Mn₆₇₅Oₓ(200) catalysts offered relatively low values, indicating that the low concentrations of Cu and Mn are not beneficial for catalysis.

The catalytic performance studies showed that the coexistence of Co, Cu, and Mn in the Co/Cu/Mn trimetal is very important for the reaction, and their molar ratios and the synergistic effects of these multicomponents are closely related to the catalytic performances, and a similar phenomenon could be found in the previous report.42

Effect of the reduction temperature of the Co₇Cu₁Mn₁Oₓ catalysts

The above characterization results indicated that the reduction temperature affected the metal valence compositions of the catalysts, and it was proved to be able to affect their catalytic performances.14,44 To verify this, the catalysts reduced at different temperatures were studied, and the results are shown in Fig. 4. Indeed, the Co₇Cu₂Mn₁Oₓ and Co₇Cu₁Mn₂Oₓ(100, 200, and 300) catalysts showed good catalytic performances during the reaction, indicating that they have similar catalyst

Fig. 4 Effect of the reduction temperature of the Co₇CuₐMnₙOₓ(T) catalysts on the catalytic performances of the photocatalytic CO₂ reduction. Reaction conditions: catalyst 50 mg, CO₂/H₂/N₂ 10%/30%/60%, 200 °C, 3 h, and 300 W Xe lamp full irradiation.
compositions and properties. However, the Co₇Cu₁Mn₁Oₓ (400 and 500) catalysts showed decreased catalytic activities, which has a great relationship with the high concentration of Co⁰ in the bulk phase but less Co₃O₄ and Mn₂O₃.

The catalysts after being used for 9 h and 21 h were characterized by XPS and XRD in Fig. 5, and the results showed that Co⁰ and Cu⁰ species could be found during the reaction. Co⁰ was widely recognized as the active site for CO₂ hydrogenation. The XRD patterns of the catalysts used for 9 h showed similar peaks to those of Co₃O₄ and CoO, revealing that Co₃O₄ still exists in the bulk phase. Compared with the Co₇Cu₆Mn₁O₇ (200) catalyst in Fig. 2, the peak at 36.6° decreased remarkably. The catalyst used for 21 h showed similar results but with more Co⁰ and Cu⁰ species. The XPS and XRD characterization studies showed that the catalyst compositions were stable during the reaction.

The highest CH₄ activity was achieved over the Co₇Cu₁Mn₁Oₓ (200) catalyst. Besides, the Co₃Cu₁Mn₁O₇ (100 and 300) catalysts also showed acceptable CH₄ formation activities. Generally, in thermal catalysis, Co⁰ species are recognized as the active components. However, the Co₇Cu₁Mn₁O₇ (500) catalyst showed the lowest activity in the reaction, which mainly contained the Co⁰ species but no Co₃O₄ or Mn₂O₃. It should be noted that in the present photothermal catalysis, the oxides including Co₃O₄, Mn₂O₃, etc., could promote the reaction via the interaction effect between the Co species and other oxides.

The H₂-TPR tests were carried out to study the interaction effect of different metal oxides, and the results are shown in Fig. 6. Pure Co₃O₄ showed two peaks at 273 °C and 336 °C, which could be assigned to the reduction peaks of Co₃O₄ to CoO and CoO to Co⁰, respectively. Mn₂O₃ showed two peaks located at 292 °C and 388 °C, which could be assigned to the reduction of Mn₂O₃ to Mn₃O₄ and Mn₃O₄ to MnO, respectively. The Co₇Cu₆Oₓ catalyst had two peaks at lower temperatures of 156 °C and 210 °C indicating that Cu could obviously promote the reduction of Co₃O₄ and CoO, which is consistent with previous reports. However, the Co₃Mn₁O₇ catalyst showed two main peaks at 280 °C and 428 °C, which could be assigned to the reduction of (Co,Mn)₃O₄ to (Co,Mn)O, and (Co,Mn)O to Co⁰ and MnO, respectively, revealing that Mn species impedes the reduction of CoOₓ. The Co₇Cu₁Mn₁O₇ catalyst had three peaks at 128, 183, and 284 °C, which could be attributed to the reduction peaks of CuO to Cu⁰, Co₃O₄ to CoO, and CoO to Co⁰ and MnO, respectively. The H₂-TPR results indicated that the Co, Cu, and Mn species show strong interaction effects, and the previous report showed that the presence of Cu could alter the electronic interactions with Co and Ni in the Co–Cu–Ni trimetallic catalysts.

