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Photocatalytic O<sub>2</sub> evolution from water over Zn-Cr layered double hydroxides  
intercalated with inorganic anions

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## **Abstract**

Zn-Cr layered double hydroxides (LDHs) intercalated with inorganic anions ( $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ ) were synthesized by the co-precipitation method and the anion exchange process. The photocatalytic activity of the LDHs was studied by  $\text{O}_2$  evolution from aqueous solution of  $\text{AgNO}_3$  as a sacrificial agent. All the prepared LDHs showed photocatalytic activity under either UV and/or visible light irradiation. Besides, the interlayer anions affected the photocatalytic activity of the LDHs. After irradiation, Ag particles were formed on the LDHs by accepting the electrons generated during the photocatalytic reaction.

**KEYWORDS:** A. inorganic compounds, A. layered compounds, B. intercalation reactions D. catalytic properties

## 1. Introduction

Photocatalysts have attracted great attention in areas of environmental and energy.  $\text{TiO}_2$  and  $\text{ZnO}$  have been addressed as common photocatalysts by many studies because of their high photocatalytic activity, good chemical stability and low cost [1, 2]. However, they only can be activated under UV light irradiation due to their large band gap. Therefore, in order to utilize maximum solar energy, the development of visible light sensitive photocatalyst has become a hottest topic [3-5].

Layered double hydroxides (LDHs) are a class of anionic clays with the general formula  $[\text{M}^{\text{II}}_{1-x}\text{M}^{\text{III}}_x(\text{OH})_2][\text{A}^{n-}_{x/n} \cdot m\text{H}_2\text{O}]$ , where  $\text{M}^{\text{II}}$  ( $\text{Mg}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ ) and  $\text{M}^{\text{III}}$  ( $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$  and  $\text{Ga}^{3+}$ ) are divalent and trivalent metal cations, respectively;  $\text{A}^{n-}$  is an interlayer anion. LDH consists of the positively charged metal hydroxide layers with anions located in the interlayer for charge compensation of the cationic layers. Because of their potential application in wide range of areas such as catalyst precursors [6], anion exchangers [7], absorbents [8, 9] and bio-active materials [10], LDHs have drawn increasing attention.

In recent years, LDHs have been demonstrated as a potential material in photocatalysis. For example, Silva et al. have reported that Zn-M (M=Cr, Ti, Ce) LDHs serve as visible-responsive photocatalysts for water splitting [11]. In addition, LDHs are found to exhibit photocatalytic activity for degradation of organic compounds [12, 13],  $\text{CO}_2$  conversion [14, 15] and so on. However, almost these reports are about LDHs intercalated

with  $\text{CO}_3^{2-}$  as the most common interlayer anion. To the best of our knowledge, few reports have described the investigations for the effects of interlayer anions of LDH on its photocatalytic property. On the other hand, we have focused attention on LDHs as ion conducting materials and reported that the ionic conductivities of Mg-Al and Ni-Al LDHs are closely related to the species of interlayer anions [16-18]. In addition, Zn-Cr LDHs intercalated with  $\text{Cl}^-$  has been reported to be proton conductor [19], while we have proved that Mg-Al and Ni-Al LDHs intercalated with  $\text{CO}_3^{2-}$  are hydroxide ion conductor [16-18].

In this study, the photocatalytic activity of Zn-Cr LDHs intercalated with various inorganic anions was examined. Zn-Cr  $\text{CO}_3^{2-}$  LDH was synthesized by the co-precipitation method. Then, Zn-Cr LDHs intercalated with  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  were prepared by the anion exchange process. The photocatalytic activity of these LDHs was studied by  $\text{O}_2$  evolution from aqueous solution of  $\text{AgNO}_3$  as a sacrificial agent, under either UV or visible light irradiation.

## **2. Experimental**

### **2.1. Preparation of samples**

Zn-Cr  $\text{CO}_3^{2-}$  LDH was synthesized by the co-precipitation method [11].  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  were dissolved in deionized water in a molar ratio of 2 : 1. The solution was dropped into 2.5 M  $\text{Na}_2\text{CO}_3$  and 3 M  $\text{NaOH}$  mixed solution with stirring. The mixture

was aged at 60 °C for 24 h. Then, the resulting purple precipitates were filtrated, washed with distilled water, and dried at 60 °C for overnight.

