Sustained CO₂-photoreduction activity and high selectivity over C, Mn-codoped ZnO core-triple shell hollow spheres

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Abstract

Solar conversion of CO₂ into energy-rich products is one of the sustainable solutions to lessen the global energy shortage and environmental crisis. Pitifully, it is still challenging to attain reliable and affordable CO₂ conversion. Herein, we demonstrate a facile one-pot approach to design core-triple shell Mn, C-codoped ZnO hollow spheres as efficient photocatalysts for CO₂ reduction. The Mn ions, with switchable valance states, function as “ionized cocatalyst” to promote the CO₂ adsorption and light harvesting of the system. Besides, they can capture photogenerated electrons from the conduction band of ZnO and provide the electrons for CO₂ reduction. This process is continuous due to the switchable valence states of Mn ions. Benefiting from such unique features, the prepared photocatalysts demonstrated remarkably selective CO₂ conversion into CH₃OH (yielding ten times higher than that of commercial ZnO). This work is endeavoured to shed light on the role of ionized cocatalyst towards sustainable energy production.

Introduction

Worldwide consumption of fossil fuels is unambiguously accountable for two critical issues *i.e.* global warming by the augmented greenhouse gases (especially CO₂) emission and depletion of such non-renewable sources.^{1–4} Nowadays, it becomes a global appeal to develop sustinable energy grids based on renewable energy sources such as solar, wind, geothermal energies.^{5,6} Reliable conversion of CO₂ by the aid of solar light to energy-rich fuels (*i.e.* artificial photosynthesis) is an ideal solution for simultaneously relieving both energy and environmental crises.^{7–9} Albeit great efforts have been devoted to exploring the potential of artificial photosynthetic materials for CO₂ conversion, its efficiency is still unsatisfactory due to difficulties in activating thermodynamically stable CO₂.^{10–12} Therefore, it is critical to construct suitable photocatalysts and coupled with active cocatalysts. Cocatalysts can effectively promote the separation and transfer of photogenerated charge carriers to attain appealing CO₂ reduction ability.^{9,13,14}

Transition metal-based materials (TMMs) such as ions, oxides, sulphides, phosphideds, exhibited outstanding potentials as cocatalysts for both oxidation and reduction reactions.^{15–17} They can not only effectively lower the barrier for CO₂ activation, but also promote the separation of photogenerated charge carriers.^{18,19} To date, most cocatalysts are in solid state. We wonder whether ionized cocatalysts which are embedded in the lattice of photocatalyst can also serve as cocatalyst. They can become active sites for the photocatalytic CO₂ reduction. Due to their multiple oxidation states, they can swap electrons with photocatalyst as well as CO₂. Besides, the introduction of ionized cocatalyst avoids the difficulty of loading cocatlyst on the photocatalyst. And the difficulty in maintaining intimate contact no longer exists.

Intricate hollow structures with tailored compositions have surpassed their solid counterparts in widespread applications. However, the fabrication of such intricate structures is still an arduous challenge. Multi-shell hollow structures (MSHSSs) are characterized by manifold features such as large

specific surface area, low density, as well as reduced mass and charge diffusion lengths.²⁰ All of these endow MSHSs with potential in multiple applications, such as photocatalysis, energy storage and conversion, drug delivery and sensors.^{21–23} Concerning CO₂ photoreduction (PR), MSHSs possess prodigious advantages over their solid counterparts. These advantages particularly spring from aesthetic shell layers. For one thing, their large surface area promotes CO₂ adsorption and surface redox reactions on both sides of the shells. For another, they provide a reduced path length for charge carriers, favoring charge migration and separation.^{24,25} All these merits make MSHSs ideal support materials for anchoring photocatalysts aiming at designing elaborate catalytic system for CO₂ PR. However, the fabrication of such MSHSs is still an arduous challenge.

