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Flower-like CoAl layered double hydroxides modified with CeO₂ and RGO as efficient photocatalyst towards CO₂ reduction



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ABSTRACT

In this article, a simple yet effective in situ hydrothermal method has been developed to synthesize a series of CeO₂ and reduced graphene oxide (RGO) stepwise-doped CoAl-LDH (CACR) composites with CoAl-LDH/ CeO₂ (CAC) as the intermediate. The smart design well integrates the photo-electrochemical merits of CoAl-LDHs and CeO₂ with conductive RGO to form an optimized formula with high light-harvesting ability, efficient charge separation, and rapid electron transfer. Owing to these features, the sample of CAC-5-R-10 containing 5 wt% CeO₂ and 10 wt% RGO, is found to be the most efficient one as the catalyst for CO₂ photoreduction with a high average CO evolution rate of 5.5 μ mol·g⁻¹·h⁻¹ at 25 °C without sacrifice reagent or extra photosensitizer under ultraviolet light, which surpasses those of the single CeO₂, CoAl-LDHs, the intermediate of CAC, and many reported LDH-based counterparts. With the assistance of Mott–Schottky curves, the Z-scheme mechanism is proposed for the significantly enhanced photo-activity of the CAC-5-R-10. The present work provides a good sample for integrating LDHs with a second semiconductor and conductive RGO for collaborative optimization of photoelectric characteristics towards enhanced CO₂ photoreduction.

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1. Introduction

Photocatalytic technology is increasingly coming to be recognized as a favorable alternative that can utilize limitless solar energy to convert CO_2 into hydrocarbon fuels, which has the potential to overcome environmental issues and the energy crisis [1,2]. Generally, the main mechanism of CO_2 photoreduction involves the excitation of electron-hole pairs by appropriate photons, and the thus extracted electrons are transported to the surface active sites where reduction of the adsorbed CO_2 molecules takes place [3,4]. However, the high energy barriers that frequently need to be overcome render the process more difficult and illustrate the need for research into practical methods to facilitate photoinduced electrons towards CO_2 photoreduction [5].

Among recently investigated photocatalysts [6,7], the layered double hydroxides (LDHs) have attracted considerable attention in photocatalytic CO_2 reduction due to their superior properties such as layered structure, high porosity, and facile synthesis [8,9]. Moreover, the anions and metal cations of LDHs can be exchanged easily

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making their composition easily adjustable, allowing for great flexibility in tuning the electron structure of these materials. In particular, Co-based LDHs have become an excellent candidate for CO₂ reduction due to its evenly distributed reductive Co²⁺ sites on the LDH layers [10]. The typical CoAl-LDH photocatalyst has also been developed in attempts to boost CO₂ reduction, but the efficiency of the pristine photocatalyst is severely limited due to high electrical resistance and relatively poor charge separation [11]. However, recent efforts using CoAl-LDH-based composite photocatalysts have yielded significantly improved outcomes [12,13], and many methods have been reported for modifying the CoAl-LDHs. For instance, Sanati et al. used g-C₃N₄/CoAl-LDH as a new electrode material for supercapacitor applications [14], while Jo et al. prepared a C dot/ CoAl-LDH photocatalyst for the highly efficient and selective reduction of CO₂ with water to from CH₄ under simulated-solar-light illumination [15]. Chen's group showed the superiority of the Z-scheme heterojunction photocatalyst AgBr@Ag/CoAl-LDH, which improved the outcome of the photocatalytic reduction of CO₂ by effectively promoting the separation of photogenerated electronhole pairs [16]. From these results, it can be inferred that introducing semiconductors to LDHs to form a Z-scheme photocatalytic system could lead to significant improvements on photocatalytic activity. Therefore, more research in the design of a Z-scheme composite

photocatalyst that incorporates CoAl-LDHs for the further improvement of photocatalytic activities for CO₂ reduction of is highly attractive and desirable.

Cerium oxide (CeO₂) is an n-type semiconductor exhibiting properties of interest such as a wide band gap, nontoxicity, stability against photo-irradiation, and chemical inertness. Its unique 4f electronic configuration makes it suitable for the fabrication of complex oxides or as a dopant to improve catalytic activity [17]. Therefore, the rational design of a Z-scheme photocatalyst incorporating dispersed CeO₂ should convert the modified CoAl-LDHs into a highly efficient photocatalyst for the reduction of CO₂. While previous research has used solid electron mediators, such as Au, Ag, and others, to fabricate Z-scheme structures [18,19], the high cost of these noble metals places a serious limitation on their practical applications, so cheaper and more widely available materials would be highly desirable as substitutes. With these considerations in mind, a viable substitute appears to be reduced graphene oxide (RGO), with its 2D structure, large specific surface area, and reported superior performance [20]. Indeed, the introduction of RGO into photocatalysts has been reported to improve the efficiency of photogenerated electron-hole pairs [21]. It is therefore proposed to combine the properties of CeO₂ with RGO as an electron mediator to construct a Z-scheme system with improved photocatalytic activity.

