Preparation of CdS-pillared $H_4Nb_6O_{17}$ and Photochemical Reduction of Nitrate under Visible Light Irradiation

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$H_4Nb_6O_{17}$/CdS nanocomposites which intercalated CdS particles, less than 0.8 nm thickness, in the interlayer of $H_4Nb_6O_{17}$ were prepared by the successive ion exchange reactions of $H_4Nb_6O_{17}$ with Cd^{2+} and $C_3H_7NH_3^+$, followed by the reaction with H_2S gas. $H_4Nb_6O_{17}$/CdS photocatalytically reduced NO_3^- to NO_2^- and NH_3 in the presence of sacrificial hole acceptor such as methanol under visible light irradiation (wavelength>400 nm), although unsupported CdS showed no noticeable photocatalytic activity for NO_3^- reduction. The catalytic activity of $H_4Nb_6O_{17}$/CdS greatly enhanced with co-doping of Pt particles in the interlayer.

Key words: $H_4Nb_6O_{17}$/CdS nanocomposite, CdS pillar, Photocatalyst, Photoreduction of NO_3^-

I. Introduction

P hotochemical reduction of nitrate has recently received special attention in view of pollution control and of photochemical energy conversion since the reduction of nitrate using water as a hydrogen source as shown by Equation (1) is an up-hill reaction.

$$2HNO_3(aq)+H_2O \rightarrow NH_4NO_3(aq)+2O_2(g) \quad \Delta G^0_{298}=269kJ \quad (1)$$
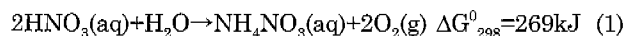
Halmann et al[1] reported that no noticeable nitrate reduction proceeded by bandgap illumination over various semiconductors without noble metals even in the presence of Na_2S as a reducing agent in aqueous solutions although nitrite was reduced to ammonia under similar conditions. On the other hand, Kudo et al.[2-4] reported the photocatalytic reduction of nitrate to ammonia over noble metal loaded TiO_2 and $SrTiO_3$ and to nitrite over oxides such as $K_4Nb_6O_{17}$, $NiO-K_4Nb_6O_{17}$, $H^+/K_4Nb_6O_{17}$ by UV light illumination with and without sacrificial hole acceptor. From the point of view of solar energy conversion, the photocatalysts should have small bandgap energy covering the solar spectrum, but the photoactivity of small bandgap semiconductors is usually modest. Incorporation of semiconductor particles in the interlayer of layered compounds is useful to enhance the photoactivity.[5-11] In the previous study[10-12] we found that the photoactivity of small bandgap semiconductors, CdS, CdS-ZnS and Fe_2O_3 could be greatly increased with incorporating them in the interlayer of layered semiconductors such as $H_2Ti_4O_9$ and $H_4Nb_6O_{17}$ due to the size effect and the inhibition of holes and electrons recombination by the electron transfer from the guest semiconductor to the host layer. In the present study, a series of tests was conducted to investigate the photoactivity for nitrate reduction of $H_4Nb_6O_{17}$/CdS nanocomposites with and without Pt loading.

II. Experimental Procedure

1. Chemicals

$H_4Nb_6O_{17}$ was prepared by the ion exchange reaction of $K_4Nb_6O_{17}$ in 1 M HCl at room temperature for 1 h, where $K_4Nb_6O_{17}$ was prepared by the calcination of the mixtures of K_2CO_3 and Nb_2O_5 at 1150°C for 10 h.

(i) Fabrication of $H_4Nb_6O_{17}$/CdS nanocomposites: $H_4Nb_6O_{17}$ was converted to $(C_3H_7NH_3)_4Nb_6O_{17}$ by stirring it in 50 vol% $C_3H_7NH_2$ aqueous solution at 60 °C for 3 days. CdS particles were incorporated into the interlayer of $H_4Nb_6O_{17}$ by reacting H_2S gas with Cd^{2+} exchanged compounds, which were obtained by the ion exchange reaction in 0.4 M Cd $(CH_3COO)_2$ solution at 50 °C for 3 days using $(C_3H_7NH_3)_4$ Nb_6O_{17}. The sample obtained was designated as $H_4Nb_6O_{17}$/CdS.

