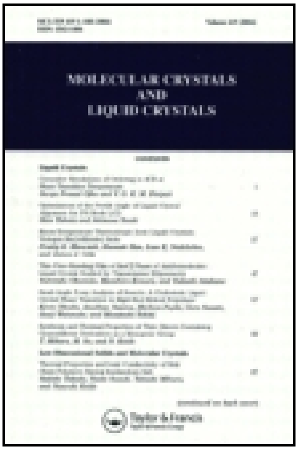

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Synthesis and Photocatalytic Property of Hectorite/(Pt, TiO_2) and $H_4Nb_6O_{17}$/(Pt, TiO_2) Nanocomposites

Sambandan Ekambaram [a], Masaru Yanagisawa [a], Satoshi Uchida [a], Yoshinobu Fujishiro [a] & Tsugio Sato [a]

[a] Institute for Chemical Reaction Science, Tohoku University, Sendai, 980-8577, JAPAN

Version of record first published: 27 Oct 2006

Mol. Cryst. and Liq. Cryst., 2000, Vol. 341, pp. 213-218
Reprints available directly from the publisher
Photocopying permitted by license only

Synthesis and Photocatalytic Property of Hectorite/(Pt,TiO_2) and $H_4Nb_6O_{17}$ /(Pt,TiO_2) Nanocomposites

SAMBANDAN EKAMBARAM, MASARU YANAGISAWA, SATOSHI UCHIDA, YOSHINOBU FUJISHIRO and TSUGIO SATO

Institute for Chemical Reaction Science, Tohoku University, Sendai 980–8577, JAPAN

(In final form July 5, 1999)

TiO_2 and Pt have been intercalated in hectorite and $H_4Nb_6O_{17}$. The height of TiO_2 and Pt pillars was less than 0.8 nm and the band gap energy of TiO_2 pillars was ca. 3.3 eV. Both hectorite/TiO_2 and $H_4Nb_6O_{17}$/(Pt,TiO_2) were capable of hydrogen evolution following irradiation from a high pressure mercury arc ($\lambda > 290$ nm) in the presence of methanol as a sacrificial hole acceptor and the hydrogen evolution was enhanced by co-incorporation of Pt, although hectorite and hectorite/Pt did not show photocatalytic activity. Incorporation of Pt or Pt and TiO_2 in the interlayer of H_4Nb_6 O_{17} has resulted in enhanced photo evolution of hydrogen, however, TiO_2 alone in the interlayer of $H_4Nb_6O_{17}$ showed adverse photocatalytic activity.

Keywords: intercalation; titania pillar; hexaniobate; photocatalyst

INTRODUCTION

Recently, there has been an upsurge of interest in nanocrystalline semiconductor oxides because of their vital applications for solar fuel production and solar detoxification. For effective utilization of photo-induced charge carriers various studies have been performed.[1-9] Semiconductor pillars constructed in layered oxides are important because of their improved photocatalytic activity compared with that of unsupported semiconductors. Recent studies, from this laboratory,[10,11] revealed that the incorporation of semiconductor in the interlayer of semiconductor sheet mitigates the recombination of photogenerated electrons and holes by separating them between the incorporated semiconductor and layer semiconductor sheet. In continuation of our studies on photofission of water, the photocatalytic activities of TiO_2 and Pt incorporated hectorite and $H_4Nb_6O_{17}$ were evaluated.

EXPERIMENTAL

(a) Synthesis of hectorite/TiO_2 and hectorite/(Pt,TiO_2) Acetic acid (211 g) was first mixed with titanium tetraisopropoxide (50 g) for 30 min followed by the addition of water (64 g) to give a clear solution of $[Ti(OH)_x(CH_3COO)_y]^z$.[12,13] Then hectorite (2 g) was dispersed in the solution to allow intercalation of $[Ti(OH)_x(CH_3COO)_y]^{z+}$ for 1 d at room temperature. The obtained sample, after being filtered off and washed with water, was calcined in air at 550°C for 2 h. The resulting materials is designated hectorite/TiO_2. Hectorite/(Pt,TiO_2) was prepared by reacting hectorite/TiO_2 (1.5 g) in 0.1 M $[Pt(NH_3)_4]Cl_2$ solution at room temperature for 3 d followed by the irradiation with UV light from a 450 W high pressure mercury lamp at room temperature for 10 h.

(b) Synthesis of $H_4Nb_6O_{17}$/(Pt,TiO_2) Procedure employed for photodeposition of Pt into the layer of $H_4Nb_6O_{17}$ was the same as described for synthesis of hectorite/(Pt,TiO_2). $H_4Nb_6O_{17}/TiO_2$ and $H_4Nb_6O_{17}$/(Pt,TiO_2) were prepared by stepwise reactions of $H_4Nb_6O_{17}$ and $H_4Nb_6O_{17}$/Pt with 50 vol.% $C_3H_7NH_2$ and $[Ti(OH)_x(CH_3COO)_y]^{z+}$ solutions followed by photodecomposition of $[Ti(OH)_x(CH_3COO)_y]^{z+}$ with UV light from a 450 W high pressure mercury lamp at room temperature for 10 h.

