Synthesis and Photochemical Properties of Semiconductor/Layered Compound Nanocomposites

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CdS and Cd0.8Zn0.2S pillars were constructed in the interlayer of hectorite, HNbWO6, H4Nb6O17 and H2Ti4O9 by the intercalation reactions. The thicknesses of the semiconductors incorporated were less than 1 nm and the band gap energies of them were slightly larger than those of normal crystalline ones. CdS and Cd0.8Zn0.2S pillared compounds showed photocatalytic activity for hydrogen evolution and nitrate reduction under visible light irradiation in the presence of sacrificial hole acceptor such as Na2S and methanol. The photocatalytic activities of the semiconductors incorporated were superior to those of unsupported ones. The incorporation of semiconductors in the interlayers of semiconductor layered compounds such as HNbWO6, H2Ti4O9 and H4Nb6O17 was much more efficient in enhancing the hydrogen production activity than when an insulator such as hectorite was used. The heterogeneous electron transfer from guest CdS to host semiconductor seemed to play an important role to enhance the photocatalytic activity.

Key Word: Semiconductor pillar, Layered compound, Intercalation, Photocatalytic property, Electron transfer

Introduction

Photoelectrochemical processes at semiconductor colloid-electrolyte interfaces have been received special attention because of their possible application to conversion of solar energy into chemical energy and pollution control. In order to achieve high efficiency in solar energy use, the photocatalyst should possess small band gap energy less than 3 eV covering the main part of solar spectrum and the surface modification of semiconductor particles to retard the quick recombination between photoinduced holes and electrons and to promote heterogeneous charge transfer is necessary. The coupling of semiconductor particles with different energy levels is useful to achieve efficient charge separation by the heterogeneous electron transfer3. Synthesis of semiconductor pillars utilizing the nanospaces (interlayers) of layered compounds4-11 may be a promising method to fabricate nanoparticulates of semiconductors uniformly dispersed and contacted well to the host layer. Therefore, in the present study a series of experiments were conducted in order to clarify the chemical properties of semiconductor pillar layered compounds.

Experimental

Chemicals: LiNbWO6 was prepared by calcining stoichiometric mixture of Li2CO3, WO3, and Nb2O5 at 800°C in air for 24 h with one intermediate grinding. Knb2O5 and K2TiO3 were prepared by calcining the mixtures of K2CO3 and Nb2O5 at 1120°C and K2CO3 and TiO2 at 1150°C, respectively. Hectorite with the cation exchange capacity (CEC) of 100 meq/100 g-sample was supplied by Coop Chemical Co.

Incorporation of CdS-ZnS in the interlayer: LiNbWO6, H4Nb6O17 and H2Ti4O9 were converted to HNbWO6, (C3H7NH3)4Nb6O17 and (C3H7NH3)2Ti4O9 by ion exchange reaction in 50 vol% C3H7NH2 aqueous solution at 50°C for 96 h in order to expand the gallery height and to enhance the following ion exchange with Cd2+ and Zn2+. CdS-ZnS particles were incorporated into the interlayer of HNbWO6, H4Nb6O17, H2Ti4O9 and hectorite by reacting H2S gas with Cd2+-Zn2+ exchanged compounds, which were obtained by the ion exchange reaction in mixed 0.4 M Cd(CH3COO)2-0.1 M Zn(CH3COO)2 solutions at 70°C for 5 h using C1H3NH3NbWO5, (C1H3NH3)2NbO5, (C1H3NH3)2TiO5 and Hectorite. The samples obtained were designated as H4Nb6O17/Cd0.8Zn0.2S, H2Ti4O9/Cd0.8Zn0.2S and HECTORITE/Cd0.8Zn0.2S. H2Ti4O9/Cd0.8Zn0.2S and Hectorite/Cd0.8Zn0.2S were also constructed by similar manner using 0.4 M Cd(CH3COO)2 solution.

Photochemical reaction:

The photocatalytic reactions were performed in a Pyrex reactor of 400 cm3 capacity attached to an inner radiation type 100 W high-pressure mercury lamp. The inner cell had thermostated water flowing through a jacket between the mercury lamp and the reaction chamber, and was constructed of Pyrex glass. In order to conduct the visible light illumination reaction, the UV emission of the mercury arc below 400 nm was filtered out by flowing 1 M NaNO2 solution between the mercury lamp and the reaction chamber. The photocatalytic hydrogen production activity of the catalyst was determined by measuring the volume of hydrogen produced.

evolved from 400 cm$^3$ of 0.1 M Na$_2$S aqueous solution containing 0.5 g of dispersed catalyst at 60°C during the irradiation from a 100 W mercury arc with a gas burette after confirming the production of hydrogen by gas chromatography (Yanagimoto G2800) using a Molecular Sieve 13X (30-60 mesh) column. On the other hand, the photocatalytic activity for the reduction of NO$_3^-$ was determined by measuring the concentrations of NO$_3^-$ remained in 400 cm$^3$ of 10 vol% methanol solution containing 0.5 g of dispersed catalyst at 60°C during the irradiation from a 100 W mercury arc.