(ii) Loading Pt particles in the interlayer of $H_4Nb_6O_{17}$ together with CdS particles: $[Pt(NH_3)_4]^{2+}$ was incorporated into the interlayer of $H_4Nb_6O_{17}$ by stirring $H_4Nb_6O_{17}$ in $[Pt(NH_3)_4]Cl_2$ aqueous solution at room temperature for 3 days. After being filtered and washed with water, the sample was dispersed in water and Pt was loaded by photodeposition with UV light of a 100 W high pressure mercury lump at room temperature for 5 h prior to incorporating CdS by successive reactions with 50 vol% $C_3H_7NH_2$ solution, 0.4 M $Cd(CH_3COO)_2$ solution and H_2S gas as shown in (i). The sample obtained was designated as $H_4Nb_6O_{17}$/(Pt,CdS).

2. Photochemical reaction

Photocatalytic reduction of NO_3^- was carried out in a Pyrex reactor of $400 \, cm^3$ 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 $NaNO_2$ solution between the mercury lamp and the reaction chamber.

3. Analysis

The crystalline phases of the samples were identified by X-ray diffraction analysis (Rigaku Denki Geiger-flex 2013) using Ni-filtered $CuK\alpha$ radiation. Chemical compositions were determined by atomic absorption spectroscopy (Hitachi Model 180-80 AAS), inductively coupled plasma-atomic emission spectroscopy (Seiko SPS-1200A) and TG-DTA analysis (Rigaku Denki TAS 200 TG-DTA). 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 concentrations of NO_3^- and NO_2^- were determined using an ion chromatograph (Dionex Qic Analyzer with a Dionex Ionpac AG4A column) and that of ammonia using an ammonium ion meter (Toa pH/ATC meter, HM-30S). The amounts of H_2 was measured using a gas burette.

III. Results and Discussion

Fig. 1 depicts powder X-ray diffraction patterns of (a) $H_4Nb_6O_{17}$ (b) $(C_3H_7NH_3)_4Nb_6O_{17}$ and (c) $H_4Nb_6O_{17}/CdS$. The main peak corresponding to (040) of $H_4Nb_6O_{17}$ significantly shifted to a lower 2θ angle for samples (b) and (c), indicating the expansion of the interlayer by incorporation of $C_3H_7NH_3^+$ and CdS. The gallery heights of (n-$C_3H_7NH_3)_4 Nb_6O_{17}$ determined by subtracting the $Nb_6O_{17}^{4+}$
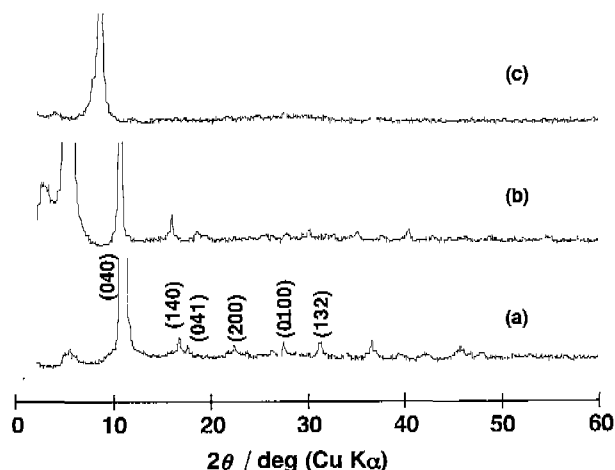
Fig. 1. Powder X-ray diffraction patterns of (a) $H_4Nb_6O_{17}$, (b) $(C_3H_7NH_3)_4Nb_6O_{17}$ and (c) $H_4Nb_6O_{17}/CdS$.
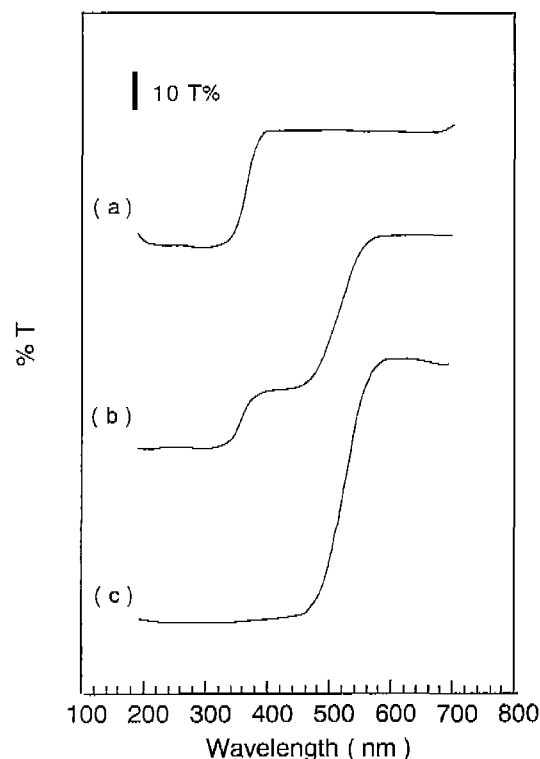
Fig. 2. UV-vis reflection spectra of (a) $H_4Nb_6O_{17}$, (b) $H_4Nb_6O_{17}/CdS$ and (c) unsupported CdS.