Herein, we developed a facile one-pot coordination polymer (CP) strategy to fabricate C, Mn-codoped ZnO core-triple shell hollow spheres (C, Mn-ZnO CTSHSs). The process involves two steps: (i) formulation of Zn, Mn CP via interaction of salicylate ligand with the corresponding metal ions in the presence of polyvinylpyrrolidone (PVP) and (ii) air calcination of the resultant Zn, Mn CP (Fig. 1). The obtained photocatalyst with fascinating core-multishell morphology and tailored composition affords adequate CO₂ reduction activity, i.e. ten times higher than commercial ZnO. Such enhanced activity is ascribed to the improved light absorption, favorable transfer of mass and charges across the thin shell layers and aided CO₂ adsorption and activation. Interestingly, Mn species formed in the system as substituent of Zn ions in the ZnO lattice play indispensable role during CO₂ PR. They act as active centers for CO₂ adsorption and subsequent reduction in a high selective manner toward CH₃OH. Most importantly, in-situ X-ray photoelectron spectroscopy (ISXPS) results revealed that Mn species can restore their primal oxidation state after CO₂ PR without external treatment or subsidiary reducing agents. Instead, Mn⁽ⁿ⁺¹⁾⁺ species can extract one photogenerated electron from the system to regenerate the original Mnⁿ⁺ moieties. The switching between Mn⁽ⁿ⁺¹⁾⁺/Mnⁿ⁺ is recognizable by virtue of the multiple oxidation states of Mn and affordability of photogenerated electrons. These results suggest that ionized Mn can act as durable and efficient cocatalyst toward practical CO₂ PR.

Results And Discussions

Formulation of C, Mn-ZnO CTSHSs. The core-triple shell hollow spheres are obtained via a facile one-pot solvothermal preparation of Zn, Mn CP spheres (Zn, Mn-CPSs) followed by controlled air-annealing as depicted in Fig. 1. The CPSs as precursor were firstly formulated by the coordination interaction between Zn- and Mn- acetate and salicylate ligands (Fig. 1a). The carboxylate groups of salicylic acid play a significant role that they can coordinate to metal ions, enabling a delicate control over the composition. Moreover, this method is universal to most of the transition metals because non-selectivity is witnessed for salicylic acid.²⁶

Fourier-transform infrared spectroscopy (FTIR) spectra of the Zn, Mn-CPSs (Supplementary Information Figure S1) evidenced the interaction between deprotonated carboxylate groups of salicylate ligands and metal ions. Such interaction is assured after distinctive intensity drop of the corresponding C = O peak

centered at 1657 cm^{-1} and a slight shift to 1654 cm^{-1} .²⁶ The deprotonation of the carboxylate groups is very critical to boost such coordination interaction. As a strong conjugated base, acetate anions can deprotonate the carboxylate groups of salicylic acid and thus enable reliable coordination between salicylate ligand and metal cations. To confirm this assumption, we replaced Zn- and Mn-acetates by their sulfates, nitrates or chlorides and followed the same preparation recipe. All of them fail to fabricate such spherical architecture. We attribute such failure to the inability of the corresponding anions to deprotonate carboxylate groups of salicylic acid. After formation of Zn, Mn-CPSs, the generation of hollow structures derives from the calcination process. In this step, the Mn, Zn-CPSs precursor is subjected to air calcination at $550\text{ }^{\circ}\text{C}$, a step that culminates the unique CTSHSs morphology by heterogeneous contraction process (Fig. 1b,c).

Transmittance electron microscopy (TEM) (Fig. 2) and field emission scanning electron microscopy (FESEM) (Supplementary Information Figure S2) images show Zn, Mn-CPSs as high uniform solid spheres with an average diameter of about $1.3\text{ }\mu\text{m}$ and smooth surface texture. After calcination for 3 h, unexpectedly, the solid Zn, Mn-CPSs were converted into unique concentric C, Mn-ZnO CTSHSs, as noticed from the high contrast between the shell edges and centered hollow regions (Fig. 2b and Fig. 3e). The CTSHSs retain the spherical shape of CPSs precursor but the diameter is dramatically shrunk to 650 nm due to the contraction upon calcination. The surface turns rough, pervaded with crystallites with invasive pores. The size of the crystallites was measured to be 25 nm from high-resolution TEM. Its porous structure was also confirmed by N_2 adsorption-desorption isotherm (Supplementary Information Figure S3 and Table S1). Additionally, uniform distribution of the constituent elements *ca.* Zn, O, Mn and C are observed from EDS elemental mapping of the calcined sample (as taken for sample calcined for 1 h, Fig. 1d-g). The elemental composition distribution is presented in Supplementary Information Figure S6.