(c) Characterization and photocatalytic reaction Formation of TiO_2 and Pt pillars was confirmed by powder X-ray diffraction, UV-Vis absorption and

ICP atomic emission spectroscopy after alkali fusion with Na_2CO_3 followed by dissolving the samples in 6 M HCl-15 wt% H_2O_2. The photoactivity of the catalyst was determined using an inner radiation type apparatus by measuring the volume of H_2 evolved from 1250 cm^3 of 20 vol% methanol solution containing 1 g of dispersed catalyst at 60°C exposed to irradiation ($\lambda > 290$ nm) from a 450 W mercury arc with a gas burette.

RESULTS AND DISCUSSION

DTA profiles of the samples are shown in Fig. 1. $[Ti(OH)_x(CH_3COO)_y]^{z+}$ incorporated hectorite showed an exothermic peak at 453°C which corresponds to the combustion of CH_3COO group. The exothermic peak disappeared after calcination (500°C, 2 h), indicating that the CH_3COO group was decomposed.

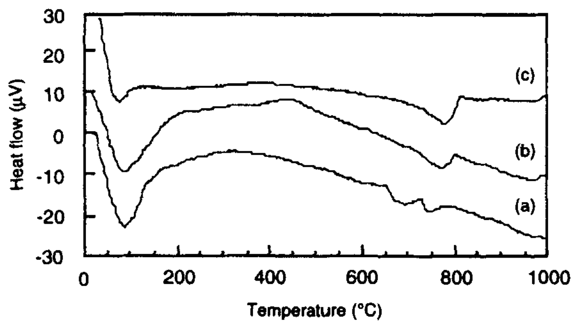

FIGURE 1 DTA profiles of (a) hectorite and (b) hectorite/ $[Ti(OH)_x(CH_3COO)_y]^{z+}$ and (c) hectorite/TiO_2.

Figure 2 shows the powder XRD patterns of (a) hectorite and hectorite/ $[Ti(OH)_x(CH_3COO)_y]^{z++}$ (b) as-prepared, (c) calcined at 500°C and (d) calcinedat 1000°C. The samples (c) showed no XRD peaks corresponding to TiO_2 although sample (d) showed diffraction peak of rutile, indicating that TiO_2 was incorporated in the interlayer.

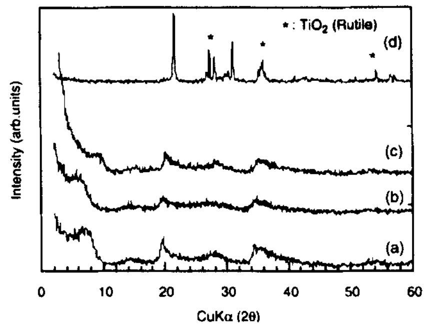

FIGURE 2 Powder X-ray diffraction profiles of (a) hectorite and hectorite/$[Ti(OH)_x(CH_3COO)_y]^{z+}$ (b) as-prepared, (c) irradiated UV-light, (d) calcined at 500°C and (e) calcined at 1000°C.

Figure 3 shows XRD patterns of (a) $H_4Nb_6O_{17}$, (b) $H_4Nb_6O_{17}$/n-$C_3H_7NH_3^+$, (c) $H_4Nb_6O_{17}$/$[Ti(OH)_x(CH_3COO)_y]^{z+}$ and (d) $H_4Nb_6O_{17}/TiO_2$. The main peak corresponding to (040) of $H_4Nb_6O_{17}$ changed significantly depending on the material incorporated.

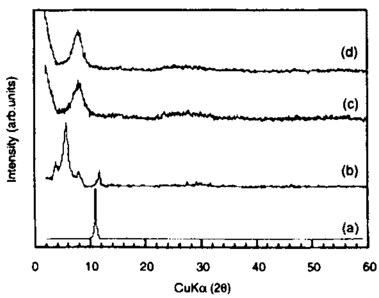

FIGURE 3 XRD patterns of (a) $H_4Nb_6O_{17}$, (b) $H_4Nb_6O_{17}$/n-$C_3H_7NH_3^+$, (c) $H_4Nb_6O_{17}$/$[Ti(OH)_x(CH_3COO)_y]^{z+}$ and (d) $H_4Nb_6O_{17}/TiO_2$.