Bearing the aforementioned aspects in mind, herein, a series of novel CeO₂ and RGO-modified CoAl-LDH composites (denoted as CoAl-LDH/CeO₂/RGO with the abbreviation of CACR) is constructed as the catalysts for CO₂ photoreduction with improved mass transfer efficiency and enhanced light-harvesting capacity and utilization of photons. The crystal, morphological, and photoelectrical characteristics of CACRs are investigated by various technologies. The optimal sample of CAC-5-R-10 shows remarkably enhanced photocatalytic performance for CO₂ reduction. A Z-scheme CO₂ photoreduction mechanism of the CAC-5-R-10 is also proposed. This work provides a new strategy and opportunity in the design of LDH-based photocatalysts for the efficient photocatalytic reduction of CO₂.

2. Experimental

2.1. Chemicals and materials

 $Co(NO_3)_2 \cdot 6H_2O$ (ACS) was supplied by ALADDIN Reagent Co., Ltd., Al(NO₃)₃.9 H₂O (AR), NH₄F (GR), and urea (AR) were all purchased from the Shanghai Chemical Reagent Company and used as the precursors for the preparation of CoAl-LDHs. $Ce(NO_3)_2 \cdot 6H_2O$ (ACS grade, 99.95% purity) was supplied by ALADDIN Reagent Co., Ltd., Shanghai and used to synthesize CeO₂. Polyethylene glycol 4000 (PEG, 4000) and ethylenediamine were purchased from Sinopharm Chemical Reagent Co., Ltd and were used the synthesis of graphene oxide (GO).

2.2. Preparation of CeO_2

A certain amount of Ce(NO₃)₂·6H₂O was grinded in an agate mortar for 25 min. Next, the prepared Ce(NO₃)₂·6H₂O powder was placed in a crucible and calcined at 300 °C for 4 h, at a heating rate of 2 °C min⁻¹. Finally, when the temperature had dropped to room temperature, the sample was removed and ground to a fine consistency.

2.3. Preparation of reduced graphene oxide (RGO)

First, graphene oxide (GO) was synthesized via a modified Hummers' method [22] with a description of synthetic protocol in Supporting Information. Then, the RGO was synthesized using ethylene glycol and ethylenediamine for reduction.

2.4. Preparation of CACRs

The procedure for the preparation of CoAl-LDH/CeO₂/RGO can be divided into two steps. First, the CoAl-LDH/CeO₂ was prepared using a hydrothermal method. Briefly, a known mass of CeO₂ was dispersed in deionized water, to which Co(NO₃)₂·6H₂O (0.006 mol), Al $(NO_3)_3$ ·9H₂O (0.002 mol), urea (0.04 mol), and NH₄F (0.01 mol) were dissolved. The resulting mixed suspension was transferred to a Teflon-lined autoclave (100 mL) at 120 °C for 24 h. The precipitate obtained was washed with deionized water until the washing's pH was neutral, then dried overnight at 60 °C in a vacuum. In this manner, CoAl-LDH/CeO₂ composites with CeO₂ weight ratios of 1%, 3%, 5%, 8%, and 10% were obtained, which were denoted as CAC-1, CAC-3, CAC-5, CAC-8, and CAC-10, respectively. Secondly, in order to prepare the RGO containing ternary composite photocatalysts (CACR), different ratios of RGO (5%, 10%, and 15%) were added to a sample of the CAC composite with the optimal photocatalytic activity of CAC-5 determined by preliminary evaluation, using the method described above. Finally, the CoAl-LDH/CeO₂/RGOs catalysts with an RGO weight ratios of 5%, 10%, and 15% were obtained and denoted as CAC-5-R-5, CAC-5-R-10, and CAC-5-R-15, respectively. In addition, the pure CoAl-LDH was prepared to compare photocatalytic activities using the similar method, but without adding CeO₂ and RGO.

2.5. Photocatalytic CO₂ reduction

The photocatalytic activity of the synthesized samples is reflected by its CO₂ reduction ability. For each test, 100 mL of deionized water (H₂O) is poured into a custom-made quartz reactor (300 mL), followed by addition of 0.05 g of photocatalyst. The reactor is sealed, and CO₂ is flowed through the sample for 10 min, and then turn on the ultraviolet (UV) light (200 W), which placed on the tops of quartz reactor about 2.0 cm. The reaction temperature was monitored at 15, 25, 35 °C using cooling circulating-water. At 60 min intervals, 500 µL of gaseous products from the reaction are sampled for measurement and analyzed by a gas chromatograph (GC-7920) with a thermal conductive detector and a flame ionization detector. To exclude the possibility of carbonaceous component on the photocatalysts (RGO) to contribute the hydrocarbon product(s), an additional isotopic labeling experiment with ¹³CO₂ instead of ¹²CO₂ as the raw gas is conducted under the identical reaction conditions by combinative analysis of gas chromatography-mass spectrometry (GC-7920 and MS-5975).