The surface adsorption capacities could significantly affect the catalytic activity. Thus, we conducted the CO₂-TPD and H₂-TPD tests for the diverse trimetallic catalysts and the results indicated that with the increase of the reduction temperature, the adsorption amounts of CO₂ and H₂ on the catalysts decreased. The Co₇Cu₁Mn₁O₇ (100 and 200) catalysts contained higher CO₂ and H₂ adsorption amounts than the others.
which is beneficial for them to catalyze the CO₂ photothermal reduction.

To investigate the effects of the Mn and Cu species on the Co-based catalysts, the CO₂-TPD tests for Co–Mn and Co–Cu bimetallic catalysts were performed (Fig. S7†). The Mn species was found to be able to improve CO₂ and H₂ adsorption for the Co-based catalysts, while the Cu species reduced their adsorption since the Co–Cu bimetallic catalyst could be deeply reduced at 200 °C. Even so, the Co–Cu₄O₅₋₄(200) catalyst exhibited a strong CO₂ adsorption peak at around 350 °C, showing that the Cu species could promote strong adsorption of CO₂ on the catalyst.

We investigated the catalytic performances of the Co–Cu and Co–Mn bimetallic catalysts reduced at different temperatures, and the results are given in Table S4.† With the increase of the reduction temperature, the activities of the Co–Cu and Co–Mn catalysts increased initially but were then reduced at high reduction temperatures of 400 and/or 500 °C. The highest activities were lower than that of the Co–Cu₄Mn₂O₇(200) catalyst (Table 1, entry 8), indicating that the Cu and Mn species were both needed for the photothermal CO₂ reduction.

**Effect of the reaction conditions**

The above investigation showed the composition and pretreatment of the catalyst affected the activity remarkably. In addition, the reaction conditions also had a great influence on the catalytic performance. The effects of the reaction conditions on the catalytic performance were also investigated, and the results are shown in Fig. 7. Almost no product was detected in the absence of CO₂ or H₂, indicating that the products are generated from CO₂. This was further confirmed by a control experiment of adding 1³CO₂ in the reaction, in which 1³CH₄ was detected with a mass spectrometer (Fig. S8†).

The best performances for CH₄ formation were achieved in CO₂/H₂ with a molar ratio of 1/3 (Fig. 6a). Surprisingly, changing the CO₂ and H₂ concentrations slightly affected the activity of CH₄ formation (around 15 mmol g⁻¹ h⁻¹), but had an influence on C₂, hydrocarbon formation. In the absence of a dilute gas, the highest C₂+, activity reached 7.5 mmol g⁻¹ h⁻¹ with a 30.8% selectivity. Generally, C₂, hydrocarbon formation involves CO₂ reduction and C–C coupling steps, and is much more difficult to achieve under photothermal conditions.‡ Thus, the present Co–Cu₄Mn₂O₇(200) catalyst could catalyze the C₂, hydrocarbon formation, but only the CO₂ and H₂ concentrations need to be enhanced. The C₂, formation is strongly linked to the amount of surface adsorbed carbon species such as CO, C–H₂, etc. A high amount of carbon species can be coupled to generate C₂, hydrocarbons over a suitable catalyst, thus an increase of the CO₂ concentration could enhance the C₂, selectivity. However, generally, to obtain C₂, products, high pressure and/or CO₂/H₂ molar ratio are always needed.‡ The present Co₇Cu₃Mn₁Oₓ(200) catalyst has a good CO₂ adsorption capacity, which was confirmed by the CO₂-TPD tests. The high C₂, selectivity indicates that the Co–Cu₄Mn₂O₇(200) catalyst possesses good CO₂ reduction and C–C coupling abilities even under ambient pressure and a low CO₂/H₂ molar ratio (1/3). These multi-functional applications of synthesis of CH₄ and C₂, hydrocarbons stemmed from the multiple interfaces created by the complicated compositions of Co⁰, CoO₄, Mn₂O₃, CuO and Cu₂O species, etc.

The reaction temperature has a significant influence on the catalytic performance, which was monitored using a thermocouple positioned above the catalyst level (Fig. S6†). As shown in Fig. 7c, high temperature promoted the reaction remarkably. With the increase of the reaction temperature, the activity of CH₄ formation increased. The C₂, selectivity increased initially and then slightly decreased at a temperature higher than 200 °C. This is probably because at high temperature, the catalyst was sintered and reduced, which affected the product distribution especially with the CH₄ selectivity increased and C₂, products decreased.