To elucidate the evolution mechanism of the CTSHSs morphology, FESEM and TEM images of the intermediates at different calcination stages were recorded (Fig. 3 and Supplementary Information Figure S2). At the initial stages of the calcination process (after 0.5 h), a significant temperature gradient (ΔT) along the radial direction of the CPSs was generated where the outermost building units are subjected to abrupt heating. Meanwhile, the carbon entities vanish and ZnO nanoparticles were crystallized at the outer surface. Thus, a core-shell structure (the first ZnO shell conjoined to the entire core) was generated (Fig. 1b, Fig. 3b). Once forming, the rigid ZnO shell plays an indispensable role in preventing further contraction of the outer diameter, even if the entire core suffers from continuous shrinkage upon the disintegration of organic moieties by further annealing, known as heterogeneous contraction.^{27–30}

With extended calcination time, both the core and the emerged new shell experienced two opposite forces. Namely, inward cohesion force (F_c) originated from the sharp contraction of the interior core upon continuous disintegration of the skeletal carbon and outward adhesion force (F_a) emanated from the cling of adjacent crystallites (Fig. 1c). The balance between both forces culminated in varied structures. When the CPSs were calcined for 1 h, the temperature gradient gets smaller. And F_c exceeds F_a , which leads to separation of the entire core from the outer shell, forming a yolk-shell structure (Fig. 1b, Fig. 3c,

and Supplementary Information Figure S2b). With calcination continued for 2 or 3 h, the entire yolk underwent similar processes described before, forming the unique second (core-double shell, Fig. 3d and Supplementary Information Figure S2c) and the third shell (core-triple shell, Fig. 3e and Supplementary Information Figure S2d).

It is noteworthy that the disintegration of the carbon moieties on both exterior and interior surfaces induces the formation of observable pores within the shell layers (Supplementary Information Figure S2e), which facilitates the mass transfer of the reactants/products.^{31,32}

All the calcined samples together with commercial ZnO (for comparison) show diffraction peaks (Supplementary Information Figure S4) that are well indexed to Wurtzite hexagonal ZnO (JCPDS PDF Card No. 36-1451).³³ Adequate purity and good crystallinity of the prepared ZnO CTSHS samples are reflected from the sharp peaks and absence of secondary peaks even with 5% Mn loading. Additionally, compared with commercial ZnO, the lattice of the prepared catalysts is mostly contracted after the doping process (see Supplementary Information for more discussion). These results suggest the successful doping of Mn and/or C within the crystal lattice of ZnO and Mn species are implemented to substitute Zn ions in the lattice.

The XPS spectra further indicate the successful doping of Mn within the crystal lattice of ZnO, originating from the distinctive Mn 2p and Mn 3 s peaks appeared in the XPS profiles and the shift of Zn 2p_{3/2} peak (see Fig. 6 and Supplementary Information Figure S5 for more details about the chemical state of Mn within the ZnO lattice). The actual compositional percentages of Mn and C in 2%Mn, C-ZnO sample are 1.8 and 8.3%, as derived from inductively coupled plasma-atomic emission spectroscopy (ICP-AES) measurements and elemental analysis, respectively, (Supplementary Information Figure S6). The presence of Mn is believed to promote catalytic conversions owing to their ability to share electrons with reactant molecules and/or intermediates.^{34–37} Besides, doping gives rise to defect states and impurity levels. They not only reduce the bandgap of the semiconductor, but also improve the light absorptivity of the photocatalyst. The defect states could support the charge separation process through obstructing the electron-hole recombination by electron trapping.^{38–41} Specifically, introduced transition metal ions could act as distinctive active sites or enrich present active sites, which evidently support reactants adsorption, activation and further chemical conversion.^{42–44}

