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Effect of Crystalline Structure of Cd(OH)₂ Precursor on the Photocatalytic Activity of Stratified CdS

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Abstract. Selective synthesis of the monoclinic Cd(OH)₂ and hexagonal Cd(OH)₂ was successfully achieved by controlling the reaction temperature and concentrations of Cd ion and NaCl in the solution. Monoclinic Cd(OH)₂ was obtained when the amount of NaCl in the solution was 3~5 mmol and hexagonal Cd(OH)₂ was synthesized for NaCl amount either above 6 mmol or 2 mmol NaCl while other parameters were fixed as follows (reaction temperature: 30 °C, 0.01 M Cd(NO₃)₂: 100 ml, 0.1 M NaOH: 100 ml). It is confirmed that the specific shape of the stratified CdS synthesized by sulphidizing Cd(OH)₂ of different crystal structures affected the photocatalytic activity.

Keywords: Cd(OH)₂, Crystalline structure, Stratified CdS, H₂S, Photocatalyst

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INTRODUCTION

The photocatalysts that respond to visible light have been studied due to their great potential for the generation the new energy (hydrogen) by photo-splitting of water. However, reaction rate of photo-splitting of water into H₂ and O₂ is relatively low since the electrolysis potential (1.229 eV) is very high. On the other hand, photocatalytic decomposition of hydrogen sulfide (H₂S) is considered as an efficient alternative route to produce H₂ compared with the splitting of water (H₂S:0.298 eV).

Recently, Arai et al. reported that the synthesis of nano-sized hollow CdS capsule for the photo-splitting of H₂S, which is referred to as “stratified CdS nanoparticles”. Stratified CdS nanoparticles was obtained by the reacting either Cd(OH)₂ or CdO nanoparticles with Na₂S [1]. The wall of these stratified nanoparticles had Cd concentration gradient and this is considered to be one of the reasons for high photocatalytic activities in decomposing H₂S [1]. It is also believed that the photocatalytic activity also depends on the crystal habits of the particles. However, neither the effect of the crystal structure nor crystallinity of the stratified CdS nanoparticles was discussed.

Therefore, in this study, the synthesis of well-crystallined and size-controlled Cd(OH)₂ precursor with different crystal structures was attempted, and their effect on the photo-splitting of H₂S is reported.

EXPERIMENTAL

Synthesis of Monophasic Cd(OH)₂ and Stratified CdS Nanoparticles

The Cd(OH)₂ precursor compounds were prepared by mixing Cd(NO₃)₂ and NaOH/NaCl solutions. Cd(OH)₂ crystallizes into two different crystalline structures, namely monoclinic and hexagonal. Thus, the synthesis of monophasic Cd(OH)₂ was attempted by controlling the reaction temperature (5~60 °C), concentration of Cd ion (0.001M~1M), and the amount of the NaCl (0mmol~90mmol) in the solution.

Stratified CdS nanoparticles was prepared by reacting Cd(OH)₂ nanoparticles in 0.1M Na₂S solution for 10 minutes. After sulphidization, the CdS particles were loaded with Pt metal by dispersing the particles in 4.825×10⁻⁷ M H₂PtCl₆ exposing the suspension to photo irradiation (500 W Hg). The crystal structure, and morphology of the synthesized materials were analyzed by X-ray diffractometer (Rigaku Co., Ltd, MULTIFLEX, XRD) and HR-TEM (Hitachi Co.,Ltd, HF-2000 Field Emission TEM) respectively.

Photocatalytic Activity Measurement

The photocatalytic activity of stratified CdS particles was evaluated from the amount of hydrogen produced when the particles were immersed in 0.1 M

$\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ solution and exposed to 500 W Xenon lamp as shown in Fig. 1.

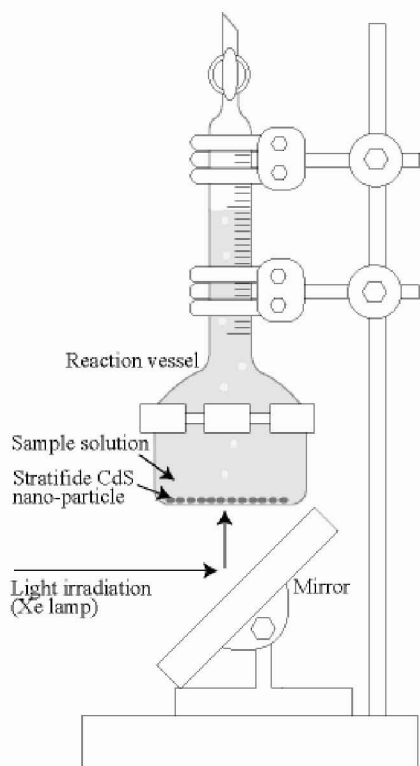


FIGURE 1. Schematic illustration of photocatalytic activity measurement system.