layer thicknesses of 0.4 nm were 1.29 nm. Since the length of n-$C_3H_7NH_3^+$ is ca. 0.5 nm, it is suspected that two molecules of n-$C_3H_7NH_3^+$ are vertically arranged in the interlayer. The peak position for sample (c) was in the middle of samples (a) and (b). These results suggested that the layer structure was still retained after intercalation of CdS and that the interlayer distance of $H_4Nb_6O_{17}/TiO_2$ is larger than that of $H_4Nb_6O_{17}$, but smaller than that of (n-$C_3H_7NH_3)_4Nb_6O_{17}$.

UV-vis reflection spectra of (a) $H_4Nb_6O_{17}$, (b) $H_4Nb_6O_{17}/CdS$ and (c) unsupported CdS are shown in Fig. 2. Sample (b) showed onsets corresponding to both $H_4Nb_6O_{17}$ layer and incorporated CdS. The onset corresponding to CdS for sample (b) shows a slight blue shift. It may be due to the size quantization effect.

The gallery height determined by XRD, the amounts of CdS and Pt incorporated, band gap energy and specific surface area of the products are listed in Table 1. Since the gallery heights of $H_4Nb_6O_{17}/CdS$ was 0.64 nm, the thickness of CdS in the interlayer is suspected to be less than 0.7 nm. The amount of Pt incorporated in $H_4Nb_6O_{17}$ were 0.32 wt% and those of CdS in $H_4Nb_6O_{17}/CdS$ and $H_4Nb_6O_{17}/(CdS, Pt)$ were determined as 40.4 and 47.5 wt%, respectively. Both $H_4Nb_6O_{17}/CdS$ and $H_4Nb_6O_{17}/(CdS, Pt)$ possessed small band gap energies, 2.56-2.58 eV, being slightly larger than that of unsupported CdS, 2.40 eV, while much smaller than that of host $H_4Nb_6O_{17}$, 3.84 eV. The specific surface area of $H_4Nb_6O_{17}/CdS$ and $H_4Nb_6O_{17}/(CdS, Pt)$ were much larger than that of $H_4Nb_6O_{17}$, indi-

Table 1. The Gallery Height Determined by XRD, the Amounts of CdS and Pt Incorporated, Band Gap Energy and Specific Surface Area of the Samples