The photocatalytic performances of the prepared catalysts were evaluated for CO₂ PR under simulated solar light at ambient conditions without photosensitizer, precious cocatalyst or sacrificial reagents. Methanol (CH₃OH) was found to be the predominant product together with small amounts of carbon monoxide (CO) (Fig. 4a). The 2%Mn, C-ZnO CTSHSs (CZ-2 in Fig. 4a) photocatalyst affords the highest PR activity with CH₃OH evolution rate 11.64 $\mu\text{mol g}^{-1} \text{h}^{-1}$, two and ten times higher than C-ZnO CTSHSs and comm. ZnO, respectively. The selectivity toward CH₃OH production is also dramatically improved from 38% (comm. ZnO) to 85% (CZ-2). The Zn in the comm. ZnO has low tendency to bind the CO intermediate.¹⁷ Therefore, the CO desorbs readily from the surface and emerges as a major product. By

contrast, in case of Mn-doped catalyst, the Mn centers were reported to show moderate adsorption affinity for CO molecules⁴⁵. This assists subsequent reduction to CH₃OH as a predominant product. These results manifest Mn ions as the more workable active centers during CO₂ PR over Mn-ZnO photocatalyst.

The time-course product evolution rate further affirms the effectiveness of the 2%Mn, C-ZnO CTSHSs sample to sustain almost the same activity even after prolonged testing time (Fig. 4b). These findings unambiguously disclose the promising potential of the prepared CTSHSs photocatalysts for CO₂ PR.

Furthermore, control experiments manifest that no detectable products are observed (either in the dark or under light irradiation) in absence of the photocatalyst and/or CO₂, suggesting that CH₃OH and CO are indeed generated from CO₂ photocatalytic reduction.^{46,47} Isotopic labeling experiment (Fig. 5a) strongly confirms that the carbon-based products are indeed derived from CO₂ reduction and not from any other carbon source. The achieved CO₂ PR rate of the prepared Mn and C-doped photocatalyst under sacrificial-reagent and photosensitizer-free conditions is superior to most state-of-the-art photocatalysts (Supplementary Information Table S3), which reflects its potential.

Additionally, the C-ZnO sample shows five times higher activity than the comm. ZnO sample (even with the same BET surface area, see Supplementary Information Table S1). To delve into the origin of such enhanced activity, UV-vis light absorption, photoluminescence (PL), time-resolved PL (TRPL) and, CO₂ adsorption isotherm and electrochemical impedance spectroscopy (EIS) measurements as controlling factors of a photocatalyst activity toward CO₂ PR were further tested and the results were depicted in Fig. 4 and Fig. 5. Appreciable enhancement of the visible light absorption was sustained by the fascinating hollow morphology, thanks to the multiple reflections of the incident light inside the interior cavities of the fascinating core-triple shell hollow structure⁴⁸ (inset of Fig. 4c). Moreover, the codoping process introduces impurity levels within the forbidden gap of ZnO, which indeed contributes to narrowing the bandgap (as depicted from Tauc plots, Supplementary Information Figure S7) and enhancing the light-harvesting ability of the doped samples. A stepwise improvement of the light absorptivity of the prepared photocatalysts is observed in line with Mn-content (Fig. 4c). This finding should be correlated to the fact that more impurity states are developed within ZnO bandgap with increasing Mn doping. In addition, the doping with Mn could initiate other electronic transitions such as ligand to metal charge transfer, metal to ligand charge transfer and d-d transition.^{49–51} All these transitions are accounted for the whole system light harvesting, which leads to enlarged absorption response.^{52,53}

