

Correlation of crystal and electronic structures with photophysical properties of water splitting photocatalysts InMO_4 ($M = \text{V}^{5+}, \text{Nb}^{5+}, \text{Ta}^{5+}$)

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Abstract

A novel series of visible light responding solid photocatalysts InMO_4 ($M = \text{V}, \text{Nb}, \text{Ta}$) were synthesized by the solid-state reaction method. The InNbO_4 and InTaO_4 photocatalysts crystallize in the same crystal structure: wolframite-type, monoclinic with space group $P2/c$, while InVO_4 belongs to the orthorhombic system with space group $Cmcm$. Under visible light irradiation ($\lambda > 420 \text{ nm}$), the native photocatalysts were found to evolve H_2 from pure water. The photocatalytic activity increases significantly by loading NiO as a co-catalyst. The bandgaps of InVO_4 , InNbO_4 and InTaO_4 were estimated to be 1.9, 2.5 and 2.6 eV, respectively. The difference in the bandgaps of the photocatalysts is supposed to come from their different conduction band levels formed by V 3d in VO_4 , Nb 4d in NbO_6 , and Ta 5d in TaO_6 , resulting in different photocatalytic activities of the photocatalysts. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Splitting water photocatalytically using oxide semiconductor under solar light irradiation to produce clean-energy hydrogen has received increasing attention because of the serious energy and environment problems. Since the first experiment of H_2 formation via photocatalysis with TiO_2 several decades ago [1], a great deal of research on the conversion of solar energy to chemical energy has been directed towards the development of photocatalytic systems capable of splitting water into H_2 and O_2 . Until now, several types of semiconductor photocatalysts such as CdS and various oxides WO_3 , In_2O_3 , Fe_2O_3 , SnO_2 , $\gamma\text{-Bi}_2\text{O}_3$ and SrTiO_3 , etc., have been developed for H_2 production from water or other aqueous solutions. However, most of them have so wide bandgap that they only respond to the ultra violet (UV) light. Furthermore, some of the semiconductors undergo photocorrosion induced by the acidity created by H^+ formed upon irradiation [2]. Yoshimure et al. [3] found that $\text{RbPb}_2\text{Nb}_3\text{O}_{10}$ of a modified perovskite type had photocatalytic behavior

and H_2 was evolved from an aqueous methanol solution under visible light irradiation using this compound. Later, Kudo et al [4–6] showed that $\text{In}_2\text{O}_3(\text{ZnO})_m$ and BiVO_4 could produce H_2 or O_2 from methanol or silver solutions under visible light irradiation. Nevertheless, the variety of applicable semiconductors for the photocatalytic production of H_2 from water under visible light irradiation has been limited.

Recently, we developed a novel series of water splitting photocatalysts, InMO_4 ($M = \text{Nb}, \text{Ta}$) [7]. We found that native InNbO_4 and InTaO_4 could evolve H_2 from pure water under visible light irradiation. In the present study, we extended our research from 5d metal Ta, 4d metal Nb, to 3d metal V, and succeeded in synthesizing a new photocatalyst InVO_4 . The new photocatalyst InVO_4 was found to have a much narrower bandgap than that of the InNbO_4 and InTaO_4 compounds, indicating that the new developed semiconductor has a prospective potential for efficiently photocatalytic production of H_2 from water under visible light irradiation. The photocatalytic activities of the new photocatalysts under visible light irradiation were investigated and the correlations of the crystal and electronic structures with photocatalytic properties of the photocatalysts are discussed in this paper.

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2. Experimental

The polycrystalline samples of InVO_4 , InNbO_4 and InTaO_4 were synthesized by a solid-state reaction method. The pre-dried In_2O_3 , V_2O_5 , Nb_2O_5 and Ta_2O_5 with purity of 99.99% were used as starting materials. The stoichiometric amounts of precursors were mixed and pressed into small columns. The columns were reacted in an aluminum crucible in air at 850°C for InVO_4 and 1100°C for InNbO_4 and InTaO_4 . The reaction time was 12 h. In order to obtain high photocatalytic activity, it is essential to load a metal or metal oxide on the surface of photocatalyst. The nickel oxide was found to be the most effective for our photocatalysts. The 1.0 wt.% nickel was loaded on surface of the catalysts powders from aqueous $\text{Ni}(\text{NO}_3)_2$ solution. The Ni-loaded photocatalysts were calcined at 350°C for 1 h in air, then prepared by H_2 (200 Torr) reaction at 500°C for 2 h and subsequent O_2 (100 Torr) oxidation at 200°C for 1 h. The double-layered structure of metallic Ni and NiO was formed on the surface of photocatalyst by the reduction–oxidation procedure.

