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650 nm-driven syngas evolution from photocatalytic CO₂ reduction over Co-containing ternary layered double hydroxide nanosheets HPSTAR 1261-2021

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ABSTRACT

The conversion of solar energy to chemical fuels by CO_2 photoreduction reaction (CO_2PR) is a promising pathway to alleviate rapid energy consumption crisis. Nevertheless, only a few systems have been reported so far by applying solar energy in visible light region in particular high wavelength (such as $\lambda \ge 650$ nm). Herein, we report an efficient 650 nm-induced CO_2 photocatalytic reduction system to syngas by introducing Co into MgAl-layered double hydroxide (COMgAl-LDH) nanosheets in conjunction with $Ru(bpy)_3]Cl_2$ · $6H_2O$ as photosensitizer, in which $[Ru(bpy)_3]Cl_2$ · $6H_2O$ could be activated to generate photogenerated electrons which further transfer to surface of COMgAl-LDH for CO_2 reduction. Under irradiation >400 nm, the COMgAl-LDH nanosheets showed excellent CO_2 conversion with TOF of 11.57 h⁻¹, 3 times higher than that of CoAl-LDH. Most importantly, up to monochromatic irradiation wavelength at 650 nm, the COMgAl-LDH nanosheets still displayed optimized syngas evolution rate, with CO rate of 0.35 µmol·h⁻¹ with quantum yield of 0.86%. Furthermore, as evidenced by X-ray absorption fine structure spectroscopy and high-resolution synchrotron X-ray powder diffraction, the proper introduction of Co promoted its dispersion on the laminate of LDH. The suitable dispersion of Co active sites into LDH nanosheets facilitates the transportation of photo-generated electrons to further promote catalytic activity for reaction. This work paves a potential way for CO_2PR to syngas under wavelength irradiation up to 650 nm.

1. Introduction

The reduction of CO_2 into high-value energy products and syngas (CO and H_2) not only could meet the demands on development of renewable energy, but also mitigate the greenhouse effect by CO_2 circulation. CO_2 photoreduction reaction (CO_2PR) is a significant way to convert solar energy into high-value energy [1,2]. In view of that, most photocatalysts up to now are traditional semiconductors activated by UV light which only occupy 3% of the whole solar spectrum, effectively widening the absorption efficiency of solar energy is a crucial task for making endeavor on efficient and stable photocatalysts/cocatalysts for CO_2 conversion [3]. In recent years, photocatalytic materials have achieved considerable progress for visible-light response [4–8], nevertheless, their weak visible light absorption above 500 nm still very

limited to the efficient utilization of sunlight due to visible–near infrared light account for about 97% of the total solar. In light of this, exploring photocatalysts for higher wavelength response (like $\lambda \geq 650$ nm) is challenging and key for further industrial application.

Layered double hydroxides (LDHs) consist of sheets in which MO_6 octahedra of bivalent and trivalent metals edge-share, and have been confirmed that they were distributed in the laminate in a highly ordered manner [9]. Due to their easily controllable metal cation composition, LDHs representing a new class of metal-to-metal charge-transfer (MMCT) system [10,11], have been considered as a very promising class of 2D photocatalysts and widely used in photocatalysis such as water splitting, fine chemical synthesis, N_2 fixation and CO₂ reduction [12–15]. Furthermore, highly-dispersing active species into the laminate could not only tailor the LDH band structure to promote the

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Received 26 September 2020; Received in revised form 22 December 2020; Accepted 28 December 2020 Available online 7 January 2021 1385-8947/© 2021 Elsevier B.V. All rights reserved. utilization of sunlight, but also may lead to the introduction of unsaturated defect sites, further promoting catalytic performance [16-25]. Cobalt oxides/complexes such as Co₃O₄ [26], Co-loaded partially oxidized graphene nanosheets (Co-G) [27], TiO_{2-x}/CoO_x [28], photosensitized porous metallic, magnetic Co-C composites [29], Co-doped TiO₂ [30], have been demonstrated that they were high efficiency catalysts for CO₂ photoreduction [26,29,31–34], However, it is still a huge challenge to avoid the agglomeration of active sites to further optimize the atomic utilization efficiency for the catalysis. Recently, our research group has proved that the introduction of Co element into the laminate of LDHs showed improved photocatalytic CO₂ reduction compared with other elements (such as Mg, Zn, Ni etc.) [35-38], nevertheless, considering that element Co is the most expensive non-noble metal, it is highly desirable to realize/optimize the atomic efficiency of Co after highly dispersing into LDH matrix through tracking the corresponding turnover frequency (TOF) value [39-43].

