



# Core-shell structured ZnO@Cu-Zn-Al layered double hydroxides with enhanced photocatalytic efficiency for CO<sub>2</sub> reduction



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## ABSTRACT

Hierarchical ZnO@Cu-Zn-Al layered double hydroxide (LDH) heterostructures were synthesized by a facial deposition-precipitation method, and it exhibited an enhanced photocatalytic efficiency for CO<sub>2</sub> reduction. The physicochemical properties of as-prepared ZnO@LDHs were studied by SEM, XRD, BET, UV-vis and TEM technique. The improvement of photocatalytic efficiency is related to two factors. On the one hand, LDH species can increase the surface areas of catalysts effectively, which means that more adsorb active sites for CO<sub>2</sub> can be provided; on the other hand, the heterojunction was formed on the ZnO/LDHs interface hindering the recombination of excited charge carriers.

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## 1. Introduction

As well known, the increase in CO<sub>2</sub> concentration in the atmosphere is responsible for the problem of global warming [1]. Converting CO<sub>2</sub> into organic fuel can attenuate the greenhouse effects and meet the increasing energy demands simultaneously. Therefore, many efforts have been made to develop an efficient photocatalyst for the conversion of CO<sub>2</sub> [2]. Although various photocatalysts such as TiO<sub>2</sub> [3], BiVO<sub>4</sub> [4], Bi<sub>2</sub>WO<sub>6</sub> [5] and Zn<sub>2</sub>GeO<sub>4</sub> [6] have been investigated for the conversion of CO<sub>2</sub> into small organic molecules (e.g. methane, C<sub>2</sub><sup>+</sup>, methanol, ethanol), most of them show a low photocatalytic efficiency. Recently, layered double hydroxides (LDHs), a class of anion clays consisting of brucite-like host layers and interlayer anions [7,8], has received considerable attention because of the high sorption capacity for CO<sub>2</sub> in the layered space [9,10] and the tunable semiconductor properties (photocatalytic activity) via changing the metal cations [11–13]. For example, Kentaro et al. [7] carried out the photocatalytic conversion of CO<sub>2</sub> in water with the presence of various LDHs. The results indicated that the basic site over the surface of photocatalyst was indispensable, which acted as the active site for CO<sub>2</sub> adsorption. Despite the high sorption capacity and the tunable semiconductor properties of LDHs, the relative low photocatalytic efficiency was still obtained for the immediate recombination of charges in the bulk and/or on the surface of semiconductor [14,15]. Proper junctions formed in semiconductor-based photocatalysts can inhibit the recombination of photoinduced electrons

and holes and lead to an enhanced efficiency in photocatalysis process [16–19]. Fabrication of junctions between LDHs and other different semiconductors has been studied in the field of the evolution of H<sub>2</sub> and the degradation of organic pollutants in more recent years [20–22]. Li et al. [22] assembled Bi<sub>2</sub>MoO<sub>6</sub>/Zn-Al LDHs hierarchical heterostructures from Bi<sub>2</sub>MoO<sub>6</sub> hierarchical hollow spheres and Zn-Al LDH nanosheets by a low-temperature hydrothermal method. The results indicated that Bi<sub>2</sub>MoO<sub>6</sub>/Zn-Al LDH heterostructure photocatalyst exhibited excellent stability and reusability, which mainly attributed to the efficient separation of photoinduced electrons and holes.

ZnO, a typical semiconductor material, has been investigated extensively for the photocatalytic reaction. The photocatalytic performance of ZnO photocatalyst is significantly influenced by its morphology due to surface defect and electronic structure [23,24]. Furthermore, a ternary Cu-Zn-Al oxide catalyst has been employed for the synthesis of methanol from CO<sub>2</sub> hydrogenation, and it shows a high activity [25–27]. In this study, rod and belt ZnO catalysts enwrapped by Cu-Zn-Al LDHs were prepared and used for the photoreduction of CO<sub>2</sub> to hydrocarbons. The catalysts were characterized with SEM, XRD, BET, TGA, UV-vis technologies and TEM. The relationship between the photocatalytic performance and the physicochemical properties, especially the adsorption of CO<sub>2</sub> and the formation of heterojunction, were discussed.