2.6. Characterization

The various characterizations of samples are presented in Supporting Information.

3. Results and discussion

3.1. Structure and morphology characteristics

The crystallinity of the synthesized samples are determined by their X-ray diffraction (XRD) patterns, as shown in Fig. 1. As previously reported, the diffraction peak at 23.9° in Fig. 1a is attributed to RGO of (002) crystal [23]. The peaks at 28.6°, 33.1°, 47.5°, and 56.4°, as observed in Fig. 1b, are ascribed to the cubic phase of CeO₂ (JCPDS No. 43-1002), corresponding to the (111), (200), (220), and (311) crystal planes [24]. The CoAl-LDHs exhibit seven diffraction peaks at 11.5°, 23.2°, 34.4°, 39.0°, 46.5°, 60.0°, and 61.3° (Fig. 1c), corresponding to the (003), (006), (012), (015), (018), (110), and (113) crystal planes, respectively [25]. The four main diffraction peaks of CeO₂ are clearly visible in CAC-5 (Fig. 1d), indicating successful incorporation of CeO₂ into the composite catalyst. For CAC-5, the



Fig. 1. XRD patterns of (a) RGO, (b) CeO_2 , (c) CoAl-LDHs, (d) CAC-5, and (e) CAC-5-R-10.

diffraction peak at 34.4° is stronger, which may indicate that CeO₂ is uniformly dispersed in the composite catalyst with a concomitant increase in crystallinity, which is also conducive to greater absorption of radiation in the visible range. In Fig. 1e, the characteristic diffraction peaks of the CoAl-LDHs, CeO₂, and RGO can be seen, while no other peaks from possible impurities are detected, indicating successful formation of the CAC-5-R-10 ternary composite.

The morphological features of the prepared materials are studied by SEM. The flower-like structure typical of layered double hydroxide is observed in the CoAl-LDHs, with 1 µm spherical agglomerates (Fig. 2a) and numerous protruding thin 2D nanoflakes, which greatly increase the number of active sites for the photocatalytic reduction of CO₂. Pure CeO₂ consist of nanometer-sized particles (Fig. 2b), while pure RGO is composed of extremely thin sheets (Fig. 2c), a feature that is further revealed by wrinkles observed to be several micrometers in length. As shown in Fig. 2d, the incorporation of CeO₂ affects the degree of dispersion of the CoAl-LDHs. Multiple CeO₂ assemblies emerge on the CoAl-LDHs surface, causing a certain degree of agglomeration. During the hydrothermal reaction, as metal ions in the precursors are hydrolyzed and gradually converted to the CoAl-LDHs in the presence of urea, CeO₂ nanoparticles are simultaneously broken down into smaller sizes and deposited onto the CoAl-LDHs surface. As shown, the addition of CeO₂ and RGO exert a significant effect on the morphology of the CAC-5-R-10 composite (Fig. 2e), transforming the hierarchical flower-like microsphere structure agglomerate observed in the CoAl-LDHs into a more rounded spherical-like structure. Further magnification of CAC-5-R-10 (Fig. 2f) depicts clear morphological features, demonstrating that CeO₂ and RGO are deposited on the surface of CoAl-LDHs. Fig. 3 illustrates the corresponding TEM images of the CAC-5-R-10. One can clearly see an individual sphere-like structure with highly-overlapped central area and zigzag brims (Fig. 3a), which is well coincident with its SEM observation (Fig. 2e). In the magnified image (white circle zone of Fig. 3a), the CeO₂ nanoparticles and RGO thin sheets are well interspersed on the hexagonal nanoflakes of CoAl-LDHs, as indicated by the orange arrows (Fig. 3b). Further HR-TEM investigation (white circle zone of Fig. 3b) ascertains the co-existences of constitutive CeO2, RGO, and CoAl-LDHs, and the measured lattice spacing are ~0.318, 0.271 and 0.191 nm for the (111), (200) and (020) crystal planes of CeO_2 , ~0.312 nm for the (002) crystal plane of RGO, and ~0.268 nm for the (012) crystal plane of CoAl-LDH, respectively (Fig. 3c). Moreover, the white circle zone

presents the high overlaps of the undistinguishable crystal planes of CeO_2 , RGO, and CoAl-LDHs, implying that the three components are heterogeneous in structure rather than a simple physical mixture of their separate phases. Such tight coupling is favorable for the separation of photogenerated carriers, thus improving the photocatalytic activity.