Herein, Co-containing CoMgAl-LDH nanosheets were fabricated by a facile one-step coprecipitation method (Scheme 1) and operated the CO₂PR to syngas (CO/H₂ = 1:1) with visible light (λ > 400 nm) combining with [Ru(bpy)₃]Cl₂·6H₂O as photosensitizer for the generation of photogenerated electrons, and the conversion rate of CO₂ to syngas for Co active sites in CoMgAl-LDH nanosheets could reach a TOF value of 11.57 h⁻¹, three times higher than that of CoAl-LDH (3.4 h⁻¹), and it still exhibited photoactivity up to 650 nm with a quantum yield of 0.86%, greatly improving the utilization of solar energy. The X-ray absorption fine structure (XAFS) indicated the dispersion of Co introduced more defects which could promote the separation and transportation of photogenerated electron holes to enhance the photocatalytic performance. This work provides an efficient strategy to facilitate the photocatalyst response of the visible–near infrared light region.

2. Results and discussion

Initially, we selected MgAl-LDH nanosheets as the candidate for the further dispersing Co atoms, since MgAl-LDH is the most classic and widely used LDH for the practical extensive applications, such as additives in polymer, non-toxic heat stabilizers of PVC, halogen-free flame retardants, anti-ultraviolet additive for asphalt, etc., and also has been successfully scaled up to several production lines in China [27,44–46]. According to XRD patterns (Fig. S2a), regular (003), (006), (012), (015), (018) and (110) reflections of the MgAl-LDH sample were observed, indicating the successful synthesis of LDH structure, and the basal spacing calculated to be 0.760 nm, illustrating that the interlayer anion is CO_3^2 –[14]. After dispersing Co atoms into MgAl-LDH, the obtained CoMgAl-LDH also displayed a similar XRD pattern to that of

MgAl-LDH. Besides, if all the Mg atoms were totally displaced by Co atoms, binary CoAl-LDH can also be obtained. As shown in Fig. S2a, compared to MgAl-LDH, the (110) diffraction peak of CoMgAl-LDH and CoAl-LDH shifted to a larger 2θ angle along with a smaller lattice, which can be attributed to the smaller ionic radius of Co^{2+} (0.065 nm) than Mg^{2+} (0.072 nm). According to the detailed calculation results of the unit cell parameters (Table S1), the unit cell lattice constant (a) which was defined by the distance between adjacent metal cations were determined to be 3.073 Å for MgAl-LDH, 3.065 Å for CoMgAl-LDH, 3.053 Å for CoAl-LDH, respectively. Through the ICP-AES analysis (Table S2), we can further confirm the successful introduction of Co atoms to MgAl-LDH, with a ratio of 0.25/1.63/1 (Co/Mg/Al) in CoMgAl-LDH, almost close to the feed ratio (0.25:1.75:1), the exact ratios of CoAl-LDH (2.02:1) and MgAl-LDH (1.93:1) were also similar to the feed ratio $(M^{2+}:M^{3+} = 2:1)$, respectively. The Fourier transform infrared (FTIR) spectra (Fig. S2b) at 1384 cm⁻¹ of all the samples demonstrated the presence of intercalation anion CO_3^{2-} . In the UV-vis spectra (Fig. S2c), MgAl-LDH did not show obviously visible absorption, being consistent with its white color (Fig. S2d), as can be well understood since the absence of any d-orbits electrons in MgAl-LDH. After dispersing Co atoms into MgAl-LDH, the CoMgAl-LDH and CoAl-LDH structure showed much broad absorption peaks for visible region centered 520 nm and 610 nm, which were consistent with d-d transitions of octahedral Co^{2+}, as originated to $^4T_{1g}$ (F) \rightarrow $^4T_{1g}$ (P) and $^3A_{2g}$ (F) \rightarrow $^3T_{1g}$ (F) transitions [47]. The increased adsorption of CoAl-LDH can be explained by the increased Co atoms in CoAl-LDH sample, corresponding to the observed actual color of the catalyst powder (Fig. S2d). The SEM images showed that all the LDHs have sheet-like structure along with the sheet size about 30 ± 10 nm and the layer thickness about 10 nm (Fig. 1a, b, S3), respectively. The HRTEM images displayed lattice stripe 0.195 nm for CoMgAl-LDH (Fig. 2c, d), which was assigned to the (018) crystal plane. These results above proved that we have successfully synthesized Co-containing LDH nanosheets.