The evolution of activity on reaction time was also studied and the results are shown in Fig. 7d. In the first 30 min of reaction, CH₄ was formed with a very low activity, indicating that the catalyst had an induction period. During this period, the surface Co species, especially the surface CoO, was reduced to the active Co⁰ species. With prolonged time, the CH₄ formation activity increased remarkably. During our experiments, we found that the pressure of the reaction gas decreased remarkably after 3 h, but further prolonging the time did not show any remarkable decrease, indicating that the reaction has reached equilibrium. Thus, we chose 3 h as the optimum reaction time. In addition, control experiments were conducted to investigate the effect of optical and thermal conditions. The reaction could hardly occur under light irradiation but without extra heating, and the sole thermal conditions offered a very low CH₄ formation activity (only one-sixth that of
the photothermal reaction). However, their combination is beneficial for the CO₂ reduction, indicating that the excellent catalytic performances stemmed from their synergistic promotion effect.

As mentioned above, the present catalytic system could achieve the photothermal CO₂ reduction to C₂, hydrocarbons, but only needs to enhance the concentrations of CO₂ and H₂ to 25% and 75%. Fig. S9† shows the catalytic performances of the reaction. Under the conditions of 200 °C and 3 h, the highest C₂ selectivity and activity reached 30.8% and 7.5 mmol g⁻¹ h⁻¹ obtained after 3 h of reaction.

The results indicated that the multifunctional applications of the trimetallic Co–Cu–Mn catalysts derive from not only the multicomponents of the catalysts, but also the interaction effects between the components.

**Photoelectric properties of the Co–Cu–Mn catalysts**

The study of the catalytic performances confirmed that Co₃O₄ and Mn₂O₃ oxides are very important for the reaction, and this differs from the fully reduced Co-based catalysts in H₂ such as Co/CoO₂⁹ and CoO/MnO₅⁵ catalysts in CO₂ thermal hydrogenation. This diversification is probably because photothermal catalysis needs more light-sensitive components such as Co₃O₄ and Mn₂O₃ due to their semiconductor nature⁵²,⁵³ while the thermal catalyst favours low-valent metals such as Co⁵⁷.

To further investigate the light-sensitive properties of the Co–Cu–Mn trimetallic catalysts, the UV-vis DRS spectra were investigated, and the results are shown in Fig. S10a.† The unreduced catalysts including Co₃Mn₁O₅, Co₇Cu₁O₅, and Co₇Cu₁Mn₁O₅ showed higher absorption than the corresponding reduced catalysts throughout the UV-vis region. This was because the former mainly contain Co₃O₄, which has strong absorption of d–d transitions.⁵⁴ Upon reduction, the Co₃O₄ amount decreased, leading to the decrease of absorption accordingly. As for the Co₇Cu₁Mn₁O₅(200, 300, 400, and 500) catalysts, with the increase of the reduction temperature, the absorption strength decreased gradually for the deep reduction of Co₃O₄ to CoO and Co⁶ species. Both the Co₇Cu₁O₅(200) and Co₇Cu₁Mn₁O₅(500) catalysts showed a lower absorbance than the other samples because they did not contain the Co₃O₄ species, which was confirmed by the XRD tests.

The band gap energies (E₉) for the tested catalysts were calculated using the Kubelka–Munk (K–M) model.⁵⁵ The Co₇Cu₁Mn₁O₅(200) catalyst had a lower E₉ value (1.86 eV) than those of the catalysts reduced at higher temperatures (Fig. S10b†). The Co₇Cu₁Mn₁O₅(500) catalyst, however, had the highest E₉ (3.26 eV) value and showed a very low activity in the reaction. The low E₉ value of the Co₇Cu₁Mn₁O₅(200) catalyst led to the feature that the electrons in the semiconductor could be easily excited under light irradiation. The lower band gap is conducive to visible light excitation, which was confirmed by the control experiments using different types of light including full irradiation (300–1100 nm), UV (300–420 nm), and visible light (420–800 nm). The catalytic performances obtained under visible light illumination are almost similar to those under UV-vis and full irradiation, as shown in Table S5.†

The photocurrent–time curves of the Co₇Cu₁Mn₁O₅(100, 200, 300, and 400) catalysts are shown in Fig. S10c†. All of these catalysts showed obvious photocurrent response behavior, indicating that they could be excited to generate electron–hole pairs.

Co₃O₄, Mn₂O₃, Cu₂O, and CoO are p-type semiconductors; however, after reduction, oxygen vacancies were created and regulated the p-type to a n-type semiconductor, which is confirmed by the Mott–Schottky curves shown in Fig. S10d†. All the catalysts showed dipolar (p-type and n-type) semiconductor properties, resulting from the multiple interfaces of the complex trimetallic catalyst.