Furthermore, the PL spectra of the prepared catalysts are step-wisely quenched after C and Mn doping. This reveals that suppressed charge recombination is achieved by doping. The 2%Mn, C-ZnO sample exhibits the lowest PL behavior (Fig. 4d), benefiting from two factors. One is (i) the defect state. The rest are (ii) the core-shell morphology and porous structure. The former could act as trapping centers, quenching the electron-hole inhalation process. Whereas the latter reduces both diffusion lengths of

charges and reactants, thus minimizing charges recombination opportunities and provide accessible channels for mass/charge transfer.⁵⁴ TRPL results also demonstrate that 2% Mn, C-ZnO can retard charge carriers recombination and prolong their lifetime (average charge carrier-lifetime ca. 1.1, 0.9 and 0.8 ns for 2%Mn, C-ZnO, C-ZnO and Comm. ZnO, respectively, Fig. 5b and Supplementary Information Table S4). These results indeed affirm the potential of Mn doping to delay charge recombination.

In addition, the prepared samples (C-ZnO and Mn, C-ZnO CTSHSs) attain very low resistance for charges transfer (R_{ct}) process compared to comm. ZnO sample (as speculated from the EIS measurements, Fig. 5d, where smaller arc diameter represents lesser resistance). Obviously, the fascinating architecture favors charge carrier separation and diffusion from bulk to surface region through few nanometer-thick shells. Especially, the Mn-doped sample shows the least R_{ct} , benefiting from charge trapping action exerted by the doping-based defect states (at optimum content) and the following interfacial charge transfer.^{55,56}

Besides, Mn species could be beneficial for enhancing the adsorption of CO₂. To authenticate such a hypothesis, the CO₂ adsorption isotherms for C-ZnO and 2%Mn, C-ZnO-CTSHSs are provided in Fig. 5c. Obviously, the 2% Mn-doped sample showed much more adsorption affinity (merely twice) toward CO₂ than the undoped sample does. This result coincides well with the photocatalytic activity of both samples (Fig. 4a). The higher the CO₂ adsorption affinity of a photocatalyst is, the better the photoreduction activity will be expected. Therefore, it is reasonable to notice such enhanced activity for Mn-doped photocatalyst. The improvement of CO₂ adsorption after Mn doping was also reported for Mn-In₂S₃ tested for CO₂ electroreduction.⁵⁷

Two plausible factors contributing to the high CO₂ adsorption affinity are proposed. One is the higher content of surface oxygen-species (see XPS interpretation, Supplementary Information for details) than C-ZnO sample. The other is the potential of Mn species replaced Zn ions in the lattice to activate CO₂ molecules.

To further explore the functional role of Mn, *in-situ* irradiated XPS (ISI-XPS) analysis for Mn, C-ZnO CTSHSs sample saturated with CO₂ was conducted under both dark and irradiated conditions. The high-resolution XPS peaks are demonstrated in Fig. 6 and supplementary Figure S5 together with the same peaks from bare sample (without CO₂ treatment). The loading of CO₂ molecules onto the surface was assured by emergence of a tiny M-CO₃ peak in C 1 s XPS (Supplementary Information Figure S5b*), suggesting the successful bonding of CO₂ molecules to metallic sites. To probe how Mn ions could assist activation of CO₂ molecules during the PR process, we calculated the average oxidation states (AOS) of Mn under test according to the following equation:⁵⁸

$$AOS = 8.95 - 1.13\Delta S \quad (1)$$

where ΔS is the multiplet splitting of Mn 3 s peak (Fig. 6a, b). By substituting ΔS values obtained from Fig. 6 in Eq. 1, the AOS of Mn species are ~ 5 , 6 and 5.5 for untreated sample, CO₂-loaded sample under dark and light irradiation, respectively. Owing to the calcination of the bare samples under open atmosphere, it is not surprising for Mn in Mn,C-ZnO CTSHSs photocatalyst (without CO₂ loading) to acquire such high AOS. Because we measure the change of AOS, further investigations are required to elucidate the actual functional oxidation state involved in CO₂ activation. For simplicity, we use Mn⁵⁺ and Mn⁶⁺ to indicate Mn species with AOS ~ 5 and 6, respectively.