**Analysis**

The crystalline phases of the samples were identified by X-ray diffraction analysis (Shimadzu KD-D1) using graphite monochromatized CuK$\alpha$ radiation. Chemical compositions were determined by atomic absorption spectroscopy (Hitachi Model 180-80 AAS), and inductively coupled plasma-atomic emission spectroscopy (Seiko SPS-1200A). The band gap energies were determined from the onsets of diffuse reflectance spectra of the powders measured using Shimadzu Model UV-2100 ultraviolet-visible spectrophotometer. The concentration of NO$_3^-$ was determined using an ion chromatograph (IC200 Yokogawa with pre-column PAX051 and separator SAX 1-251).

**Results and Discussion**

Figure 1 depicts powder X-ray diffraction patterns of (a) HNbWO$_6$, (b) C$_3$H$_7$NH$_3$NbWO$_6$, (c) Cd$_{0.5}$NbWO$_6$, (d) HNbWO$_6$/CdS and (e) CdS, where CdS was prepared by the reaction of 0.4 M Cd(C$_3$H$_5$COO)$_2$ and 0.1 M Na$_2$S solutions. The main peak corresponding to (002) of HNbWO$_6$ significantly shifted depending on the species incorporated. The sample (e) showed broad diffraction peaks corresponding to a zinc-blende structure, but no diffraction peak corresponding to CdS was observed for sample (d), indicating that CdS was incorporated in the interlayer. Interlayer distance of HNbWO$_6$/CdS determined from (002) peak was 1.15 nm. Since the thickness of NbWO$_6$ layer is 0.76 nm, the thickness of CdS seemed to be less than 1 nm.

UV-Vis reflectance spectra of (a) HNbWO$_6$, (b) HNbWO$_6$/CdS and (c) CdS are shown in Figure 2. HNbWO$_6$/CdS showed two onsets corresponding to host HNbWO$_6$ and guest CdS. The onset corresponding to guest CdS slightly blue shifted. It may be due to the size quantization effect.

Contents of Cd and Zn element, interlayer distances, band gap energies and specific surface areas of the samples prepared are summarized in Table 1. It is seen that significant amounts of Cd and Zn elements were incorporated in the interlayer. The specific surface area of H$_2$Ti$_4$O$_9$ and H$_4$Nb$_6$O$_{17}$ greatly increased by the incorporation of CdS and Cd$_{0.8}$Zn$_{0.2}$S, indicating the construction of CdS and CdS-ZnS pillars. The interlayer distances of semiconductor pillared compounds were less than 1.94 nm. Since the layer thicknesses of HNbWO$_6$, H$_2$Nb$_6$O$_{17}$, H$_2$Ti$_4$O$_9$ and hectorite are 0.76, 0.4, 0.4 and 0.98 nm, the height of the pillars must be less than 1 nm. The band gap energies of semiconductor pillars were slightly larger than those of unsupported semiconductors, but were smaller than that expected for such small size semiconductor by the quantum size effect$^{12,13}$. Similar results were reported for iron oxide pillared montmorillonite$^{7,9}$, titanium oxide pillared montmorillonite$^8$ and cadmium sulfide/zinc sulfide pillared various
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Table 1 Band gap energies, interlayer distance, specific surface, areas and contents of Cds and ZnS in the samples prepared