RESULT AND DISCUSSION

Crystalline Structure and Crystal Shape Of $\text{Cd}(\text{OH})_2$ and Stratified CdS Synthesized from $\text{Cd}(\text{OH})_2$

Figure 2 shows the XRD profiles of the particles synthesized under varying amount of NaCl while other parameters were fixed as follows (reaction temperature: $30\text{ }^\circ\text{C}$, $0.01\text{ M Cd}(\text{NO}_3)_2$: 100 ml , 0.1 M NaOH : 100 ml). It should be noted that the peaks corresponding to monoclinic $\text{Cd}(\text{OH})_2$ (JCPDS#40-0760) was clearly observed when 3~5 mmol NaCl added, while peaks of hexagonal $\text{Cd}(\text{OH})_2$ (JCPDS#31-0228) was observed when the amount of NaCl was either above 6 mmol or under 2 mmol as shown in the above Fig. Thus, it can be said that crystal phase of $\text{Cd}(\text{OH})_2$ precursor can be freely controlled by controlling the loading amount of NaCl. Moreover, the crystal shape and size of monoclinic

$\text{Cd}(\text{OH})_2$ and hexagonal $\text{Cd}(\text{OH})_2$ could be controlled by adjusting these factor as shown in Fig. 3 (TEM micrographs).

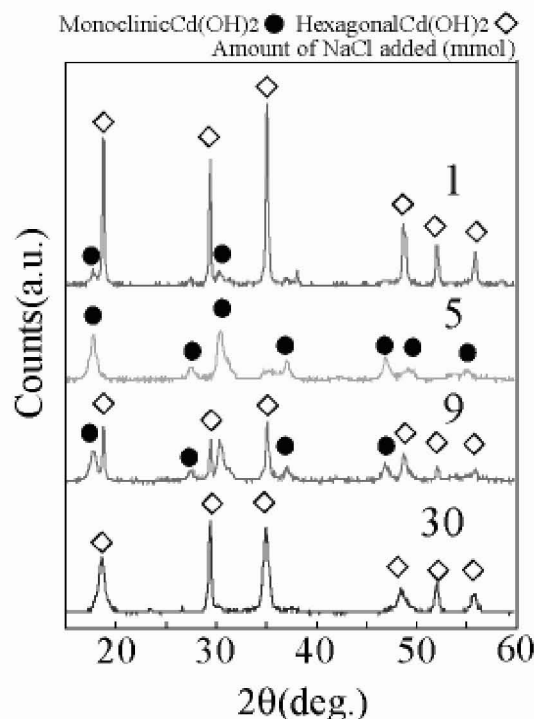


FIGURE 2 XRD profiles of $\text{Cd}(\text{OH})_2$ precursor compounds synthesized using various amounts of NaCl. (● - monoclinic $\text{Cd}(\text{OH})_2$ and ◇ hexagonal $\text{Cd}(\text{OH})_2$)

Figure 3 shows the TEM micrographs of monoclinic and hexagonal $\text{Cd}(\text{OH})_2$ synthesized, and stratified CdS nanoparticles synthesized by using corresponding $\text{Cd}(\text{OH})_2$ precursor. When monoclinic $\text{Cd}(\text{OH})_2$ was used as starting materials (Fig. 3(a)), the shape of stratified CdS was semi-spherical capsule-like structure (Fig. 3(b)). On the other hand, the shape of the stratified CdS particle was plate-like capsule structure when hexagonal $\text{Cd}(\text{OH})_2$ was used as the starting material. Thus, TEM micrographs clearly demonstrated that the shape of the stratified CdS nanoparticles was influenced very much by the shape and also the size of starting material.

All the dark field images showed that the stratified CdS particle were polycrystalline irrespective of the structure of the starting material. It is well known that the reaction rate from $\text{Cd}(\text{OH})_2$ to CdS is rather fast. Moreover, the $\text{Cd}(\text{OH})_2$ precursor has low crystalline structure as shown in Fig. 3(a) and (c). Therefore, it can be conceived that the sulphidization of $\text{Cd}(\text{OH})_2$ did not progress uniformly. As a consequence, polycrystalline CdS was formed. The formation of

poorly crystallined CdS is also believed to have an influence on the photocatalytic activity. Thus, it is important to improve the crystallinity of the starting material as well as control the rate of sulphidization for the synthesis of well-crystallized stratified CdS.