Typical atomic force microscopy (AFM) analysis is performed to determine the thicknesses of the as-prepared samples, as shown in Fig. 4. The thickness obtained for the selected regions of CAC-5 is 3.7 nm (Fig. 4b₂), much greater than that for the CoAl-LDHs (1.5 nm) (Fig. 4a₂). This may be the result of the high-degree of dispersion exhibited by CeO₂, which is deposited in large scale on the skeleton of CoAl-LDHs during the hydrothermal reaction process. Meanwhile, compared with the CoAl-LDHs and CAC-5, the CAC-5-R-10 has the greatest thickness at 6.5 nm (Fig. 4c₂) indicating that RGO and CAC-5 are closely joined together. Overall, the AFM measurements serve as further evidence to confirm successful formation of the CAC-5-R-10. The roughness and three-dimensional structure of the as-prepared samples are further illustrated in Fig. 4a₃-c₃. On the basis of the three-dimensional images and the calculated results, the CoAl-LDHs is found to have the lowest roughness (Rb = 1.33), follows by CAC-5 (Rb = 2.45), while in contrast the CAC-5-R-10 (Rb = 5.51) has the highest roughness. This result shows that incorporation of both CeO₂ and RGO in CAC-5-R-10 leads to architectures with increased roughness on the surface, in good accordance with the obtained AFM images. Moreover, the specific surface areas (SSAs) of different samples depend on their roughness, and therefore N₂ adsorption/ desorption experiments are carried out (Fig. 5a).

The N₂ adsorption–desorption isotherms and the corresponding pore size distribution (PSDs) are depicted in Fig. 5a. It is found that the CoAl-LDHs, CAC-5, and CAC-5-R-10 display the type-IV isotherms, indicating their essentially mesoporous structures, well consistent with their average pore sizes listed in Table S1. However, the PSDs of CAC-5 and CAC-5-R-10 show a backward tendency to smaller mesorpores sizes (inset of Fig. 5a) accompanying with the obvious decrease of peak intensity, suggesting the relatively low proportion of mesopores of the two samples. The calculated SSAs by the Barrett-Joyner-Halenda method of CAC-5 and CAC-5-R-10 are 19.3 and 9.9 m² g⁻¹, respectively, much lower than that of the CoAl-LDHs (89.7 m² g⁻¹). With cage-like MIL-101 as substrate, Meng et al. prepare a CdS quantum dots and carbon nanodots (CDs) co-immobilized ternary photocatalyst (CD/CdS@MIL-101) for H₂ evolution by a one-step double solvents method. Compared with the pure MIL-101, CdS@MIL-101, and CD@MIL-101, the CD/CdS@MIL-101 possesses the lowest SSA but the highest photocatalytic activity for H₂ evolution. They attribute the SSA decrease of CD/CdS@MIL-101 to the pore blockage by the introduction of CDs and CdS [26]. Similar as the case, the introduced CeO₂ and RGO also scatter on the nanoflakes surface of CoAl-LDHs (Figs. 2a, d, and e) and obstruct some of the inner interstitial spaces, and thus leading to the decrease in SSA of the corresponding samples. The following photocatalytic evaluations of CO₂ reduction exhibit the optimal activity of the CAC-5-R-10. These results mean that high SSA does not correspond to high photocatalytic activity, and there is no necessarily relationship between the two. To figure out this, CO₂ adsorption-desorption experiments are carried out to assess the CO₂ adsorption capacity of the three samples (Fig. 5b). In contrast to low absorbed amounts of CO₂ of the CoAl-LDHs and CAC-5, the CAC-5-R-10 shows a higher value, further shedding light into the N2-sorption results that a photocatalyst with a high SSA does not mean to absorb more CO₂ molecules for enhanced photocatalytic activity. The suitable band structure for more light absorption and utilization, efficient separation of photogenerated electron-hole pairs, and strong interaction with CO₂ molecules of the photocatalyst also plays critical roles on determining the photocatalytic performances, especially for the multi-component one.



Fig. 2. FESEM images of (a) the CoAl-LDHs, (b) CeO₂, (c) RGO, (d) CAC-5, (e) CAC-5-R-10, and (f) partial amplified CAC-5-R-10.

3.2. Surface chemical composition and group analysis

The FT-IR spectra of the as-prepared samples are shown in Fig. 6. In the CoAl-LDHs, the broad absorption peak at 3520 cm^{-1} is attributed to the O-H stretching modes of interlayer water molecules and H-bonded OH groups, while the weak peak at 1640 cm^{-1} corresponds to the bending mode of water molecules. The strong peaks at 1380 and 766 cm^{-1} belong to the v₃ vibrational and bending modes of CO_3^{-2} , respectively [27]. The absorption peaks from 800 to 500 cm⁻¹ correspond to the lattice vibrations present in the M-O and O-M-O (where M = Co, Al) groups [28]. For pure CeO₂, the wide peak at 3450 cm^{-1} is ascribed to

the asymmetrical -OH stretching vibration [29]. The region from 1600 to 1300 cm⁻¹ is attributed to the O–H bending vibration of physically adsorbed water molecules [30]. There is little change in the FT-IR spectrum of CAC-5 compares to the CoAl-LDHs, illustrating that the chemical structure of CoAl-LDHs is virtually unchanged by the hydrothermal treatment. However, a slight reduction in the intensity of the O-H absorption band is observed in the CAC-5-R-10, which may be due to deposition of RGO species between the CoAl-LDHs nanosheets, resulting in a decrease of interlayer water molecules.

