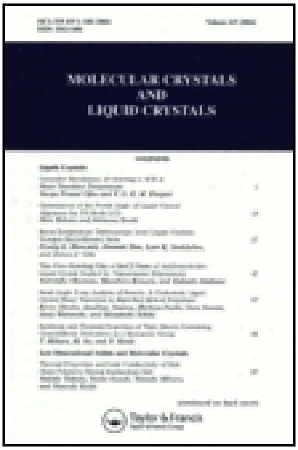

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Photoreduction of NO_3^- and NO_2^- under Visible Light Irradiation with Layered $H_4Nb_6O_{17}$/CdS and $H_2Ti_4O_9$/CdS Nanocomposites

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Photoreduction of NO_3^- and NO_2^- under Visible Light Irradiation with Layered $H_4Nb_6O_{17}$/CdS and $H_2Ti_4O_9$/CdS Nanocomposites

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The photoreduction of NO_3^- and NO_2^- was performed at 60 °C under irradiation of visible light (λ >400 nm) in the presence of unsupported CdS, $H_2Ti_4O_9$/CdS and $H_4Nb_6O_{17}$/CdS in 10 vol.% aqueous methanol solution. The photoreduction rate of NO_3^- proceeded in the presence of $H_4Nb_6O_{17}$/CdS and $H_2Ti_4O_9$/CdS nanocomposites although unsupported CdS, $H_4Nb_6O_{17}$ and $H_2Ti_4O_9$ did not show photocatalytic activity for nitrate reduction under visible light irradiation. The photoreduction rate of NO_3^- and NO_2^- changed significantly depending on solution pH, i.e., with increasing solution pH the reduction rate of NO_3^- increased, on the orther hand, that of NO_2^- decreased.

Keywords: cadmium sulphide; $H_4Nb_6O_{17}$/CdS; $H_2Ti_4O_9$/CdS; photoreduction; nitrate; nitrite

INTRODUCTION

Photocatalytic decomposition of organic or inorganic pollution has been studied extensively[1]. Nitrate and nitrite ions were the major contamination of the watershed in areas under intense agricultural use. High concentration of nitrate and nitrite promote the growth of algae, which rob the oxygen being necessary for animal life[2]. The removal or elimination of nitrate and nitrite from the wastewater has been studied in many techniques such as reverse osmosis, ion exchange, electrodialysis etc[3]. The major problem of these techniques was that the reaction efficiency decreases at low concentration of nitrite and nitrate. The photoreduction of nitrate and nitrite ion by using TiO_2 as photocatalyst has been studies. These results showed that TiO_2 has low efficiency of reduction of nitrate and nitrite ion [4]. To improve its efficiency, TiO_2 was loaded with noble metal and/or used with the hole scavenger reagent [5]. Its disadvantage is large bandgap energy (3.2 eV) which does not cover the main part of sunlight. The photoreduction of nitrate in the presence of small bandgap semiconductor, CdS (2.5eV) at neutral pH was studied [6]. The overall quantum yields was up to 4 % for 2-mercaptoethyl-amine-caped CdS nanocrystals (~20Å) under illumination by sunlight condition. In the present study $H_4Nb_6O_{17}$/CdS and $H_2Ti_4O_9$/CdS nanocomposites and unsupported CdS were prepared and their photocatalytic activities for the reduction of nitrate and nitrite ion were studied under the visible light (λ >400nm) irradiation.

EXPERIMENTAL

Chemicals

$H_2Ti_4O_9$ was converted to $(C_3H_7NH_3)_2Ti_4O_9$ by stirring in 50 vol.% $C_3H_7NH_2$ aqueous solution at 60 °C for 3 days, whereas $H_4Nb_6O_{17}$ was converted to $(C_3H_7NH_3)_4Nb_6O_{17}$ by reflux in 50 vol.% $C_3H_7NH_2$ aqueous solution for 6 h. After that CdS was intercalated by ion exchange reaction of them with $Cd(CH_3COO_2)_2$ solution followed by reacting with H_2S gas. The samples obtained were designated $H_2Ti_4O_9$/CdS and $H_4Nb_6O_{17}$/CdS, respectively.

Photochemical reaction

Photoreduction of NO_3^- and NO_2^- was studied in 500 ml of 0.2 mM KNO_3 and KNO_2 aqueous solution containing in 10 vol.% methanol and 0.5 g photocatalyst using an inner radiation type 100 W high-pressure mercury lamp. The pH of solution was adjusted by 0.005 M H_2SO_4 and 0.01 M KOH. Before irradiation the solution was purged with argon gas for 30 min in order to remove oxygen. The UV emission of the mercury arc below 400 nm was filtered out by flowing 0.1 M of $NaNO_2$ solution between the mercury lamp and the reaction chamber.