## 2. Experimental

For the sample preparation, characterization and photocatalytic test have been shown in the Supporting information.

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### 3. Results and discussion

#### 3.1. Characterization of catalysts

The SEM pictures of the as-prepared ZnO were presented in Fig. 1 (a) and (d). It can be seen that the ZnO materials exhibited typical rod-like and belt-like structure. The rod-like ZnO has regular shape with an average diameter of  $\sim 600$  nm and a length of  $\sim 3.5$   $\mu\text{m}$ . The width of the belt-like ZnO varies from 50 nm to 200 nm, and the length of the belt is more than 10  $\mu\text{m}$ . Fig. 1 (b) and (e) show the morphology of ZnO wrapped by Cu–Zn–Al layered double hydroxides (LDHs). Obviously, a coating of LDHs was covered on the surface of ZnO materials indicating that the ZnO@Cu–Zn–Al LDHs with a core-shell-like structure were obtained by the facile deposition-precipitation method in this study. Therefore, the rod-like and belt-like ZnO were marked R-ZnO and B-ZnO. Meanwhile, the rod-like and belt-like ZnO wrapped by LDHs were noted R-ZnO@LDHs and B-ZnO@LDHs in the following description, respectively. To further investigate the morphology of ZnO@LDHs, the magnifications of Fig. 1 (b) and (e) were presented in Fig. 1 (c) and (f), respectively. It can be seen that the stacked LDH nano-sheets intercross each other with a diameter  $\sim 200$  nm.

Fig. 2 shows the XRD patterns of ZnO and ZnO@LDHs. Similar diffraction patterns are presented for the R-ZnO and B-ZnO, and the peaks at  $31.7$ ,  $34.4$ ,  $36.2$ ,  $47.5$ ,  $56.5$ ,  $62.8$  and  $67.9^\circ$  correspond the (100), (002), (101), (102), (110), (103) and (112) planes of hexagonal ZnO (JCPDS files 89–1397), respectively. Moreover, no diffraction peaks of secondary phase were observed, which indicates that these two hexagonal ZnO are phase-pure. As for the ZnO@LDHs, the peaks that appeared at  $11.9$ ,  $23.7$  and  $39.4^\circ$  are assigned to the characteristic diffractions of Cu–Zn–Al LDHs with the interlayer anion of  $\text{CO}_3^{2-}$  (JCPDS files 48–1024). Furthermore, with the coating of LDHs, except for a small decrease in the intensity of diffraction peaks, there is no change for the characteristic peaks of ZnO phase.

Fig. S2 shows the TGA curves of the as-prepared ZnO and ZnO@LDHs. The weight loss is less than 2 wt.% for these two ZnO material, which is ascribed to the evaporation of adsorbed water. There are three weight loss stages for Cu–Zn–Al LDHs. The first step ( $< 150^\circ\text{C}$ ) corresponds to the evaporation of adsorbed and interlayer intercalated water. In the range of  $150$ – $350^\circ\text{C}$ , the weight loss is related to two overlapping events of the dehydroxylation and the decomposition of the interlayer  $\text{CO}_3^{2-}$  [28,29]. As the temperature is higher than  $400^\circ\text{C}$ , the layered LDH structure began to collapse. The TGA curves of ZnO@LDHs are similar to that of LDHs, suggesting that the LDHs are coated successfully on

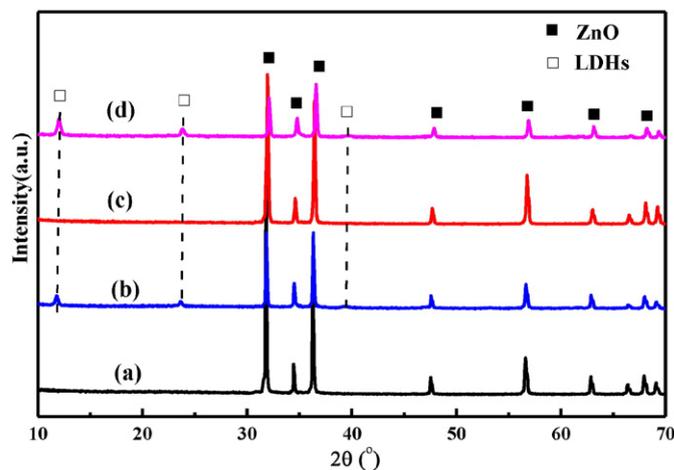


Fig. 2. XRD patterns of ZnO and ZnO@LDHs (a) R-ZnO; (b) R-ZnO@LDHs; (c) B-ZnO; (d) B-ZnO@LDHs.