The chemical states and surface elemental composition of CAC-5-R-10 are examined using XPS, as shown in Fig. 7. The survey XPS



Fig. 3. TEM and HR-TEM images of the CAC-5-R-10 with increasing magnification.

spectrum of CAC-5-R-10 in Fig. 7a indicates that Co, Al, C, Ce, and O are all present. The XPS spectrum of Co 2p (Fig. 7b) displays the spinorbit splitting of Co 2p into Co $2p^{1/2}$ (797.2 and 804.1 eV) and Co $2p^{3/2}$ (781.9 and 787.6 eV), suggesting that both Co²⁺ and Co³⁺ are simultaneously present [28]. The peak at 75.2 eV (Fig. 7c) in the spectrum of Al 2p suggests the existence of Al³⁺ species present as Al-OH [25]. The complex pattern of the C 1 s peak can be deconvoluted into five peaks center at 284.6, 285.3, 286.8, and 290.4 eV, which may be attributed to sp²-C, sp³-C, C-O, and O=C-O, respectively, derive from the adsorbed organic molecules and CO₃²⁻ groups (Fig. 7d) [28]. The Ce 3d spectrum exhibits four peaks, as can be observed in Fig. 7e. The peaks at 885.3 eV and 888.6 eV are ascribed to the binding energies of Ce $3d^{5/2}$, while the remaining peak at 904.6 eV and 906.6 eV are ascribed to that of Ce $3d^{3/2}$, indicating a configuration corresponding to Ce⁴⁺ present in the material [31,32]. The O1s XPS spectrum shows one peak at 532.4 eV (Fig. 7f), which is assigned to the hydroxyl groups [33]. This result is due to the low

 ${\rm CeO_2}$ content in CAC-5-R-10, so that most of the oxygen presents in LDHs exists as interlaminar hydroxide.

3.3. Photo-electrochemical analysis

To understand the light absorption ability of the as-prepared samples, the UV–vis DRS spectra of the CoAl-LDHs, CeO₂, CAC-5, and CAC-5-R-10 are record. As shown in Fig. 8a, the CoAl-LDHs exhibit two distinct absorption bands, a broad band in the visible region centers around 558 nm, and a sharper UV band around 300 nm. Delamination shifts the middle band to ~520 nm, resulting in the appearance of an additional absorption band around 670 nm. The bands from 520 to 558 nm are indicative of the $4T1g(F) \rightarrow 4T1g(P)$ transition of Co²⁺ octahedrally coordinate by weak field ligands [34], while the 670 nm band corresponds to a $3A2g(F) \rightarrow 3T1g(F)$ transition arising from spin-orbit coupling [35]. The UV absorption may have arisen from ligand \rightarrow metal charge transfer at the CoAl-LDHs



Fig. 4. AFM images, height profiles along the lines of AFM, and the corresponding three-dimensional models drawn from AFM images of CoAl-LDHs (a_1-a_3) , CAC-5 (b_1-b_3) , and CAC-5-R-10 (c_1-c_3) .

surface. These absorption features translate to an optical band gap of 2.10 eV (Fig. S1a), consistent with previous findings in the literature [36]. CeO₂ exhibits a typical absorption edge at about 427 nm, with a calculated optical band gap of 2.84 eV (Fig. S1b). For the CAC-5, the light absorption ability is significantly enhanced compares with the CoAl-LDHs, the absorbance edge has been taken place distinct redshift, up to of 530 nm, the results could demonstrate that the enhanced light absorption is due to the introduction of CeO₂ species. In addition, it deserve to note that the DRS spectra of CAC-5-R-10 are stronger than CAC-5. The significantly enhanced light absorption prove that the introduce CeO₂ and RGO play a crucial role in improvement of photocatalytic activity. Photoluminescence (PL) is another well-known and widely accepted technique for investigating the separation efficiency of electron-holes in semiconductor [37–39]. As shown in Fig. 8b, a strong PL emission peak is observed in CeO₂ at around 480 nm (in accordance with the previously reported value) [40]. A strong PL emission peak is also observed in the CoAl-LDHs, located nearby at around 490 nm [41]. Meanwhile, it is clear that the main emission peak of CAC-5 around 490 nm is of much weaker intensity compares to those of the CoAl-LDHs and CeO₂, suggesting that the separation rate of electrons/ holes and the photocatalytic activity is higher in CAC-5 compares to the pure non-composite materials. Furthermore, the PL emission peak in CAC-5-R-10 at around 490 nm is the weakest from among all

the samples. In general, a more intense spectrum indicates a higher efficiency for the recombination of electrons-holes, while the opposite holds true for lower intensity spectra. Therefore, the PL spectrum suggests that CAC-5-R-10 has the highest separation rate of electron-holes. This illustrates that the charge transfer between CoAl-LDHs and CeO₂ is remarkably improved after the incorporation of RGO and the decreased recombination of photogenerated electrons and holes, which is the main reason for improving photocatalytic activity. To further figure out this point, TRPL decay spectra are detected to measure the average lifetimes of the photogenerated charge carriers. As shown in Table S2 and Fig. S2, the average lifetimes of the entire decay in the CAC-5 and CAC-5-R-10 are 6.04 and 10.67 ns, respectively, quantitatively explaining the great advantage of the incorporation of RGO on retarding the recombination of charge carriers for efficient photocatalysis.