Zn-Cr Cl<sup>-</sup> LDH was prepared by anion exchange process with Zn-Cr CO<sub>3</sub><sup>2-</sup> LDH as a starting material [20]. First, Zn-Cr CO<sub>3</sub><sup>2-</sup> LDH was added to an aqueous solution containing 0.005 M HCl and 5 M NaCl with stirring at room temperature under a N<sub>2</sub> flow. After stirring for 24 h, the resulting suspension was filtered and washed with distilled water under a N<sub>2</sub> flow. The remaining precipitates were collected and dried in a vacuum.

The obtained Zn-Cr Cl<sup>-</sup> LDH was subjected to further anion exchange [21]. Zn-Cr Cl<sup>-</sup> LDH was added to aqueous solution of 0.85 M Na<sub>2</sub>SO<sub>4</sub> or 5 M NaNO<sub>3</sub>. The solution was stirred at room temperature for 24 h. Filtration and drying were conducted as described above. Consequently, Zn-Cr LDHs intercalated with SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> were obtained.

## 2.2. Characterization

X-ray diffraction (XRD) measurements were performed to identify crystalline phases. Presence of intended anion in the samples was confirmed by Fourier Transform Infrared (FT-IR) spectra. The KBr pellet technique was used for IR measurement. The morphology of the samples was investigated using a scanning electron microscopy (SEM). Optical absorption characteristic was collected using a UV-vis diffuse-reflectance spectroscopy. The specific surface areas were measured by N<sub>2</sub> adsorption on the basis of the Braunauer-Emmett-Teller (BET) equation.

### 2.3. Photocatalytic reaction

The photocatalytic reaction was carried out in a quartz reaction cell. The prepared LDH powder (40 mg) was dispersed in 0.01 M AgNO<sub>3</sub> aqueous solution (40 mL). Prior to irradiation, the suspension was purged with Ar for 30 min in order to remove dissolved air. Then, the suspension was irradiated using a 300 W Xe lamp for 3 h. In the case of visible light irradiation, a wavelength pass filter ( $\lambda > 400$  nm) was employed and the light was irradiated for 5h. The amount of O<sub>2</sub> evolved was estimated by gas chromatograph (GC-8A; Shimadzu Corp.) with Ar as carrier gas. The amount of N<sub>2</sub> measured by gas chromatograph at the same time was regarded as the results of the residual air. Thus, the amount of O<sub>2</sub> from the residual air was estimated from the amount of N<sub>2</sub>, and was subtracted from the measured O<sub>2</sub> amount.

## 3. Results and discussion

Figure 1 shows XRD patterns of Zn-Cr LDHs prepared by the co-precipitation method and the anion exchange process. The XRD patterns exhibit a series of 00l (l=3, 6) peaks attributed to the layered structure of LDH. The basal spacing of Zn-Cr LDHs is affected by the anion species, suggesting that an interaction between hydroxide layer and interlayer anions is different among the kind of anions.

FT-IR spectra of the obtained Zn-Cr LDHs were measured to identify the interlayer anions, as shown in Figure 2. Zn-Cr  $\text{CO}_3^{2-}$  LDH prepared by the co-precipitation method shows a strong  $\nu_3$  band at around  $1380\text{ cm}^{-1}$  with a shoulder at around  $1450\text{ cm}^{-1}$ . The intensity of the band at around  $1380\text{ cm}^{-1}$  remarkably decreases for the  $\text{Cl}^-$ -exchanged Zn-Cr LDH. In Zn-Cr LDH exchanged with  $\text{SO}_4^{2-}$ , a strong band at  $1120\text{ cm}^{-1}$ , which is assigned to the  $\nu_3$  band of  $\text{SO}_4^{2-}$ , is observed. In Zn-Cr LDH exchanged with  $\text{NO}_3^-$ , a band without split is observed at around  $1380\text{ cm}^{-1}$ . However, from the XRD results, the basal spacing of Zn-Cr  $\text{NO}_3^-$  LDH is different from that of Zn-Cr  $\text{CO}_3^{2-}$  LDH. Thus, the band at around  $1380\text{ cm}^{-1}$  in the Zn-Cr LDH exchanged with  $\text{NO}_3^-$  can be assigned to the  $\nu_3$  band of  $\text{NO}_3^-$ . Although small bands due to  $\text{CO}_3^{2-}$  ion are still observed in FT-IR spectra of Zn-Cr  $\text{Cl}^-$  LDH, Zn-Cr  $\text{SO}_4^{2-}$  LDH and Zn-Cr  $\text{NO}_3^-$  LDH, these results reveal that Zn-Cr LDHs intercalated with  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  are obtained by anion exchange process.