Analysis

The crystalline phases of the products were identified by X-ray diffraction analysis (Shimadzu KD-01) using graphite monochromatized CuK α radiation. Chemical compositions were determined by inductively coupled plasma-atomic emission spectroscopy (Seiko SPS-1200A). The bandgap energies were determined by a Shimadzu Model UV-2100 ultraviolet-visible spectrophotometer. The concentrations of NO_3^- and NO_2^- were determined by an ion chromatograph (IC200 Ion Chromatographic Analyzer YOKOGAWA with pre-column PAX051 and separator SAX 1-251) and amount of NH_3 was determined by ammonia selective electrode (AE-235). The amount of N_2 was determined by subtracting the amounts of NO_3^-, NO_2^- and NH_3 from the initial amount of NO_3^-.

RESULTS

Figure 1 shows powder X-ray diffraction patterns of (a) $H_4Nb_6O_{17}$, (b) $(C_3H_7NH_3)_4Nb_6O_{17}$, (c) $H_4Nb_6O_{17}$/CdS, (d) $H_2Ti_4O_9$, (e) $(C_3H_7NH_3)_2Ti_4O_9$, and (f) $H_2Ti_4O_9$/CdS. The main peak corresponding to (002) of $H_4Nb_6O_{17}$ (a) and $H_2Ti_4O_9$ (b) significantly shifted to a lower 2 θ angle for sample (b) and (e), indicating the expansion of the interlayer by incorporation of $C_3H_7NH_3^+$. Although the color of samples (b) and (e) were white, the samples (c) and (f) were yellow. The samples (c) and (f) showed XRD peaks corresponding to the

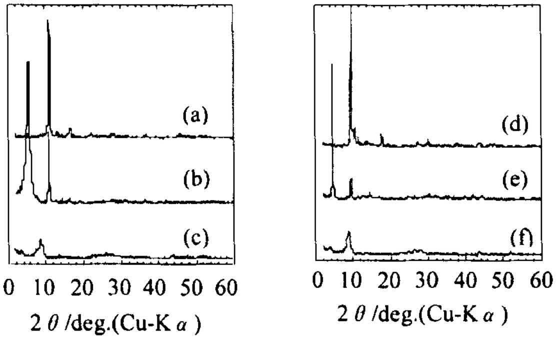

FIGURE 1 Powder X-ray diffraction patterns of the sample. (a) $H_4Nb_6O_{17}$, (b) $(C_3H_7NH_3)_4Nb_6O_{17}$, (c) $H_4Nb_6O_{17}$/CdS, (d) $H_2Ti_4O_9$, (e) $(C_3H_7NH_3)_2Ti_4O_9$, and (f) $H_2Ti_4O_9$/CdS

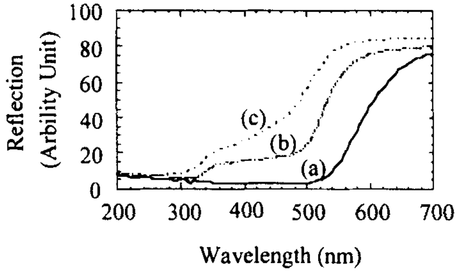

FIGURE 2 UV-VIS reflectance spectra of (a) CdS, (b) $H_2Ti_4O_9$/CdS and (c) $H_4Nb_6O_{17}$/CdS.

TABLE I CdS contents and bandgap energies of the samples

Photocatalyst	CdS content (wt%)	Bandgap energy (eV)
CdS	100	2.32
$H_2Ti_4O_9$/CdS	27.2	2.51
$H_4Nb_6O_{17}$/CdS	16.8	2.66

host materials but no XRD peaks corresponding to CdS was detected. These results indicated that CdS was intercalated in the layer of host material. UV-VIS diffuse reflectance spectra of (a) CdS, (b) $H_2Ti_4O_9$/CdS and (c) $H_4Nb_6O_{17}$/CdS are shown in Figure 2 and the CdS contents and band gap energies of the catalysts used are summarized in Table I. The bandgap energies of $H_2Ti_4O_9$/CdS and $H_4Nb_6O_{17}$/CdS were 2.51 (494 nm) and 2.66 eV(466 nm), respectively, and were slightly larger than that of unsupported CdS (2.32 eV, 534 nm). The amount of CdS incorporated in the $H_2Ti_4O_9$ and $H_4Nb_6O_{17}$ were 27.2 and 16.8 wt%, respectively.