The chemical composition of the samples was determined by scanning electron microscope–X-ray energy dispersion spectrum (SEM–EDS) with accelerating voltage of 25 kV. The crystal structure was decided by powder X-ray diffraction method using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). UV–Vis diffuse reflectance spectrum of samples was measured by using an UV–Vis spectrometer (Shimadzu UV-2500).

Photocatalytic reactions were carried out in a closed gas circulation system. A 0.5 g powder sample was suspended in a 270 ml pure water using a Pyrex glass cell (350 ml). A 300W Xe arc lamp was focused through a shutter window and a 420 nm cut filter was placed onto the window face of the cell. The gases evolved were analyzed with a TCD gas chromatograph, which was connected to a gas circulating line.

3. Results and discussion

Along with the InNbO_4 and InTaO_4 compounds, native InVO_4 gave only very low photocatalytic activity under visible light irradiation, showing a normal behavior of photocatalyst. However, the photocatalytic activity increased significantly when a co-catalyst such as NiO_x , RuO_2 , or Pt was loaded on the surface of the InMO_4 ($M = \text{V, Nb, Ta}$) photocatalysts. Fig. 1 shows the H_2 evolution from pure water with InVO_4 photocatalyst suspension under visible light irradiation ($\lambda > 420 \text{ nm}$) using NiO_x co-catalyst. The formation rate of H_2 evolution was about $5.0 \mu\text{mol g}^{-1} \text{ h}^{-1}$, larger than the other two In-containing photocatalysts $\text{NiO}_x/\text{InNbO}_4$ and $\text{NiO}_x/\text{InTaO}_4$ (3.5 and $4.0 \mu\text{mol g}^{-1} \text{ h}^{-1}$, respectively). The activities in pure water for all the three new photocatalysts are much larger than that of $\text{In}_2\text{O}_3(\text{ZnO})_m$ even though it works in aqueous methanol/Pt

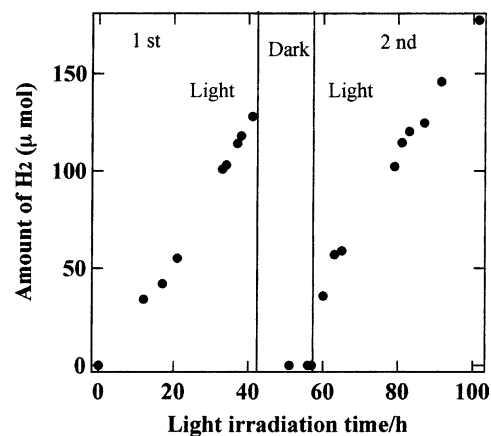


Fig. 1. Photocatalytic H_2 evolutions from pure H_2O using 1.0 wt.% NiO_x - InVO_4 under visible light irradiation. Catalyst: 0.5 g, pure H_2O : 270 ml, $\lambda > 420 \text{ nm}$.

solution [4]. The effect of visible light illumination was also investigated by light on/off shutter studies (see Fig. 1). The H_2 evolution stopped when irradiation was terminated, showing that the photocatalytic reaction is induced by the absorption of visible light irradiation. After evacuating the system, almost the same rate was reproduced in the second run, indicating that the reaction occurs catalytically.

The crystal structures of the InMO_4 ($M = \text{V, Nb, Ta}$) compounds were investigated by the powder X-ray diffraction method. Fig. 2 shows the X-ray diffraction patterns of the InMO_4 compounds. Those of the 5d and 4d transition metal compounds InTaO_4 and InNbO_4 appear very similar, but 3d transition metal compound InVO_4 shows a totally different feature. The further structure investigations revealed that the InTaO_4 and InNbO_4 compounds crystallize in the same wolframite-type structure, monoclinic system with space group of $P2/c$, lattice parameters $a = 5.1552(1) \text{ \AA}$, $b = 5.7751(1) \text{ \AA}$, $c = 4.8264(1) \text{ \AA}$, $\beta = 91.373(1)^\circ$ for