The CO₂PR was performed for all the LDHs in acetonitrile/H₂O solvent under visible light irradiation (400 nm $< \lambda < 800$ nm, Beijing Perfect Light, PLS-SXE300D, China) with conditions (30 °C and 1.8 atm CO₂). And a typical [Ru(bpy)₃]Cl₂ played the role of photosensitizer, TEOA was chosen for sacrificial agent. The controlled experiment showed the catalytic performance of CoMgAl-LDH under various reaction conditions (Fig. 2a), when not adding [Ru(bpy)₃]Cl₂ or TEOA, no CO, H₂ could be obtained, confirming the both of them played essential roles in the reaction. When using Ar replacing CO₂, fewer H₂ was produced with no CO, confirming that CO came from the CO₂ conversion. Fig. 2b showed the photocatalytic activity of all as-prepared LDHs. For the MgAl-LDH, the obtained catalytic performance showed a slight



Scheme 1. Schematic diagram for MgAl-LDH and Co dispersed in MgAl-LDH (CoMgAl-LDH) for CO₂ photoreduction to generate CO and H₂ on under $\lambda \ge 650$ nm combining with a Ru complex. Mg (blue), Co (pink), Al (green). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 1. SEM (a, b), HRTEM (c, d) images for CoMgAl-LDH.

evolution rate of CO (0.17 μ mol·h⁻¹) and poor yield rate H₂ (0.19 μ mol·h⁻¹) along with CO/H₂ ratio of 0.89; after dispersed Co atoms into MgAl-LDH (CoMgAl-LDH), interestingly, the rate of CO (7.70 μ mol·h⁻¹) and evolution rate 5.80 μ mol \cdot h⁻¹ for H₂ increased 45 times and 30 times than that of MgAl-LDH, respectively, with the syngas (CO/H₂) ratio of 1.32. Further increasing the loading amount of Co to LDH for the synthesis of binary CoAl-LDH, the highest evolution rate 14.90 μ mol·h⁻¹ of CO and generation rate 14.27 μ mol·h⁻¹ for H₂ were expectedly obtained (with the syngas CO/H₂ ratio of \sim 1.04). The obvious enhancement of catalytic activity in reaction could be ascribed to the promoted effect of Co atoms, demonstrated that Co atoms were considered to be the main active sites for CO₂ photoreduction, consistent to the results of previous studies [27,48]. It is noteworthy that the total Co amount of CoAl-LDH reached 8 times than that of CoMgAl-LDH (Table S2), nevertheless, when focusing on the catalytic efficiency of Co atoms, the TOFs value of CO production came to 11.57 h^{-1} for CoMgAl-LDH, 3 times than that of CoAl-LDH (3.4 h^{-1}) (Fig. 2c), further indicating that only a part of dispersed Co in CoAl-LDH played as catalytic site in reduction, while CoMgAl-LDH with a suitable amount of Co could realize exactly the more efficient utilization of Co atoms in the CO₂ photoreduction. What's more, the higher syngas (CO / H₂) ratio of 1.32 for CoMgAl-LDH than 0.89 for MgAl-LDH, 1.04 for CoAl-LDH indicated that the suitable introduction of Co promoted the hydrogenation of CO_2 molecules absorbed on the surface of catalyst by the active H* for the evolution of CO along with simultaneously limiting the coupling of surface active H* for generation of H₂. Therefore, one conclusion could be drawn that the improvement in the catalytic efficiency of Co atoms should be due to the suitable dispersion of Co on the CoMgAl-LDH, while for CoAl-LDH structure, most of the Co in LDH structure did not participate in the

catalytic cycle.