The significant increase in AOS of Mn after CO₂ loading and before illumination could be explained in terms of electron transfer from Mn to adsorbed CO₂ molecules^{34,35}. In our system, we noticed that the AOS of Mn in CO₂-loaded photocatalyst can be restored again under light irradiation. This is due to that photogenerated electrons transfer from ZnO to Mn⁶⁺ centers to regenerate the primal Mn⁵⁺ again (Fig. 7). This light-switchable conversion between Mn⁵⁺/Mn⁶⁺ is very critical for restoring the original activity of the Mn-doped catalyst without external treatment or activation steps. In addition, this conversion holds a promising potential for all-in-one CO₂ reduction technology. Concisely, Mn⁶⁺ species can capture the photogenerated electrons from the CB of ZnO, yielding Mn⁵⁺. Mn⁵⁺ functions as the active centers for CO₂ adsorption and activation via one electron transfer process to yield CO₂^{•-} and Mn⁶⁺. At the same time, if more electrons are captured at Mn⁶⁺, the generation of CH₃OH becomes possible. This finding authenticates the role of Mn species as ionized cocatalyst in the system.

In fact, the regeneration of the Mn species after the activation step is very critical to maintain the activity (Fig. 4b). Moreover, the charge trapping action is of great essence for charge carrier's separation. Thus the optimal doping from Mn results in lowest charges recombination as revealed from PL results (Fig. 4d).

In this vein, Mn functions as Lewis base center, which supports the adsorption of acidic CO₂ molecules and further transfer of one electron thus culminates activated CO₂^{•-} (Fig. 7). This electron transfer process is typically mimicking the electron transfer process involved in Photosystem II during natural photosynthesis.³⁵ Such a process is followed by multiple proton-coupled electron transfer reactions to produce the desired CH₃OH molecules (Eqs. 2–6, Supplementary Information).

The adsorption, activation and subsequent reduction of CO₂ molecules over Mn-doped ZnO photocatalyst is further confirmed by *in-situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) results (Supplementary Information Figure S8, see supporting information for more details), which assures the adsorption, activation and successful conversion of activated CO₂ molecules onto CH₃OH at the photocatalyst surface (Fig. 7).

All these results unambiguously disclosed the potential of the prepared and light-switchable ionized cocatalyst (Mn⁵⁺/Mn⁶⁺) integrated C, -ZnO CTSHSs as an efficient photocatalyst for CO₂ PR under

ambient conditions without sacrificial reagents, precious cocatalysts or external treatment set up for activity restoration.

In summary, core-triple shell C, Mn-codoped ZnO hollow spheres were rationally fabricated via a one-pot synthetic protocol. In addition, they were tested as a highly active and selective catalyst for CO₂ photoreduction under simulated sunlight and ambient conditions. The unique core-triple shell hollow structures codoped with Mn and C, hold manifold structural and functional features. These unique features culminated improved light absorption capability, enhanced charge separation and migration efficiency, suppressed e⁻/h⁺ pairs undesired recombination probability and abundant adsorption and activation active sites for effective photoredox catalysis. All of these accounted for the superior activity of the prepared photocatalyst. The Mn species played a significant role to activate CO₂ molecules through an electron-transfer mechanism, assembling that occur within Photosystem II in natural photosynthesis. We have observed that the ionized Mn species can restore their primal oxidation state and hence their activity by virtue of the photogenerated electrons. Therefore, it can be operated as a light-switchable ionized cocatalytic system. These findings will support the design of efficient photocatalytic materials for sustainable clean energy production and beyond. The present study sheds light on the significance of hollow structure materials as active photocatalyst for CO₂ reduction as well as the importance of light-switchable ionized cocatalysts during this process.

Methods

Materials.

All chemicals are of analytical grade and used without additional purification. Zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O) and absolute ethanol were purchased from Beijing Sinopham Chemical Reagent Co., Ltd. Manganese acetate tetrahydrate (Mn(CH₃COO)₂·4H₂O) and salicylic acid (C₇H₆O₃) were purchased from Tianjin BODI Chemical Co., Ltd. Polyvinylpyrrolidone (C₆H₉NO)_n (K23-27, M.Wt ~ 24000) was supplied by Aladdin Industrial cooperation, Shanghai, China.