Figure 3 shows the SEM images of Zn-Cr LDHs intercalated with  $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ . All the samples exhibit agglomerated morphology with diameter ranging from 1 to 5  $\mu\text{m}$ . The images prove that the morphology and size of the LDHs did not change obviously during anion exchange process. The UV-vis diffuse reflectance spectrum of Zn-Cr  $\text{CO}_3^{2-}$  LDH is shown in Figure 4. There are two absorption bands at 410 and 570 nm in the visible region, which can be attributed to the d-d transition  ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{F})$  and  ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$  of  $\text{Cr}^{3+}$ , respectively [22, 23]. As for Zn-Cr LDHs intercalated with other inorganic anions,

similar spectra were also obtained.

Figure 5 shows the amount of O<sub>2</sub> evolved per hour over Zn-Cr LDHs intercalated with inorganic anions. In all samples, O<sub>2</sub> evolution was confirmed under UV and/or visible light irradiation, and the photocatalytic activity did not change during light irradiation. It can be seen that interlayer anions of the LDH play a key role in determining its photocatalytic property. Zn-Cr Cl<sup>-</sup> LDH showed the highest photocatalytic activity among all the prepared samples. After photocatalytic reactions, XRD measurements for Zn-Cr LDHs intercalated with Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> were examined (Figure 6). Both of the patterns show the coexistence of LDH and Ag phases, indicating that Ag<sup>+</sup> accepted the photogenerated electrons and Ag particles were formed. For Zn-Cr Cl<sup>-</sup> LDH, AgCl is also observed after photocatalytic reaction because Cl<sup>-</sup> in the LDH interlayer reacted with Ag<sup>+</sup>. Recently, Ag/AgX/LDH (X=Br, Cl) composites have been developed as new visible active photocatalysts for the degradation of organic pollutants [24, 25]. Thus, precipitated AgCl on the LDH may also contribute to photocatalytic O<sub>2</sub> evolution. Zn-Cr NO<sub>3</sub><sup>-</sup> LDH as well as Zn-Cr Cl<sup>-</sup> LDH showed better photocatalytic performance than Zn-Cr LDHs intercalated with divalent anions. The BET surface areas of Zn-Cr LDHs intercalated with CO<sub>3</sub><sup>2-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> were 55.4, 27.6, 16.4 and 28.7 m<sup>2</sup>/g, respectively. Although the surface area of Zn-Cr NO<sub>3</sub><sup>-</sup> LDH is about a half of that of Zn-Cr CO<sub>3</sub><sup>2-</sup> LDH, NO<sub>3</sub><sup>-</sup> intercalated LDH accelerated the photocatalytic O<sub>2</sub> evolution compared with CO<sub>3</sub><sup>2-</sup> intercalated LDH. Above results imply that the photocatalytic

reaction over the LDH is closely connected with the intercalated anions. The difference in photocatalytic activity is probably related to the reaction between interlayer anions of the LDH and photogenerated holes [26-28]. However, it remains unclear how interlayer anions contribute to the photocatalytic reaction over LDH and further experiments are necessary to elucidate it.

#### **4. Conclusions**

Zn-Cr LDHs intercalated with various inorganic anions ( $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ ) were synthesized. All the prepared LDHs showed photocatalytic activity for  $\text{O}_2$  evolution from aqueous  $\text{AgNO}_3$  solution, under UV and/or visible light irradiation. In addition, interlayer anions affect the photocatalytic properties of Zn-Cr LDHs. In particular, monovalent anion-intercalated LDHs comparatively showed good photocatalytic performance. After the photocatalytic reaction, Ag particles were formed on the LDH, indicating that  $\text{Ag}^+$  acted as an electron scavenger.

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## Figure captions

**Figure 1** XRD patterns of Zn-Cr LDHs intercalated with inorganic anions.

**Figure 2** FT-IR spectra of Zn-Cr LDHs intercalated with inorganic anions.

**Figure 3** SEM images of Zn-Cr LDHs intercalated with (a)  $\text{CO}_3^{2-}$ , (b)  $\text{Cl}^-$ , (c)  $\text{SO}_4^{2-}$ , (d)  $\text{NO}_3^-$ .

**Figure 4** UV-vis diffuse reflectance spectrum of Zn-Cr LDH intercalated with  $\text{CO}_3^{2-}$ .

**Figure 5** Yields of  $\text{O}_2$  from aqueous solution of  $\text{AgNO}_3$  over Zn-Cr LDHs intercalated with inorganic anions.

**Figure 6** XRD patterns of Zn-Cr LDHs before and after photocatalytic  $\text{O}_2$  evolution reactions from aqueous solution of  $\text{AgNO}_3$  under UV light irradiation.