To further confirm the carbon source of CO, as shown in Figs. 2d and S4, GC–MS was used to detect the generated gas of 13 CO₂ photoreduction. One peak at the m/z = 29 in MS was assigned to produced 13 CO, and fragment peak centering m/z = 13 was ascribed to the 13 C origin originating from 13 CO₂. This result confirmed that CO was indeed generated from the conversion of CO₂. In addition, no other liquid products (such as HCHO, CH₃OH, HCOOH) could be obtained in reduction system (Fig. S5). What's more, the catalyst could maintain stable catalytic activity in four cycles of reaction testing without any structure change, proving the stability of CoMgAl-LDH as catalyst (Figs. 2e and S6).

In order to investigate why the CoMgAl-LDH showed a better catalytic efficiency on TOF performance than that of CoAl-LDH, the X-ray absorption fine structure (XAFS) spectroscopy was advantageous for exploring the local coordination environment of Co atoms in CoMgAl-LDH (Fig. 3). A similar absorption edge position to each other of Co Kedge XANES spectra exhibited that the valence of Co atom did not change significantly for the CoAl-LDH and CoMgAl-LDH (Fig. 3a), consistent with XPS results (Fig. S7). The Co K-edge $k^{3}\chi(k)$ spectra (Fig. 3b) for CoMgAl-LDH showed the lower oscillation intensity than CoAl-LDH, confirming that Co atoms in CoMgAl-LDH had a different coordination surrounding (Fig. 3b). The Fourier-transformed (FT) k³weighted EXAFS spectra (Fig. 3c) displayed main peak centered at 1.6 Å, which could be assigned to the Co-O coordination shell, the smaller coordination number (N) of CoMgAl-LDH (N = 4.98) than 6.0 of CoAl-LDH (Table S3), demonstrating hydroxyl vacancies (V_{OH}) existed in the layer (Fig. 3d). Furthermore, CoMgAl-LDH possessed the bigger Debye–Waller factor of coordination shell Co–O (0.0085 Å²) than CoAlC. Ning et al.



Fig. 2. a) Yields of CO and H₂ with various conditions; b) Yield rates of CO and H2 on LDHs; c) TOFs of CO production on CoMgAl-LDH and CoAl-LDH; d) GC-MS analysis on carbon products of ¹³CO₂ photoreduction; e) CO, H₂ selectivity using recycled CoMgAl-LDH; f) CO, H2 yield rates on CoMgAl-LDH with different wavelengths irradiation ($\lambda > 400$ nm, 500 nm, 600 nm, 700 nm) and UV-visible spectra of the photosensitizer Ru (bpy)₃Cl₂·6H₂O; g) CO, H₂ yield rates for CoMgAl-LDH along with monochromatic lights irradiation ($\lambda = 600$ nm, 630 nm, 650 nm); h) AQYs of CO on CoMgAl-LDH along with monochromatic lights irradiation ($\lambda = 405$ nm, 440 nm, 470 nm, 550 nm, 600 nm, 630 nm, 650 nm).

LDH (0.0084 Å²), which revealed the more disordered structure of CoMgAl-LDH compared to CoAl-LDH. As exhibited in Fig. 3e, f, wavelet transform (WT) showed one WT maximum around at 5.8 Å⁻¹, which corresponded with Co-O-M (M = Mg/Co/Al) bonding [49,50], and the WT maximum corresponding to the Co-O-M (M = Mg/Co/Al) bonding showed a shift from 6.8 Å⁻¹ for CoMgAl-LDH to 7.4 Å⁻¹ for CoAl-LDH, which can be assigned to the smaller average atomic number surrounding Co atoms of CoMgAl-LDH, demonstrated that the Co atom was dispersed by the Mg and Al atoms. From the above XAFS discussion, it can be concluded that CoMgAl-LDH with abundant V_{OH} provided the coordinatively unsaturated active site for the efficient CO₂ reduction, while CoAl-LDH with higher amount of Co atoms exhibited lower TOF in the reaction, mainly due to the relatively complete/perfect structure without exposing unsaturated sites. What's more, in order to further understand the specific distribution of the laminate atoms within the