In order to gain further insights into the separation efficiency of electron-hole pairs in the composite photocatalysts, photocurrent tests of the three samples are further performed. In general, a higher photocurrent indicates a higher efficiency of electron-hole separation, which further indicates a higher photocatalytic activity [42–44]. Fig. 9 shows the photocurrent-time curves of the as-prepared samples with on-off intermittent UV irradiation cycles. The weakest photocurrent is clearly shown on the CoAl-LDHs, indicating that it has the lowest electron-hole separation rate. Meanwhile, the



Fig. 5. (a) N2 adsorption-desorption isotherms and (b) CO2 adsorption-desorption isotherms of the CoAl-LDHs, CAC-5 and CAC-5-R-10.



Fig. 6. FT-IR spectra of (a) the CoAl-LDHs, (b) CeO₂, (c) CAC-5, and (d) CAC-5-R-10.

CAC-5 composite displays a significantly improved photocurrent with the intensity approximately 1.2 times higher than that of the CoAl-LDHs. The highest photocurrent intensity is observed in CAC-5-R-10, which is approximately 1.5 times higher than on the CoAl-LDHs, confirming CAC-5-R-10 as a superior catalyst in terms of its stronger light harvesting capacity and the highest separation efficiency of electron-hole pairs. In addition, the EIS of as-prepared samples (Fig. S3) also verify that the incorporation of CeO₂ and RGO can effectively accelerate the transfer of photogenerated carriers to enhance the photocatalytic activity.

3.4. Photocatalytic CO₂ reduction activities

The photocatalytic activities of the as-prepared samples as photocatalysts are evaluated by CO₂ reduction with neutral H₂O as reducing agent at 25 °C under UV lamp irradiation in absence of any sacrificial reagents or photosensitizers, in which the predominant product is CO with negligible trace amount of CH₄ for the different samples. On the other hand, the reduction of CO₂ competes with the reduction of H₂O which means that the splitting of H₂O into O₂ and H₂ would unavoidably proceed together with the reduction of CO₂. It would not be regarded as the photocatalytic reduction of CO₂ if H₂ was dominantly evolved as compared to the reduction products of CO₂. In order to affirm the former is the dominant reaction in our case, we also monitor the evolution of H₂. Fig. 10a compares the photocatalytic activity among all the CAC samples. The CoAl-LDHs without \mbox{CeO}_2 exhibits limited activity. The total yield of CO is 2.91 µmol·g⁻¹ after 5 h reaction with the corresponding average CO evolution rate of $0.58 \,\mu mol \cdot g^{-1} \cdot h^{-1}$. Meanwhile, trace amount of O_2 and H₂ evolutions are also detected. With the increasing CeO₂ content in the CACs, the total yield of CO is significantly enhanced during the time course compared with that of the CoAl-LDHs with the better one (CAC-5) delivering a yield of CO of $11.5 \,\mu mol \cdot g^{-1}$. After RGO is incorporated into the CAC, the total yield of CO is further boosted with the best one (CAC-5-R-10) conveying a yield of CO up to $27.5 \,\mu\text{mol}\cdot\text{g}^{-1}$ (Fig. 10b), which can be attributable to the positive enhancements on absorbed amount of CO2 and generation of electron-hole pairs with rapid electrons transfer from CeO₂ and RGO. The corresponding average CO evolution rate is calculated to be of 5.5 µmol·g⁻¹·h⁻¹, which is superior to many reported LDH-based counterparts under the similar evaluation conditions (Table S3). Moreover, XRD analysis of the CAC-5-R-10 after the photocatalytic reaction reveals that no significant change of the crystal structure occurs after UV irradiation for 5 h compared with its original