The characteristics of the samples are summarized in Table 1. The gallery height which indicates the pillar height was less than 0.8 nm. The band gap energy of TiO_2 incorporated was slightly larger than that of unsupported TiO_2. Photocatalytic hydrogen evolution behaviors from methanol solutions dispersed

TABLE 1 Summary of the characteristics of the prepared samples

Compound	Content (wt%)		Gallery height	Band gap
	Ti	Pt	(nm)	(eV)
hectorite/TiO_2	4.63	0	0.78	3.3
hectorite/(Pt, TiO_2)	4.63	0.06	0.78	3.3
$K_4Nb_6O_{17}$	0	0	0.50	3.4
$H_4Nb_6O_{17}$	0	0	0.40	3.3
$H_4Nb_6O_{17}/TiO_2$	10.9	0	0.52	3.2
$H_4Nb_6O_{17}$/Pt	0	0.26	0.40	3.3
$H_4Nb_6O_{17}$/(Pt,TiO_2)	11.6	0.26	0.52	3.2
TiO_2 (P-25)	59.9	0	-	3.1

various catalysts are shown in Fig. 4. Hectorite/TiO_2 was capable of hydrogen evolution and the activity was increased by co-incorporation of Pt, although hectorite and hectorite/Pt did not show photocatalytic activity. The activity of hectorite/TiO_2 was almost the same with that of P-25, although the TiO_2 content was 4.63 wt%. $K_4Nb_6O_{17}$ showed photocatalytic activity similar to P-25. The activity of $H_4Nb_6O_{17}$ is ca. 3.5 times greater than that of $K_4Nb_6O_{17}$. Interestingly photocatalytic activity of $H_4Nb_6O_{17}$ was improved 4.2 and 8.5 times by the incorporation of Pt and co-incorporation of TiO_2 and Pt, but slightly decreased by incorporating TiO_2 alone. The promotion of hydrogen evolution in the

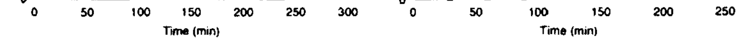

FIGURE 4 Cummulative amounts of hydrogen evolved by irradiating 450 W mercury arc (λ>290 nm) from the suspension of 1 g catalyst in 1250 cm^3 of 20 vol% methanol solution. (A) ○: hectorite/TiO_2, ●: hectorite/(TiO_2, Pt), ▲: TiO_2 (Degussa P-25), (B) ▲: $K_4Nb_6O_{17}$, △: $H_4Nb_6O_{17}$, ●: $H_4Nb_6O_{17}/TiO_2$, □: $H_4Nb_6O_{17}$/Pt, ■: $H_4Nb_6O_{17}$/(Pt, TiO_2)

presence of Pt may be due to the electron transfer from $H_4Nb_6O_{17}$ and/or TiO_2 to Pt. When $H_4Nb_6O_{17}/TiO_2$ was photoirradiated in methanol solution, the color of the samples changed from white to blue, indicating the reduction of TiO_2. It might be the reason why the incorporation of TiO_2 alone showed adverse photocatalytic activity.

CONCLUSION

The photocatalytic activity for H_2 evolution from methanol solution was in the order $H_4Nb_6O_{17}$/(Pt,TiO_2)>$H_4Nb_6O_{17}$/Pt > $H_4Nb_6O_{17}$> $H_4Nb_6O_{17}/TiO_2$ >>hectorite/ (Pt,TiO_2)> hectorit /TiO_2=$K_4Nb_6O_{17}$ = unsupporte TiO_2 (P-25).

References

[1] P. V. Kamat, in *Studies in Surface Science and Catalysis* edited by B. Delmon and J.T. Yates (Elsevier Science B.V., 1997), Vol. 103, p.237.
[2] K.R. Gopidas, M. Bohorquez and P. V. Kamat, *J. Phys. Chem.*, **94,** 6435 (1990).
[3] Y.I. Kim, S.J. Atherton, E. S. Brigham and T.E. Mallouk, *J. Phys. Chem.*, **97**, 11802 (1993).
[4] T. Sato, K. Masaki, K. Sato, Y. Fujishiro and A. Okuwaki, *J. Chem. Tech. Biotechnol.*, **67,** 339 (1996).
[5] T. Takata, Y. Furumi, K. Shinohara, A. Tanaka, M. Hara, J. N. Kondo and K. Domen, *Chem. Mater.*, **9,** 1063 (1997).
[6] G. B. Saupe, T.E. Mallouk, W. Kim and R.H. Schmehl, *J. Phys. Chem. B*, **101,** 2508 (1997).
[7] W. Choi, A. Termin and M. R. Hoffmann, *Angew. Chem. Int. Ed. Engl.*, **33,** 1091 (1994).
[8] W. Choi, A. Termin and M.R. Hoffmann, *J. Phys. Chem.*, **98,** 13669 (1994).
[9] J. Moser, M. Gratzel and R. Gallary, *Helvetica Chimica Acta,* **70,** 1596 (1987).
[10] T. Sato, Y. Yamamoto, Y. Fujishiro and S. Uchida, *J. Chem. Soc., Faraday Trans.*, **92,** 5089 (1996).
[11] S. Uchida, Y. Yamamoto, Y. Fujishiro, A. Watanabe, O. Ito and T. Sato, *J. Chem. Soc., Faraday Trans.*, **93,** 3229 (1997).
[12] S. Doeuff, M. Henry, C. Sanchez and J. Livage, *J. Non-cryst. Solids.*, **89,** 206 (1987).
[13] C. Kao and W. Yang, *Ceramics International*, **22,** 57 (1996).