Sample	Interlayer distance (nm)	Content (wt%)		Bang gap (eV)	Specific surface area (m^2g^{-1})
		CdS	Pt		
$H_4Nb_6O_{17}$	0.40	0	0	3.84	6.6
$H_4Nb_6O_{17}$/CdS	0.76	40.4	0	3.84 2.56	98.0
$H_4Nb_6O_{17}$/(CdS, Pt)	0.75	47.5	0.32	3.84 2.58	102
CdS		100	0	2.40	121
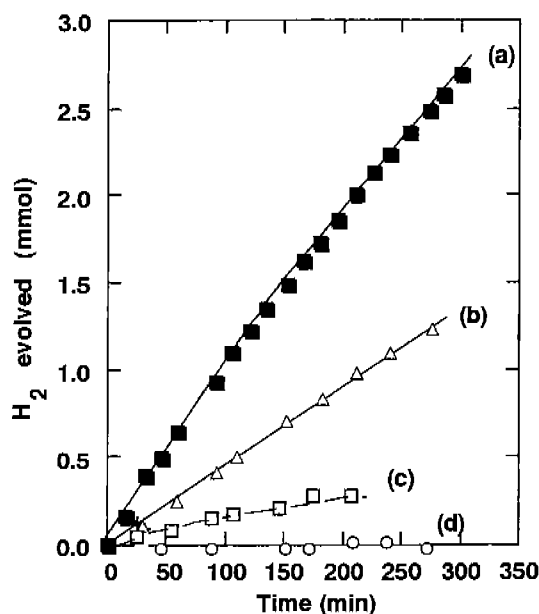
Fig. 3. Amounts of hydrogen gas produced from 400 cm³ of 0.1 M Na_2S solutions which contained dispersed 1 g of (a) $H_4Nb_6O_{17}$/(CdS,Pt), (b) $H_4Nb_6O_{17}$/CdS, (c) unsupported CdS and (d) $H_4Nb_6O_{17}$, at 60 °C exposed to irradiation of visible light of wavelength longer than 400 nm.

Fig. 4. Time dependence of (a) NO_3^-, (b) NO_2^- and (c) NH_3 concentrations at 60°C under irradiation of visible light in the presence of $H_4Nb_6O_{17}$/(Pt,CdS) catalyst and 10 vol% methanol.

cating the construction of CdS pillars.

The photocatalytic activity of (a) $H_4Nb_6O_{17}$/(CdS,Pt), (b) $H_4Nb_6O_{17}$/CdS, (c) unsupported CdS and (d) $H_4Nb_6O_{17}$ were determined by measuring the amount of hydrogen gas produced from 400 cm³ of 0.1 M Na_2S solution which contained dispersed 1 g of sample at 60 °C exposed to irradiation of visible light of wavelength longer than 400 nm. The results are shown in Fig. 3. The amount of hydrogen evolved in the presence of $H_4Nb_6O_{17}$ alone was negligibly small under radiation of visible light. It was notable that the amount of hydrogen gas evolved in the presence of $H_4Nb_6O_{17}$/CdS and $H_4Nb_6O_{17}$/(CdS,Pt) were respectively ca. 3.0 and 5.3 times as much as when unsupported CdS was used, although the amounts of CdS in the samples were about 40 wt% of unsupported CdS (see Table 1). The improvement in the photocatalytic activity of CdS with $H_4Nb_6O_{17}$ might be due to the surface modification of CdS which retards the quick recombination between photoinduced holes and electrons, as was observed in $H_4Nb_6O_{17}$/ TiO_2 and $H_2Ti_4O_9$/CdS systems.[12]