counterpart, suggesting the crystal structure stability of CAC-5-R-10 during reaction. (Fig. S4). The samples obtained by overwhelming introduction of CeO₂ to CoAl-LDHs (CAC-8 and CAC-10) and RGO to CAC-5 (CAC-5-R-15) greatly deteriorate the activity of the CAC and CAC-5-R, whose yields of CO present striking decays compared with those of the CAC-5 and CAC-5-R-10, respectively. This arises presumedly from the broad coverage of RGO to the CAC-5, inhibiting the light absorption and utilization. Simultaneously, it can be clearly found the O₂ evolution with a yield of 14.7 μ mol \cdot g⁻¹ for the CAC-5-R-10. The stoichiometric ratio of CO to O_2 , in terms of CO evolution rate to O_2 evolution rate (ratio of μ mol·g⁻¹·h⁻¹), is calculated to be 1.87, approaching to the theoretical value of 2. Accordingly, the detected yield of H₂ evolution is as low as to $1.6 \,\mu\text{mol} \cdot \text{g}^{-1}$, well confirming that most of the photogenerated electrons from the valence band (VB, $H_2O \rightarrow 1/2O_2 + 2H^+ + 2e^-$) of the CAC-5-R-10 are involved in the reaction for the reduction of CO₂ but not for the reduction of H₂O. Furthermore, a couple of the blank evaluations without a photocatalyst, photoirradiation (in dark) or under an Ar atmosphere do not show the CO evolution, implying that the CO in this case is indeed originated from CO₂ photoredcution. Considering the fact that the interlayer CO_3^{2-} in the CoAl-LDH of CACRs are an underlying carbon source contributing to the evolved CO, we perform an ionexchange treatment for the CAC-5-R-10 using a NaH₂PO₄ aqueous solution (0.5 M) to remove the interlayer CO_3^{2-} as much as possible, and the treated CAC-5-R-10 is denoted as CAC-5-R-10-Dc. After the photocatalytic activity evaluation, the amount of CO generated on the CAC-5-R-10-Dc in 5 h is $25.2 \,\mu mol \, g^{-1}$, indicating that most of the evolved CO (91.6%) originate from the photoreduction of CO₂, and the interlayer CO_3^{2-} in the CoAl-LDH has a minor contribution to the production of CO. The carbon-13 isotopic labeling results of the CAC-5-R-10-Dc in Fig. 10c disclose the origin of carbon in the generated CO. Two signals at m/z = 29 and 32 in the MS are observed, which can be assigned to ¹³CO from the used ¹³CO₂ and O₂ from H₂O oxidation, respectively. These results well verify that the production of CO is exactly originated from the introduced ¹³CO₂ excluding its potential possibility from both oxidation of RGO and degradation of interlayer CO_3^{2-} , and further confirm the simultaneous reactions of CO_2 reduction to CO and holes oxidation of H₂O to O₂. In order to investigated the contribution of thermal reduction to CO₂ photoredcution, the yields of CO are also evaluated at two other temperatures of 15 °C and 35 °C, respectively. As shown in Fig. 10d, the average CO evolution rate of CO are 5.1 (15 °C) and 7.3 (35 °C) μ mol·g⁻¹·h⁻¹, respectively, presenting slight increment with the increasing reaction temperature. It is commonly recognized that the increase of temperature will greatly decrease the adsorbed amount of CO₂, thus leading to the activity decay of the used photocatalyst. Evidently, our results prove the existence of the thermal reduction of CO_2 as a positive supplement to the photoreduction of CO_2 .

3.5. Mechanism of photocatalytic CO₂ reduction

Mott–Schottky curves are applied to determine the CB potential of CeO₂ and CoAl-LDHs (Fig. S5). It can be found that the Mott–Schottky curves possess a positive slope at different frequencies from 1500 to 2000 Hz, indicating that CeO₂ is a typical n-type semiconductor. The flat band potential derived from the intercept of the tangent of the Mott–Schottky curves on the X-axis is -0.43 V (vs Ag/AgCl, pH = 7). Generally, the CB potential of n-type semiconductor is near the flat band potential. According to the conversion formula of normal hydrogen electrode potential (NHE) and Ag/AgCl electrode potential: E (NHE) = E (Ag/AgCl) – E⁰ + 0.059 pH, where E⁰ (Ag/AgCl, at pH = 7) = 0.197 V, the CB potential (E_{CB}) of CeO₂ is therefore determined to be -0.21 V (vs NHE, pH = 7). The same algorithm is used to calculate the E_{CB} of Co-Al LDHs to be -0.62 V. Both are very close to the previously reported values [45,46]. Along with the values of the band gap (Eg) from UV–vis DRS for CeO₂



Fig. 7. XPS spectra of the CAC-5-R-10: (a) all survey spectrum, (b) Co 2p, (c) Al 2p, (d) C 1s, (e) Ce 3d, and (f) O 1s.

(2.84 eV) and CoAl-LDHs (2.10 eV), the VB potential (E_{VB}) of CeO₂ and CoAl-LDHs can be converted into 2.63 and 1.48 V, respectively, following the formula of $E_{VB} = E_{CB} + E_g$ [47]. Based on these, two possible CO₂ photoreduction mechanisms, the type-II heterojunction and Z-scheme, have been proposed for the optimal CAC-5-R-10, as illustrated in Fig. 11. If the former works, the photogenerated

electron-hole pairs can be simultaneously excited on the CoAl-LDHs and CeO₂, during which the photoexcited electrons from the CB of CoAl-LDHs tend to transfer to the CB of CeO₂, meanwhile, the produced holes migrates correspondingly from the VB of CeO₂ to the VB of CoAl-LDHs. As a result, the photogenerated electrons in the CB of CeO₂ can not reduce CO₂ to CO because the E_{CB} of CeO₂ (-0.21 V) is



Fig. 8. (a) UV-vis DRS and (b) PL spectra of the CoAl-LDHs, CeO₂, CAC-5, and CAC-5-R-10.