hydroxide layers, we carried out the high-resolution synchrotron X-ray powder diffraction ($\lambda = 0.6887$ Å) of LDHs. As shown in Fig. S8, Bragg peaks representing (003), (006), (015), (018), (110) and (113) planes of CoAl-LDH and CoMgAl-LDH (Fig. S8a) could be observed, consistent with XRD results. Total scattering data was converted to pair distribution function (Fig. S8b) and analyzed to get short/medium-range structural information. The peaks attributed to interatomic distances below the interlayer distance d(003) (\sim 7.7 Å) were ascribed to M–M or M–O distances in the layers, and peak intensity changes could reflect different population of the corresponding atomic pairs. The lower peak intensity of CoMgAl-LDH than CoAl-LDH at a (\sim 3.1 Å) for Co-Co/Mg/Al pairs in the first metal shell, $\sqrt{3}a$ (\sim 5.2 Å) for Co-Co/Mg pairs in the second metal shell, and 2a (\sim 6.2 Å) for Co-Co/Mg/Al pairs in the third metal shell (Fig. S8c), respectively, indicated the fewer Co-Co/Mg/Al atomic pairs for CoMgAl-LDH than CoAl-LDH [51–53], corresponding



Fig. 3. a) X-ray absorption near-edge structure (XANES) spectra; b) Fourier transform (FT); c) EXAFS oscillation functions of CoMgAl-LDH, CoAl-LDH, CoO and Co metal of Co K-edge; d) Schematic illustration of CoMgAl-LDH; e) The wavelet transform (WT) plot; f) the WT maximum corresponding to the Co-O bonding shift of CoMgAl-LDH and CoAl-LDH.

to the XAFS results. And the lower peak intensity of CoMgAl-LDH than CoAl-LDH at ~2.0 Å could be attributed to the fewer Co-O pairs in CoMgAl-LDH, in which the existence of hydroxyl defects may also be one of the reasons for this result. Therefore, a suitable dispersion of Co atoms in CoMgAl-LDH with more $V_{\rm OH}$ could maintain a much efficiently promoted TOF for the CO₂ reduction.

Furthermore, we explored how the catalytic activity of CoMgAl-LDH responsed to the different wavelengths irradiation, since CoMgAl-LDH showed much wider visible light absorption to 700 nm, when compared to [Ru(bpy)_3]Cl₂ (200–650 nm) (Figs. S2c, f). The production rate 7.30 µmol·h⁻¹ of CO and 5.49 µmol·h⁻¹ of H₂ under the irradiation with $\lambda > 500$ nm were slightly lower than $\lambda > 400$ nm. Excitingly, it was worth exploring that CoMgAl-LDH also exhibited good catalytic activity under irradiation with $\lambda > 600$ nm with evolution rate of CO (2.41 µmol·h⁻¹) and H₂ (2.87 µmol·h⁻¹), and the syngas (CO/H₂) ratio of 0.85, and we could not detect any production under irradiation with $\lambda > 700$ nm. The slight change of syngas ratio can be explained by the balance of the competitive reaction over water splitting into H₂, as discussed

below. Therefore, we could get that the catalytic performance agreed to some extent with the changing trend of the absorption intensity of [Ru (bpy)₃]Cl₂ under visible light, demonstrating that light absorption of [Ru(bpy)₃]Cl₂ made a considerable effect on catalytic activity. Furthermore, we took further tests using different monochromatic lights between 400 and 650 nm to explore the catalytic activity of CoMgAl-LDH (Figs. 2g and S9, S10), and more interestingly, compared with the previously reported photocatalysts toward CO₂PR (Table S4), CoMgAl-LDH still obviously showed good activity response to monochromatic irradiation of 650 nm with evolution rate 0.35 μ mol·h⁻¹ for CO and 0.26 $\mu mol {\cdot}h^{-1}$ for H_2 with the CO/H_2 ratio of 1.35. And compared with the generation of 1.60 μ mol \cdot h⁻¹ for CO and 1.80 μ mol·h⁻¹ for H₂ under irradiation of monochromatic light 600 nm, the decreased evolution rate of CO and H₂ for monochromatic light 630 nm and 650 nm could be ascribed to the lower absorption strength of [Ru (bpy)₃]Cl₂·6H₂O around 630 nm and 650 nm than that of 600 nm. The apparent quantum yields (AQYs) of CO on CoMgAl-LDH corresponding with different monochromatic light were given in Fig. 2h, the reaction