Photochemical reduction of NO_3^- was carried out by adding methanol as a sacrificial reductant. Time dependence
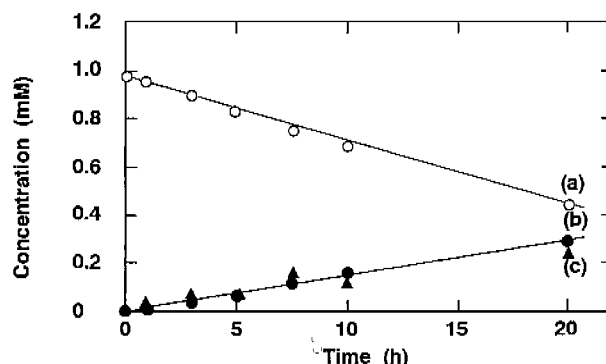
of (a) NO_3^-, (b) NO_2^- and (c) NH_3 concentrations at 60 °C under irradiation of visible light in the presence of $H_4Nb_6O_{17}$/(Pt,CdS) catalyst and 10 vol% methanol is shown in Fig. 4. Under present experimental conditions, the amounts of SO_4^{2-} and Cd^{2+} dissolved in the solution were negligibly small, indicating that methanol acted as a reductant of NO_3^- and depressed the reaction between NO_3^- and CdS. Since both NO_2^- and NH_3 were formed, NO_3^- seemed to be reduced to NH_3 via NO_2^-.

Time dependence of degree of NO_3^- decomposition under visible light illumination in the presence of (a) $H_4Nb_6O_{17}$/ (CdS,Pt), (b) $H_4Nb_6O_{17}$/CdS and (c) unsupported CdS with 1 mM NO_3^- and 10 vol% methanol is shown in Fig. 5. The
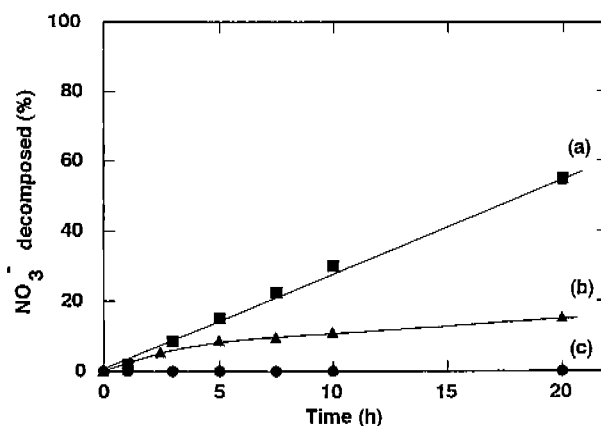
Fig. 5. Time dependence of degree of NO_3^- decomposition under visible light illumination in the presence of (a) $H_4Nb_6O_{17}$/(CdS,Pt), (b) $H_4Nb_6O_{17}$/CdS and (c) unsupported CdS with 1 mM NO_3^- and 10 vol% methanol.

degree of NO_3^- reduction linearly increased with time in the presence of $H_4Nb_6O_{17}$/CdS and $H_4Nb_6O_{17}$/(Pt,CdS), but no noticeable NO_3^- reduction was observed in the presence of unsupported CdS. As was suspected from the results shown in Fig. 3, the photoactivity of $H_4Nb_6O_{17}$/(Pt,CdS) was much higher than that of $H_4Nb_6O_{17}$/CdS. Therefore, it may be concluded that although unsupported CdS showed no photocatalytic activity for NO_3^- reduction even in the presence of the hole scavenger, $H_4Nb_6O_{17}$/CdS nanocomposite possesses photoactivity for NO_3^- reduction and the photoactivity was greatly increased with Pt loading in the interlayer.

IV. Conclusions

From the results of tests described, the following conclusions may be drawn:

(i) $H_4Nb_6O_{17}$/CdS nanocomposites which intercalated CdS particles, less than 0.8 nm thickness, in the interlayer of $H_4Nb_6O_{17}$ were prepared by the successive ion exchange reactions of $H_4Nb_6O_{17}$ with Cd^{2+} and $C_3H_7NH_3^+$, followed by the reaction with H_2S gas.

(ii) Although unsupported CdS showed no noticeable photocatalytic activity for NO_3^- reduction, NO_3^- was reduced by band gap illumination in the presence of $H_4Nb_6O_{17}$/CdS nanocomposites.

(iii) The photocatalytic activity of $H_4Nb_6O_{17}$/CdS increased with doping Pt particles in the interlayer.

(iv) Addition of methanol as a sacrificial hole acceptor was useful to depress the oxidation of CdS with NO_3^-.

Acknowledgement

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