<table>
<thead>
<tr>
<th>Sample</th>
<th>Band gap (eV)</th>
<th>Interlayer distance (nm)</th>
<th>Specific surface area (m² g⁻¹)</th>
<th>Content (wt%)</th>
<th>Cd</th>
<th>Zn</th>
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<tr>
<td>HNbWO₄</td>
<td>3.1</td>
<td>1.04</td>
<td>4.2</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>HNbWO₄/CdS</td>
<td>3.2</td>
<td>2.66</td>
<td>1.15</td>
<td>9.5</td>
<td>12.2</td>
<td>0</td>
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<td>HNbWO₄/Cd₀.₈Zn₀.₂S</td>
<td>3.3</td>
<td>2.69</td>
<td>1.14</td>
<td>9.9</td>
<td>9.0</td>
<td>3.8</td>
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<tr>
<td>HNb(NO₃)₄</td>
<td>3.8</td>
<td>0.80</td>
<td>16.1</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>HNbWO₄/CdS</td>
<td>3.84</td>
<td>2.56</td>
<td>1.16</td>
<td>8.0</td>
<td>31.4</td>
<td>0</td>
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<tr>
<td>HNbWO₄/Cd₀.₈Zn₀.₂S</td>
<td>3.84</td>
<td>2.98</td>
<td>1.20</td>
<td>96.0</td>
<td>9.5</td>
<td>2.09</td>
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<td>HClO₄</td>
<td>3.54</td>
<td>0.80</td>
<td>20.7</td>
<td>0</td>
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<td>0</td>
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<tr>
<td>HClO₄/CdS</td>
<td>3.54</td>
<td>2.64</td>
<td>1.02</td>
<td>95.0</td>
<td>11.8</td>
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<td>HClO₄/Cd₀.₈Zn₀.₂S</td>
<td>3.54</td>
<td>2.75</td>
<td>1.02</td>
<td>93.5</td>
<td>14.5</td>
<td>1.75</td>
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<tr>
<td>Hectorite/CdS</td>
<td>-</td>
<td>1.20</td>
<td>10.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>Hectorite/Cd₀.₈Zn₀.₂S</td>
<td>2.64</td>
<td>1.94</td>
<td>35.5</td>
<td>6.21</td>
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<tr>
<td>Hectorite/Cd₀.₈Zn₀.₂S</td>
<td>2.88</td>
<td>1.94</td>
<td>36.0</td>
<td>2.79</td>
<td>0.56</td>
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<tr>
<td>Unsupported CdS</td>
<td>2.40</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>77.8</td>
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<tr>
<td>Unsupported Cd₀.₈Zn₀.₂S</td>
<td>2.55</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>62.3</td>
<td>13.4</td>
</tr>
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</table>

Unpressed Cds and Cd₀.₈Zn₀.₂S were prepared by adding a 0.1 M Na₂S aqueous solution to a 0.1 M CdS and a 0.08 M CdS-0.02 M ZnS aqueous solutions, respectively.

layered compounds[6,10,11] although the reason has not been clarified yet. Recently, it has been reported that the iron oxide pillars constructed in montmorillonite are in fact pancake shape with 0.3 nm in height and a diameter of <10nm[14,15]. It was also reported that the organic dyes incorporated in the interlayer showed red shift in the absorption spectrum due to the low symmetry ligand distortions in the spatially restricted environment of galleries[16,17]. Therefore, the large diameter of the semiconductor pillared and distortion of the pillars are likely to contribute for retaining the small band gap energy. It is also probable that the crystal structures of semiconductors incorporated in the interlayer are different with those of unsupported ones. Further study is necessary to clarify it.

Since the host layered compounds were large band gap semiconductor or insulator, they showed no photocatalytic activity under visible light irradiation, but CdS and Cd₀.₈Zn₀.₂S pillared compounds showed photocatalytic activity for hydrogen evolution and nitrate reduction. The cumulative amounts of hydrogen evolved from 0.1 M Na₂S solution with (a) H₂TiO₄/Cd₀.₈Zn₀.₂S, (b) hectorite/Cd₀.₈Zn₀.₂S and (c) unsupported Cd₀.₈Zn₀.₂S catalysts by irradiating visible light above 400nm are shown in Figure 3. It is interesting to note that the photocatalytic activities of the Cd₀.₈Zn₀.₂S pillared compounds were superior to that of unsupported crystal. Namely, the catalytic activity of unsupported Cd₀.₈Zn₀.₂S decreased with time. It may be due to the agglomeration of the samples. On the other hand, no degradation was observed for Cd₀.₈Zn₀.₂S pillared compounds.

The photocatalytic hydrogen gas evolution activities of the samples are summarized in Figure 4. The incorporation of CdS and Cd₀.₈Zn₀.₂S in semiconductor layered compounds such as HNbWO₄, H₂TiO₄ and HNbO₂ · H₂O was much more efficient in enhancing the hydrogen production activity than when an insulator such as hectorite was used as host material.

Since the nitrate reduction potential is more positive than that of water reduction potential and the conduction band of CdS as shown in Figure 5, it can be expected that nitrate is photocatalytically reduced using CdS. The time dependences of the degree of photoreduction of nitrate under visible light irradiation in methanol solution dispersed with CdS, H₂TiO₄/CdS and Hectorte/CdS are shown in Figure 6. No photoreduction of nitrate proceeded in the presence of unsupported CdS as reported by Kogel et al.[18] It may be due to the large overpotential for nitrate reduction. On the other hand, nitrate concentration linearly decreased in the presence of H₂TiO₄/CdS and Hectorte/CdS. The incorporation of CdS pillars in the Cd₀.₈Zn₀.₂S was much more efficient in
enhancing the nitrate reduction activity than when hectorite was used. The photoreduction of nitrate with Hectorite/CdS may be attributed to the rise of conduction band level by size quantization effect to overcome the overpotential for nitrate reduction. On the other hand, the promotion by the semiconductor layered compound, \( \text{H}_2\text{Ti}_4\text{O}_9 \), may be attributed to the surface modification of CdS which retards the quick recombination between photoinduced holes and electrons by the heterogeneous charge transfer from CdS to the host layers.