the surface of ZnO materials. The amount of LDHs coated on ZnO was evaluated by calculating weight loss of TGA, and the data were summarized in Table S1. It can be seen that the amount of LDHs for R-ZnO@LDHs and B-ZnO@LDHs is approximately 17 wt.% and 27 wt.%, respectively.

The  $\text{N}_2$ -adsorption/desorption isotherms were carried out to study the surface area and porosity of ZnO, Cu–Zn–Al LDHs, and ZnO@LDHs materials. As shown in Fig. 3, LDH and ZnO@LDH samples present the type IV isotherms with a H3 hysteresis loops ( $P/P_0 > 0.8$ ), indicating the presence of a porous structure, which is ascribed to the formation of slit-shaped pores. The specific surface area and pore volumes determined from the Brunauer–Emmett–Teller (BET) isotherms are summarized in Table S1. The surface areas of  $21.8$  and  $26.8 \text{ m}^2 \text{ g}^{-1}$  were obtained for R-ZnO@LDHs and B-ZnO@LDHs, respectively. Obviously, the values of the surface areas are significantly higher than that of ZnO. Moreover, the pore volumes of the materials increase greatly after the LDHs coating. The increase in the surface area and pore volume of ZnO@LDHs is attributed to the existence of hierarchical LDHs, which has been illustrated in Fig. 1 (c) and (f).

Fig. S3 shows the UV–vis diffuse reflectance spectra of the samples. Only one absorption region is observed for ZnO material, and the absorption peak appears at UV light region ( $\lambda < 360 \text{ nm}$ ). The absorbance

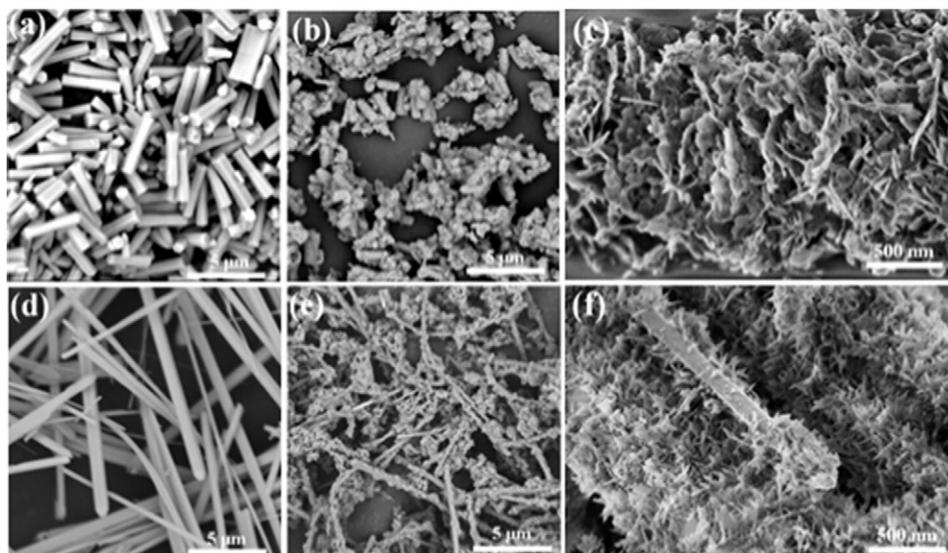


Fig. 1. SEM images of bare ZnO and ZnO@Cu–Zn–Al LDHs composites (a) R-ZnO; (b) R-ZnO@LDHs; (c) magnification of Fig. (b); (d) B-ZnO; (e) B-ZnO@LDHs; (f) magnification of Fig. (e).

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