Synthesis of Mn, C-ZnO CTSHSs

The Mn, Zn CPSs were firstly prepared by a solvothermal step. Typically, 1 mmol Zn(CH₃COO)₂·2H₂O, x mmol Mn(CH₃COO)₂·4H₂O corresponding to the desired Mn²⁺/Zn²⁺ mole ratio (0, .01, .02, .05 or .1) and (2 + x) mmol salicylic acid were magnetically dissolved in 50 mL absolute ethanol. Afterward, a calculated amount of PVP (to keep the concentration ratio M_{PVP}/M_M²⁺ = 5, M of PVP was calculated based on the molecular weight of its monomer) was added to the above solution and further stirred for 30 minutes. The mixture was transferred into a 100 mL Teflon-lined stainless steel autoclave, heated at 160 °C for 12 h and then air-cooled to room temperature. The precipitate was separated by centrifugation, washed three times with absolute ethanol and dried under vacuum at 60 °C overnight. The as-obtained

Mn, Zn CPSs were calcined at 550 °C for 3 h by 5 °C/min rate under air atmosphere. The samples with 0, 1, 2, and 5% Mn were denoted as C-ZnO (CZ), 1%Mn,C-ZnO (CZ-1), 2%Mn,C-ZnO (CZ-2) and 5%Mn,C-ZnO (CZ-5), respectively.

Characterization

TEM, HRTEM and elemental mapping were obtained by Titan G2 60–300 operated at 300 kV. FESEM images were taken by JSM-7500F, JEOL, Japan, equipped with X-Max 50 energy-dispersive X-ray spectroscopy (EDS) unit (Oxford Instruments, UK). XRD patterns of the prepared samples were recorded using D/Max-RB X-ray diffractometer (Rigaku, Japan) with CuK α radiation ($\lambda = 1.5406 \text{ \AA}$) and scan rate = $0.05^\circ (2\theta) \text{ S}^{-1}$. The surface composition and chemical states of C-ZnO and 2%Mn, C-ZnO CTSHSs samples were analyzed by XPS analysis (Thermo ESCALAB 250). The UV–visible light absorption spectra of the samples were recorded by UV-2600, Shimadzu spectrophotometer (Japan) where BaSO $_4$ was used as the reflectance standard. The Brunauer–Emmett–Teller (BET) specific surface area and porosity of the prepared samples, nitrogen adsorption-desorption isotherms were measured on a Micromeritics ASAP 2020 apparatus (USA) and the adsorption data at relative pressure (P/P_0) range of 0.05–0.3 was used. The average pore size and pore volume of the samples were calculated through the Barret-Joyner-Halender (BJH) method using the adsorbed nitrogen volume at the relative pressure of 0.994. Photoluminescence (PL) spectra were recorded on a Hitachi F-7000 (Japan) fluorescence spectrophotometer. FLS920 fluorescence lifetime spectrophotometer (Edinburgh, Instruments, UK) was employed to record TRPL spectra of the prepared samples.

FTIR and DRIFTS analyses were obtained by an FTIR spectrometer (Thermo Scientific, Nicolet iS50, USA). For DRIFT test, the prepared sample was placed into the reaction chamber then, the chamber was sealed and purged with the mixed CO $_2$ and H $_2$ O gases. The DRIFTS analysis was conducted under both dark and light irradiation (3 W 365 nm LED) conditions.

Photocatalytic and electrochemical measurement

The electrochemical measurements were performed in a standard three-electrode configuration analyzer (CHI660C instruments, CHI, China) system with Pt wire and Ag/AgCl (saturated KCl) utilized as counter and reference electrodes, respectively, while the working electrode was prepared using the as-synthesized samples deposited on FTO glass, and the three electrodes were immersed in 0.5 M Na $_2$ SO $_4$ aqueous solution as electrolyte.