could get higher AOYs under monochromatic irradiation from 405 nm (16.50%) to 550 nm (9.91%), and the lower AQY for 440 nm than 470 nm may be attributed to that the less generation rate of CO at 440 nm than 470 nm (Fig. S10) and the stronger absorption intensity of [Ru (bpy)₃]Cl₂·6H₂O at 440 nm than that of 470 nm (Fig. S2c) according to the AQY calculation equation (Eq. (S2)). And an AQY (0.86%) can be obtained under 650 nm irradiation, further improved the light energy utilization to a certain extent. The decreased AQYs could be attributed to the weak light intensity. Although CoAl-LDH exhibited slightly higher evolution rate 0.42 μ mol·h⁻¹ for CO and 0.35 μ mol·h⁻¹ for H₂ with AQY (0.95%) for CO evolution under the monochromatic irradiation of 650 nm (Fig. S11, Table S5), however, the lower TOF of CoAl-LDH made it unable to give full play to the catalytic efficiency of Co atoms. Therefore, CoMgAl-LDH with abundant active sites owned the more advantage for improving the utilization of sunlight (up to 650 nm) for the evolution of syngas. Furthermore, inspired by recent excellent works on photocatalytic reduction coupled with organic oxidation reactions [54–56], when we tried to replace the sacrificial agent TEOA by 4-fluorobenzyl alcohol, the evolution rate 0.086 μ mol h⁻¹ of CO and generation rate 0.013 μ mol·h⁻¹ for H₂ can be obtained for CoMgAl-LDH (Table S4), indicating the successful replacement for TEOA and the formation of oxidation product (like 4-fluorobenzaldehyde), beneficial for the future industry application.

To further comprehend the promoted catalytic activity of CoMgAl-LDH in reaction, we explored the photo-induced electron hole separation efficiency under light irradiation. As shown in Fig. 4a, The CoMgAl-LDH exhibited higher photocurrent, indicated that the enhanced mobility of photoinduced carrier in CoMgAl-LDH when dispersing Co atoms into MgAl-LDH. The photoluminescence (PL) spectra in Fig. 4b proved that the weaker photoluminescence intensity of CoMgAl-LDH could make a better effect on suppressing the electron-hole radiative recombination, promoting more photo-induced electron transfer to the surface of catalyst, which could be assigned to the introduction of Co active sites on CoMgAl-LDH. Furthermore, by the EIS analysis (Fig. 4c), CoMgAl-LDH possessed a smaller impedance radius, facilitating the transportation of photoinduced electrons to participate in CO_2PR . Furthermore, as shown in Fig. S12, the increased SPV intensity of CoMgAl-LDH (Fig. S12a) and longer carrier lifetime (Fig. S12b) for CoMgAl-LDH (371 ns) compared with MgAl-LDH (364 ns) confirmed directly that Co introduction was beneficial for the efficient separation of photogenerated electron–hole pairs [27,57,58].