The EIS Nyquist plots of the tested samples including Co₇Cu₁Mn₁O₅(100, 200, 300, and 500) showed similar arc radii, revealing that they have similar impedance values and electron transfer rates (Fig. S10e†).⁵⁶

The photothermal effect was investigated via testing the stable temperature of the samples under vacuum (Fig. S11†). Under similar conditions, the catalyst temperatures were monitored using an infrared camera. Among the tested catalysts, the MnO₂ catalyst showed the highest temperature (104.6 °C) under the full irradiation, while the CuO catalyst offered the lowest (88.3 °C). The Co₇Cu₁Mn₁O₅(200) catalyst showed a higher temperature (102.2 °C) than that of the Co₇Cu₁Mn₁O₅(500) (95.8 °C), indicating that the Co₇Cu₁Mn₁O₅(200) catalyst could provide a higher local heating environment. The results revealed that the presence of Mn could provide a higher local temperature for the catalyst.

In summary, the results obtained due to the photoelectrical characteristics indicated that the Co₇Cu₁Mn₁O₅(200) catalyst is a p-type and n-type semiconductor, showing a low band gap. All of these properties are closely related to the excellent catalytic activity in photothermal CO₂ reduction. However, it should be noted that the unique catalytic performances of the Co₇Cu₁Mn₁O₅(200) catalyst were derived from the synergistic effect of the adsorption effect, light-response properties, and photothermal effect.

**Light effect and the proposed mechanism for photothermal CO₂ reduction**

In the present catalytic system, the synergistic effect between light and heat had a great influence on the catalytic activity. Under light irradiation, the electrons of the Co₇Cu₁Mn₁O₅(200) catalyst could be excited to generate the electron–hole pairs. Generally, in photocatalysis, the excited electrons and holes can participate in reactions.⁵⁷ However, under photothermal conditions, the E₉ value of the semiconductor is normally found to be lower, and the excited electrons recombine more easily with the photogenerated holes than under the traditional photocatalysis without heating.

To investigate the effects of the generated electron–hole pairs, we carried out two control experiments by adding sacrificial electron donors including p-xylene (~2.18 V vs. Ag/AgClₛₑₐ) and anisole (1.92 V vs. Ag/AgClₛₑₐ) in the absence of H₂.¹⁸,²⁵ As shown in Fig. S12†, both the reactions gave a very low CH₄
yield despite the fact that p-xylene and anisole could quench the photogenerated holes more efficiently than H₂. These results indicated that photocatalysis plays a minor role in the present photothermal CO₂ reduction. In this aspect, similar to the Ru-,18 Rh-,58 Au-,58 and Ag-based59 catalysts, the charge separation and recombination under light irradiation resulted in a local thermal effect at the surface of the catalyst, offering more energy to promote CO₂ reduction.

The mechanism for the photothermal CO₂ reduction to hydrocarbons is still unclear, and two reaction routes are generally accepted.60 The first involves a CO intermediate, in which CO₂ is initially converted to CO, and CO could be further hydrogenated to hydrocarbons.61 The other route is the direct CO₂ conversion. In this route, CO₂ is hydrogenated to carbonate, formate, and methoxy intermediates, and then hydrogenated to hydrocarbons. In this work, the CO formation activity was very low. To study the reaction pathway, we conducted the control experiments of replacing CO₂ by CO under the conditions given in Table 1, entry 8. Interestingly, the activities of CH₄ and C₂⁺ were 4.9 and 7.3 mmol g⁻¹ h⁻¹, and their selectivities were 40.2% and 59.8%, respectively (Table 1, entry 8, Fig. S13, S14 vs. Table S6, entry 2, Fig. S15f). To exclude that the high CO concentration may occupy the active sites on the catalyst surface, a mixed gas of 2% CO/8% CO₂ (total 10%) was also reacted (Table S6, entry 3 and Fig. S16f). However, the activities of CH₄ and C₂⁺ were 7.2 and 2.8 mmol g⁻¹ h⁻¹ with the selectivities of 72.0% and 28.0%, respectively. The results implied that the presence of CO could not improve but reduce the CH₄ activity, meaning that in the photothermal CO₂ reduction, CH₄ is probably not formed via the CO intermediate route. However, CO was found to be beneficial for the C₂⁺ synthesis, revealing that it is probably an intermediate for the formation of the C₂⁺ hydrocarbon product.