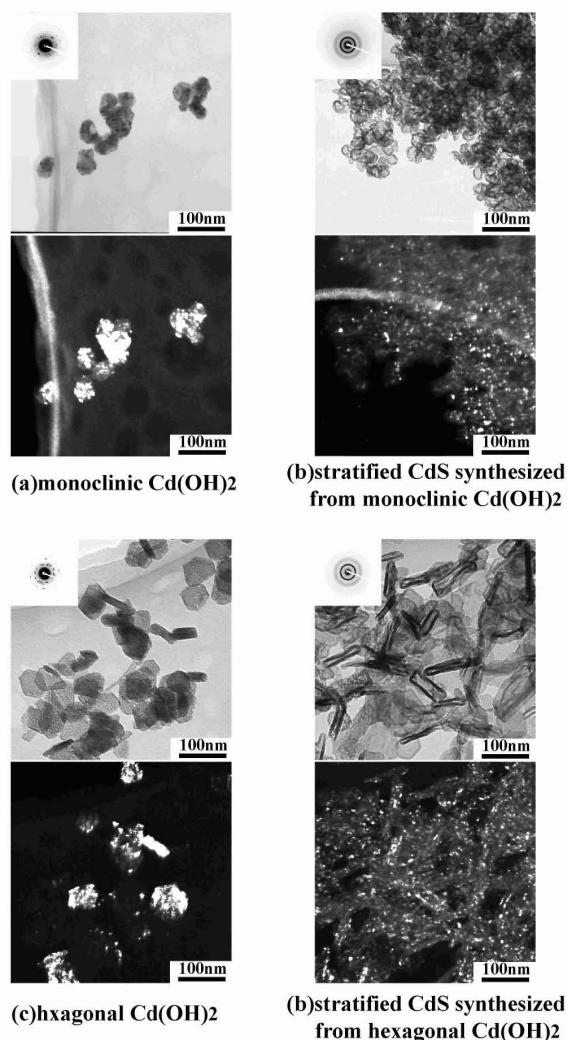


FIGURE 3 TEM micrographs of $\text{Cd}(\text{OH})_2$ precursors with (a) monoclinic and (c) hexagonal crystal phases and stratified CdS particles prepared from respective precursors (b), (d).

Photocatalytic Activity of Stratified CdS

Figure 4 shows the photocatalytic activities of the stratified CdS particles synthesized from monoclinic $\text{Cd}(\text{OH})_2$ (\blacklozenge), hexagonal $\text{Cd}(\text{OH})_2$ (\blacksquare), and co-deposited CdS particles (\bullet). It was confirmed that the stratified CdS particles showed higher catalytic activities than that of co-deposited CdS particles, even though the surface area of all the three samples was almost the same. Thus, it is concluded that the specific

shape of the stratified materials seriously affected the photocatalytic activity. In addition, the stratified CdS synthesized from monoclinic $\text{Cd}(\text{OH})_2$ performed better than hexagonal $\text{Cd}(\text{OH})_2$. Thus, it could be concluded that the crystal structure of the precursor and the crystallinity of CdS derived by the sulphidization of the precursor is vital in determining the photocatalytic activity of CdS.

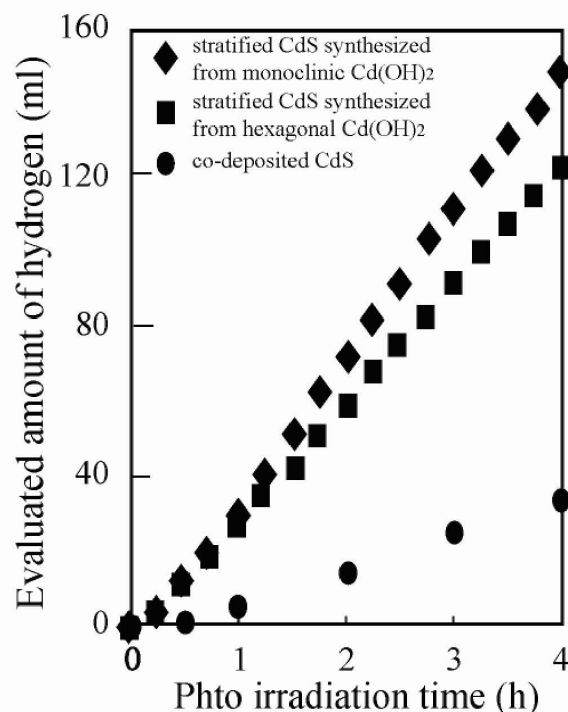


FIGURE 4. Photocatalytic activities of the CdS samples were evaluated by measuring the amount of H_2 evolved from 0.1M $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ solution exposed to Xe lamp irradiation of stratified CdS particle synthesized from monoclinic $\text{Cd}(\text{OH})_2$ and hexagonal $\text{Cd}(\text{OH})_2$ precursors and co-deposited CdS particle.

CONCLUSION

The selective synthesis of the monoclinic $\text{Cd}(\text{OH})_2$ and hexagonal $\text{Cd}(\text{OH})_2$ has been successfully achieved by controlling the reaction temperature, concentration of Cd ion in the solution, and the amount of the NaCl added. It is confirmed that the specific shape of the stratified CdS nanoparticles, which depended on the $\text{Cd}(\text{OH})_2$ precursor compounds, seriously affected the photocatalytic activity.

REFERENCE

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