The photoreduction of nitrate proceeded under visible light irradiation in the presence of (a) $H_2Ti_4O_9$/CdS and (b) $H_4Nb_6O_{17}$/CdS (see Figure 3), although unsupported CdS, $H_2Ti_4O_9$ and $H_4Nb_6O_{17}$ showed no photocatalytic activity for the reduction of nitrate. The amount of NO_3^- linearly decreased with time in the presence of both $H_2Ti_4O_9$/CdS and $H_4Nb_6O_{17}$/CdS. NO_3^- was reduced to NO_2^- and N_2 in the presence of $H_2Ti_4O_9$/CdS and to NO_2^-, NH_3 and N_2 in the

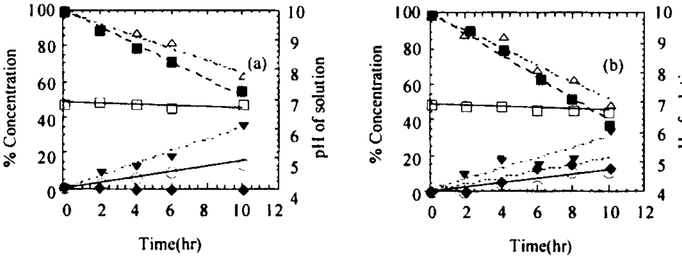

FIGURE 3 Time dependence of NO_3^- (■), NO_2^- (○), NO_2^-+NO_3^- (△), NH_3 (◆) and N_2 (▼)concentrations and pH (□) at 60 °C by irradiating visible light (λ >400 nm) to 0.2 mM KNO_3 and 10 vol.% methanol solution in the presence of (a) $H_2Ti_4O_9$/CdS and (b) $H_4Nb_6O_{17}$/CdS.

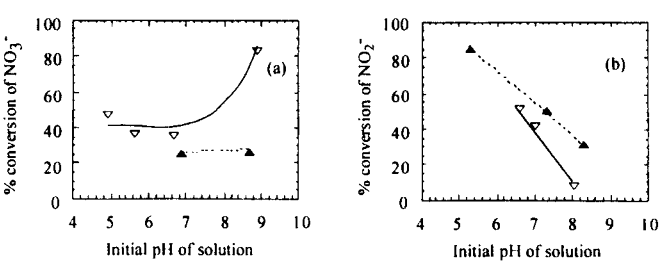

FIGURE 4 The % conversion of (a) NO_3^- after irradiation of a 100 W high pressure mercury arc (λ > 400 nm) for 6 h and (b) NO_2^- after irradiation for 2 h versus pH with 0.5 g photocatalyst. ▲:$H_2Ti_4O_9$/CdS, ▽:$H_4Nb_6O_{17}$/CdS

presence of $H_4Nb_6O_{17}$/CdS. The rate of NO_3^- reduction was in the order $H_4Nb_6O_{17}$/CdS>$H_2Ti_4O_9$/CdS, and that of total amount of NO_3^- and NO_2^- in the presence of $H_4Nb_6O_{17}$/CdS was twice larger than that of $H_2Ti_4O_9$/CdS. The effect of initial pH on the %conversion of NO_3^- and NO_2^- after 6 h in the presence of $H_2Ti_4O_9$/CdS and $H_4Nb_6O_{17}$/CdS are shown in Figure 4(a) and (b). The % conversion of NO_3^- was almost constant at pH 4-7 and greatly increased above pH 8.5. On the other hand, the % conversion of NO_2^- monotonously decreased with increasing pH. These results agreed with the fact that NO_2^- is thermodynamically more stable at higher pH.

CONCLUSIONS

Both $H_4Nb_6O_{17}$/CdS and $H_2Ti_4O_9$/CdS nanocomposites showed photocatalytic activity for the photoreduction of NO_3^- under visible light irradiation in the presence of methanol as sacrificial hole acceptor, although unsupported CdS, $H_2Ti_4O_9$ and $H_4Nb_6O_{17}$ showed no photocatalytic activity. NO_3^- was reduced to NO_2^-, NH_3 and N_2 in the presence of $H_4Nb_6O_{17}$/CdS and to NO_2^- and N_2 in the presence of $H_2Ti_4O_9$/CdS. The reduction rate of NO_3^- increased with increasing the solution pH in both catalysts whereas the reduction rate of NO_2^- decreased.

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