The photocatalytic CO $_2$ reduction test was carried out in a 200 ml Pyrex reactor at room temperature. Firstly, 50 mg of the prepared samples and 10 mL deionized water were added to the reactor and ultrasonically dispersed for 10 minutes. Then, the dispersion was dried at 80 °C for 6 h to form a thin film at the bottom of the reactor. Furthermore, the reactor was sealed and purged with nitrogen gas for 30 minutes. A 0.3 mL of 4 M HCl was then injected to the sidearm of the reactor which contains 84 mg NaHCO $_3$ (added to the reactor before sealing) to allow *in-situ* generation of CO $_2$ and H $_2$ O vapor inside the

reactor. A 300 W simulated solar light Xe arc lamp was used as light source and placed 10 cm above the Pyrex reactor. After a definite time of light irradiation, 1 ml of mixed gas was withdrawn from the reactor and analyzed by a gas chromatograph (PGC-80, Changzhou Panna Instrument, China) equipped with a flame-ionized detector (FID) and methanizer to determine the composition of the product mixed gas. High purity nitrogen gas was used as a carrier gas in the PGC-80. Isotopic labeling test was accomplished on TILON LC-D200M gas chromatography-mass spectrometer following similar procedures but pure Ar gas was employed for purging purpose instead of N₂ gas.

Declarations

Author contributions

M.S., P.K., J.L., L.Z and J.Y. conceived and designed the experiments. M.S. and P.K. carried out the synthesis of the materials, the photocatalytic test and the characterizations of the materials. M.S., J.L., L.Z. and J.Y. conducted data analysis. J.Y. supervised the project. M.S., L.Z. and J.Y. wrote the paper. All authors discussed the results and commented on the manuscript.

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Figures

Figure 1

Schematic illustration of C, Mn-ZnO CTHSs formation process. a Preparation of Mn, Zn CPSs from solvothermal treatment of zinc acetate and manganese acetate with salicylic acid in the presence of PVP. b Step-by-step conversion of Mn, Zn CPSs into C, Mn-codoped ZnO CTHSs upon calcination at 550 °C for 3 h. c The underlying driving force for such hollow structure formation.

Figure 2

Morphology of the prepared materials. TEM images of the Zn, Mn-CPSs a before calcination and b after calcination for 3 h. c HAADF-STEM image of Mn, C- ZnO and EDS mapping of the sample show the constituent elements Zn, O, Mn and C.

Figure 3

TEM images of Zn, Mn-CPSs a before calcination and after calcination for b 0.5 h, c 1 h, d 2 h and e 3 h. f depicts the HR-TEM of C, Mn-codoped ZnO with lattice fringes of 0.248 nm corresponds to the (101) plane of Wurtzite ZnO.

Figure 4

The photoresponse of the prepared photocatalysts. a Photocatalytic CO₂ reduction performance of comm. ZnO and the prepared samples. b Time-course products yield over the 2%Mn, C-ZnO CTSHSs photocatalyst. c UV-vis light absorption of the prepared samples and the inset represents the multiple reflection effect of the incident light inside the hollow cavities. d PL spectra of samples at excitation wavelength=380 nm.

Figure 5

a Isotopic labeling test using $\text{NaH}^{12}\text{CO}_3$ and $\text{NaH}^{13}\text{CO}_3$ as the CO_2 source, b TRPL spectra of the samples, c adsorption isotherm of, C-ZnO CTSHSs and 2%Mn, C-ZnO-CTSHSs samples and d EIS measurements for the photocatalysts.

Figure 6

In-situ XPS analysis showed Mn 3s profiles for a untreated and b CO₂-adsorbed Mn, C-ZnO CTSHS samples. The multiplet splitting of Mn 3s (ΔS) is used to calculate oxidation state of Mn ions within the structure (Eq. 1).

Figure 7

Schematic illustration of CO₂ activation and reduction over Mn, C-codoped ZnO sample. The CO₂ molecules are firstly activated at the confined Mn active centers to the highly active radical anion. Such intermediate anion is then subjected to successive electron-coupled proton transfer process (electrons from ZnO CB and protons from water) to finally produce methanol. The photogenerated holes are consumed for water oxidation (oxygen evolution reaction).

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