The characterization results confirmed that the trimetallic Co₇Cu₃Mn₁O₉(200) catalyst contains CoO, Co₉O₄, Cu₂O, Mn₃O₄, etc. During the reaction, the CoO species could be reduced to Co⁰, which was recognized as the active site. The CoO and Cu₂O species could be reduced by H₂ to Co⁰ and Cu⁰ during the reaction, which was confirmed by the XPS results (Fig. 5). In the present photothermal CO₂ hydrogenation, metal oxides such as Co₉O₄ and Mn₃O₄ were very important for the reaction because they are semiconductors, which could generate electrons and holes under light illumination. A quick recombination of electrons and holes provides a local heating environment for the catalysts, and further promotes the reaction.7 In addition, Mn₃O₄ could offer Lewis acidic sites to enhance CO₂ and H₂ adsorption capacity of the catalyst.

Cu species could promote the partial reduction of cobalt oxides to CoO and Co⁰ and maintain the presence of CoO and Co₉O₄ prior to and during the reaction, and reduce the temperature of catalyst reduction. Besides, the CO₂-TPD tests and the control experiments confirmed that the Cu species or the Cu–Co interfaces could provide strong CO₂ adsorption sites to convert CO₂ to CO, and further form C₂⁺ hydrocarbons.

It should be mentioned that, although CH₄ was probably not formed via the CO route, CO could be produced with an activity of 1.1 mmol g⁻¹ h⁻¹ (entry 8, Table 1). Importantly, the higher concentration of CO could make it easily coupled into the C₂⁺ products over the same Co₇Cu₃Mn₁O₉(200) catalyst. Thus, C₂⁺ hydrocarbons could be formed by increasing the CO₂ concentration.

In addition, the present protocol could be extended to photothermal CO hydrogenation. We conducted the reaction over the Co₇Cu₃Mn₁O₉(200) catalyst under the similar conditions given in Table 1, entry 8, and the results are shown in Fig. S17.† The photothermal activity is about 7 times higher than that of the thermal activity, and the selectivity of the C₂⁺ products is higher than that of CH₄, which is similar to CO₂ hydrogenation. The results indicated that the present trimetallic Co–Cu–Mn catalyst has multifunctional applications as shown in photothermal CO hydrogenation.

The reusability and stability studies of the Co₇Cu₃Mn₁O₉(200) catalyst

The reusability of the Co₇Cu₃Mn₁O₉(200) catalyst was investigated, and the results are shown in Fig. 8a. For comparison, the CO₂ reduction reactions were alternatively conducted under photothermal and thermal conditions. The results revealed that the present catalyst possesses good reusability in the reaction, and after using for 18 times, it still showed an activity of higher than 10 mmol CH₄ g⁻¹ h⁻¹. Besides, the results also confirmed that the activities under photothermal conditions were much higher than those under thermal conditions. The used catalysts were characterized by XRD and XPS, and the results are shown in Fig. 5, respectively.

The activity loss is probably caused by catalyst agglomeration, which was confirmed by the TEM images of the catalyst after being used 18 times (Fig. S18).† The size of the used catalyst increased in the range 40–90 nm.

Fig. 8b shows the temporal stability of the Co₇Cu₃Mn₁O₉(200) catalyst in a continuous flow operation (details are given in the ESI†). The catalyst offered approximately 20 mmol g⁻¹ h⁻¹ of CH₄ after a short induction period of 3 h, and maintained higher than 18 mmol g⁻¹ h⁻¹ activity.
even after 25 hours of reaction. The result showed that the present Co-Cu-Mn catalysts have a long-term temporal stability, confirming that it has a potential industrial application.

Conclusions

In summary, a trimetallic Co–Cu–Mn catalytic system for photothermal CO₂ reduction was constructed by a simple co-precipitation method. The metal compositions and reduction temperatures of the catalysts affected their activities remarkably, and the screened Co-Cu-Mn catalyst could offer 14.5 mmol g⁻¹ h⁻¹ of CH₄ at low CO₂ (10%) and H₂ (30%) concentrations. Importantly, the catalyst system could produce C₂, hydrocarbons with an activity of 7.5 mmol g⁻¹ h⁻¹ and a selectivity of 30.8% by only improving the CO₂ and H₂ concentrations to 25% and 75%, respectively. High activities stemmed from the multicomponents of the catalyst, especially the metallic Co₀, Cu₀, and CoO, Co₃O₄, Cu₂O, and Mn₂O₃ semiconductors. The Cu species could tune the reduction characteristics, and further tune the balance of Co²⁺ and Co³⁺. The Mn species could enhance the CO₂ and H₂ adsorption, and also offer a high local temperature for the nanocatalyst. The present strategy of partial reduction of the Co–Cu–Mn trimetallic catalyst not only highlights the route for using solar energy to produce valuable chemicals under mild conditions especially low CO₂ concentration, but also constructs the highly efficient trimetallic catalysts with multifunctional applications in photothermal catalysis.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

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