In order to confirm the guest-to-host charge transfer, the fluorescence intensity and life time were measured. Namely, when semiconductor is excited by band gap irradiation, electron and hole are formed and the deactivation of excited semiconductor occurs by radiative (reaction 1) and nonradiative (reaction 2) processes. The fluorescence yield and emission life time can be equated to expressions (4) and (5), where \( k_r \) and \( k_n \) are the rate constants of electron-hole recombination by radiative and nonradiative processes, respectively, and \( k_{et} \) is the heterogeneous electron transfer rate constant. Therefore, it is suspected that the emission intensity and life time decrease with increasing the charge transfer rate.

\[
\begin{align*}
\text{CdS} & \rightarrow \text{CdS} (e^- \cdots h^+) \\
\text{CdS} (e^- \cdots h^+) + \text{H}_2\text{Ti}_4\text{O}_9 & \rightarrow \text{CdS} (h^+) + \text{H}_2\text{Ti}_4\text{O}_9 (e^-) \\
\phi &= k_r/(k_r + k_n + k_{et}) \\
\tau &= 1/(k_r + k_n + k_{et})
\end{align*}
\]

Emission spectra of (a) CdS, (b) \( \text{H}_2\text{Ti}_4\text{O}_9/\text{CdS} \), (c) hectorite/CdS obtained by excitation using 375 nm pulse corresponding to a quantum energy of 3.3 eV of an argon ion laser pumped Ti-sapphire laser are shown in Figure 7, where no emission was observed with \( \text{H}_2\text{Ti}_4\text{O}_9 \).

All samples (a)-(c) showed emission at wavelengths greater than 550 nm caused by the excitation of CdS. It is notable that the emission intensity of hectorite/CdS was much stronger than that of unsupported CdS. The increase of emission intensity can be attributed to the decrease of \( k_n \). On the other hand, the emission intensity of \( \text{H}_2\text{Ti}_4\text{O}_9/\text{CdS} \) was much smaller than that of hectorite/CdS.
The quenching by H2Ti4O9 may be attributed to the injection of electrons from CdS in the interlayer to the conduction bands of H2Ti4O9, since H2Ti4O9 is an n-type semiconductor while hectorite is an insulator. The emission decay profiles of (a) unsupported CdS, (b) H2Ti4O9/CdS and (c) hectorite/CdS obtained by excitation from the 375 nm pulse are shown in Figure 8. It is seen that the emission intensity of hectorite/CdS was much stronger than that of the unsupported one. The increase of the emission intensity may be due to the decrease of the defects which act as nonradiative electron and hole recombination centre. As expected, the emission life time of hectorite/CdS was much longer than that of H2Ti4O9/CdS.

If we consider that the quenching by H2Ti4O9 is entirely due to the charge injection process and that the values of k+ and k-, in the H2Ti4O9/CdS and hectorite/CdS systems are the same, the values of ket in the H2Ti4O9/CdS system can be calculated. The results are shown in Table 2 together with those in the H4Nb6O17/CdS system, where the emission decay profiles were fitted with a double-exponential decay law shown by expression (6) and the average emission life time \( <\tau> \) was calculated by equation (7). The rate constants for the charge injection process were estimated to be \( 10^7 \) s\(^{-1}\) in the both H4Nb6O17/CdS and H2Ti4O9/CdS systems. These values are comparable to those observed in the systems CdS-TiO2.

Conclusions

From the experimental results following conclusions may be drawn. (1) CdS and CdS-ZnS pillars could be incorporated in the interlayer of layered compounds, (2) CdS and CdS-ZnS pillars showed excellent photocatalytic activity and (3) the guest-to-host electron transfer seems to play an important role to improve the photocatalytic activity.

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References


<table>
<thead>
<tr>
<th>Compound</th>
<th>(&lt;\tau&gt; &gt; (\text{ns}))</th>
<th>(k_+\times10^7 (\text{s}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsupported CdS</td>
<td>19.9</td>
<td>-</td>
</tr>
<tr>
<td>Hectorite/CdS</td>
<td>29.1</td>
<td>0</td>
</tr>
<tr>
<td>H2Ti4O9/CdS</td>
<td>16.4</td>
<td>26.7</td>
</tr>
<tr>
<td>H4Nb6O17/CdS</td>
<td>9.01</td>
<td>76.6</td>
</tr>
</tbody>
</table>

Figure 8 Emission decay profiles of (a) unsupported CdS, (b) H2Ti4O9/CdS and (c) Hectorite/CdS obtained by excitation from the 375 nm pulse.