Fig. 9. Photocurrent response curves of the CoAl-LDHs, CAC-5, and CAC-5-R-10 under UV light irradiation.

higher than that of the theoretical reduction potential of CO_2/CO (-0.53 V). Evidently, the type-II heterojunction mechanism deduced easily from the Mott-Schottky plots conflicts with our results of the CAC-5-R-10 with a high yield of CO, implying its unavailability in this

case. Therefore, we postulate the Z-scheme mechanism is feasible for the present system as the following steps. After light irradiation onto the CAC-5-R-10, the conventional generation of electron-hole pairs and electron transition occur from VB to CB of the constitutive CeO₂ and CoAl-LDHs. With the assistance of RGO for conduction, the electrons at the CB of CeO₂ can rapidly transfer to the VB of CoAl-LDHs and combine with the holes of it through the interface contact of CeO₂ and CoAl-LDHs. So the electrons at the CB of CoAl-LDHs are effectively employed for reduction of CO₂, which well meets the photocatalytic Z-scheme mechanism. In order to further confirm this, the electron spin resonance (ESR) data are collected to the generated radicals ($\cdot O_2^-$ and $\cdot OH$) with 5,5-dimethyl-1-pyrroline Noxide (DMPO) as spin-trapping agent to capture under UV-visible light irradiation [48]. As shown in Fig. S6, the CoAl-LDHs exhibits strong regular ESR signals for DMPO- \cdot O₂, but the counterpart of the CeO₂ is invisible. Contrarily, there are significant ESR signals for DMPO-•OH on the CeO₂, and the counterpart of the CoAl-LDHs disappears. Such phenomena is attributed to the functions of the sufficiently negative E_{CB} of the CoAl-LDHs ($E_{CB} = -0.62 \text{ V} < O_2/\bullet O_2^- =$ -0.33 V vs NHE) and sufficiently positive E_{VB} of the CeO₂ (E_{VB} = +2.63 V > $H_2O/\bullet OH = +2.4 V$ vs NHE) [49] to generate $\bullet O_2^-$ and $\bullet OH$ after the recombination of the electrons from CB of CeO₂ with the holes from VB of the CoAl-LDHs, in very good agreement with the Z-scheme mechanism. Therefore, the Z-scheme charge transfer process efficiently improves the separation of photoinduced



Fig. 10. CO yields of various photocatalysts under UV irradiation: (a) the CoAl-LDHs and CACs; (b) CAC-5 and CAC-5-Rs; (c) isotope analysis of ¹³CO with ¹³CO₂ as the raw gas by GC-MS for the CAC-5-R-10-Dc; (d) temperature-dependent photocatalytic activity of the CAC-5-R-10.



Fig. 11. Proposed photoinduced carrier transfer mechanism over the CAC-5-R-10: (a) type-II heterojunction and (b) Z-scheme.

electrons and holes of the CAC-5-R-10 with superior activity for CO_2 photoreduction. Base on the above discussion, the following individual steps in the mechanism of the reduction process are proposed by the following equations:

CoAl- LDHs + $hv \rightarrow$ Co-Al LDHs ($e^- + h^+$) (1)

$$\operatorname{CeO}_2 + h\upsilon \to \operatorname{CeO}_2 \left(e^- + h^+ \right) \tag{2}$$

$$\operatorname{CeO}_2(e^-) \xrightarrow{\operatorname{transfer}} \operatorname{Co} - \operatorname{Al} \operatorname{LDHs}(e^-)$$
 (3)

$$2H_2O + h^+ \to 4H^+ + O_2 + 4e^- (E^0 = +2.4 V)$$
(4)

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O (E^0 = -0.53 V)$$
 (5)

4. Conclusions

In this work, CeO₂ and RGO are incorporated onto the flower-like CoAl-LDHs to form catalysts with superior activity for CO₂ photoreduction. Benefiting from the cooperation of the highly dispersed CeO₂ nanoparticles and conductive RGO with enhanced photoelectric characteristics, the sample of CAC-5-R-10 exhibits both high photocatalytic selectivity and activity towards CO₂-to-CO ($5.5 \,\mu$ mol $\cdot g^{-1} \cdot h^{-1}$) under ultraviolet light, much higher than those of the single CeO₂, CoAl-LDHs, and the intermediate of CAC-5 counterparts, respectively. More importantly, our findings demonstrate the relationship between multi-component modified-LDHs and CO_2 photoreduction behavior, providing a valuable attempt to overcome the intrinsic deficiencies of LDH-based photocatalyst in photocatalysis.

CRediT authorship contribution statement

Zhao Li: Conceptualization, Methodology, Software, Data curation, Writing - original draft. **Yang Li:** Conceptualization, Methodology, Investigation. **Zhi Liu:** Conceptualization, Resources, Supervision, Writing - review & editing, Funding acquisition, Supervision. **Qiu Wang:** Validation, Supervision.

Declaration of Competing Interest

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

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Appendix A. Supporting information

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