Density functional theory (DFT) calculations were performed to gain atomic-level insight and understand the dispersion effect of Co atom in MgAl-LDH. Firstly, the density of states was conducted to confirm the electronic structure and band gap for LDHs (Figs. 5 and S3, S14). According to Figs. 5a and S14, the band gap of MgAl-LDH and CoAl-LDH was calculated to be 3.12 eV and 2.0 eV, respectively. After introducing Co atoms into MgAl-LDH, the band gap CoMgAl-LDH was reduced from 3.12 eV (MgAl-LDH) to a value of 2.11 eV (Fig. 5c). Moreover, an new intermediate band existed in the forbidden zone, indicating that the introduction of Co into LDH reduced the band gap and facilitated electron transfer [17]. In addition, when adding hydroxyl vacancies into CoMgAl-LDH (denoted as CoMgAl-LDH (V_{OH})), an additional defect level was observed between conduction band and valence band (Fig. 5c). Such reduced band gap was beneficial to improve the corresponding electrical conductivity and further promote the electron transfer efficiency, in accordance to the EIS result (Fig. 4c). Thus, defectcontaining CoMgAl-LDH provided much more efficient charge transportation due to the hydroxyl vacancies, similar to the previous studies, in which the increased number of oxygen vacancies in LDHs could significantly increase the electron conductivity to further promote catalytic performance [59,60]. Furthermore, we also calculated the hydroxyl vacancies (V_{OH}) formation energy of different LDHs. The V_{OH} formation energy of MgAl-LDH (4.31 eV), CoAl-LDH (2.51 eV), CoMgAl-LDH (2.09 eV) was shown in Fig. 5d, such lowest energy indicated that V_{OH} can be much easily formed in CoMgAl-LDH structure, as mainly due to the hetro-elements dispersed in LDH structure [61], consistent with the XAFS results. Therefore, we can conclude that Co dispersed in MgAl-LDH could adjust the electronic structure with the formation of more defects (V_{OH}), and then improved the photocatalytic syngas evolution.



Fig. 4. a) Photocurrent responses under UV-vis illumination; b) Room-temperature photoluminescence (PL) spectra; c) Electrochemical impedance spectra of CoMgAl-LDH and MgAl-LDH; d) The proposed possible reaction mechanism.



Fig. 5. The calculated density of states plots of (a) MgAl-LDH (b) CoMgAl-LDH and (c) CoMgAl-LDH (V_{OH}); (d) Formation energy of hydroxyl vacancy (V_{OH}) in three LDHs.

Based on previous works [26,27] and the understanding of the catalytic system, we pointed out a feasible possibly mechanism (Fig. 4d), photosensitizer $[Ru(bpy)_3]^{2+}$ was converted to $[Ru(bpy)_3]^{3+}$ under irradiation along with the photogenerated electrons transferring to arrive at the surface of CoMgAl-LDH, followed by that, the photoelectrons could further reduced H₂O to active hydrogen (H*), which could promote the hydrogenation of CO2 and further generate CO, and H* coupled to generate H₂. The competition competition between the hydrogenation over CO₂ and coupling of H* for the H₂ evolution gives the effect on the ratio of syngas evolution. Besides, TEOA could reduce [Ru $(bpy)_3]^{3+}$ to initial state $[Ru(bpy)_3]^{2+}$ to complete the whole cycle by providing electron. In terms of charge transfer, it could be considered that the matching band structure of CoMgAl-LDH catalyst and photosensitizer was responsible for good response at 650 nm of catalyst. What's more, through the analysis of the band structure (Figs. S15–S18), due to the lower conduction band minimum (CBM) of CoMgAl-LDH (4.39 eV) than LUMO of photosensitizer [Ru(bpy)₃]Cl₂ (3.19 eV), photoexcited electrons from LUMO of photosensitizer could effectively transfer to the CBM of CoMgAl-LDH, further participated in CO2 reduction, thereby promoting the catalytic reaction. These results indicated that higher carrier concentrations and facile charge transport could be assigned to the dispersed Co active sites on CoMgAl-LDH and the appropriate band structure matching [Ru(bpy)₃]Cl₂, efficiently promoting the separation and transportation of photo-generated electron holes to participate in the reaction.

3. Conclusion

In summary, we reported a facile one-step coprecipitation method to introduce Co species into MgAl-LDH nanosheets. The CoMgAl-LDH nanosheets showed the efficient syngas evolution under visible light, with an optimized TOFs of CO production (11.57 h⁻¹) compared to CoAl-LDH nanosheets, further promoting catalytic efficiency of Co active sites. Most importantly, up to 650 nm, the as-prepared CoMgAl-LDH nanosheets still exhibited catalytic activity with CO evolution rate of 0.35 μ mol·h⁻¹. The dispersed Co active sites and appropriate band structure well-matched with [Ru(bpy)₃]Cl₂ facilitated the efficient transportation of photo-generated electrons to promote the reaction. This work may propose a view for photocatalyst design to promote the utilization of solar energy and catalytic efficiency for CO₂PR to syngas.

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. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2020.128362.

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