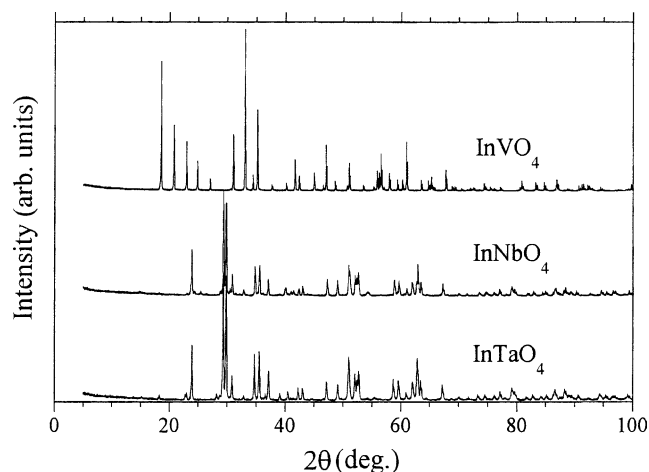


Fig. 2. X-ray powder diffraction patterns of the InMO_4 ($M = \text{V, Nb, Ta}$) photocatalysts.

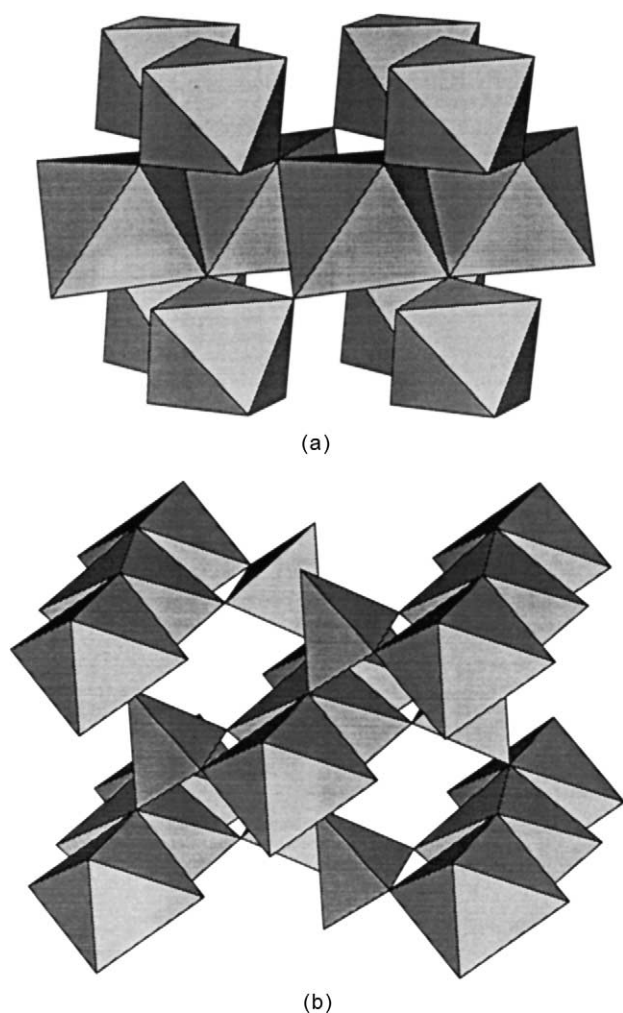


Fig. 3. Schematic structures of (a) InTaO₄, InNbO₄ and (b) InVO₄.

InTaO₄ and $a = 5.1440(8) \text{ \AA}$, $b = 5.7709(6) \text{ \AA}$, $c = 4.8355(6) \text{ \AA}$, $\beta = 91.13(1)^\circ$ for InNbO₄. In contrast, the 3d metal compound InVO₄ belongs to the orthorhombic system, space group *Cmcm*, $a = 5.765(4) \text{ \AA}$, $b = 8.543(5) \text{ \AA}$ and $c = 6.592(4) \text{ \AA}$. Fig. 3 shows the schematic structural diagrams of the InTaO₄, InNbO₄ (a) and InVO₄ (b) compounds. In structure of InTaO₄ and InNbO₄, there are two kinds of octahedron, NbO₆(TaO₆) and InO₆. The InO₆ octahedron connects to each other to form zigzag chains by sharing edges. These InO₆ chains are connected through NbO₆(TaO₆) octahedron to form the three-dimensional network. In InVO₄, the structure is composed of chains of the InO₆ octahedra linked together by the VO₄ tetrahedra [8].

Although the V, Nb and Ta transition metals are all belonging to the 5B group in the periodic table, the 5d metal Ta and 4d metal Nb are often reported to form compounds with similar structures, while the 3d transition metal V behaves in a more complicated manner [9]. It is not surprising that the InMO₄ (M = V, Nb, Ta) compounds form in different structures and hence exhibit different physical and chemical properties. Fig. 4 shows the diffuse reflection spectra of

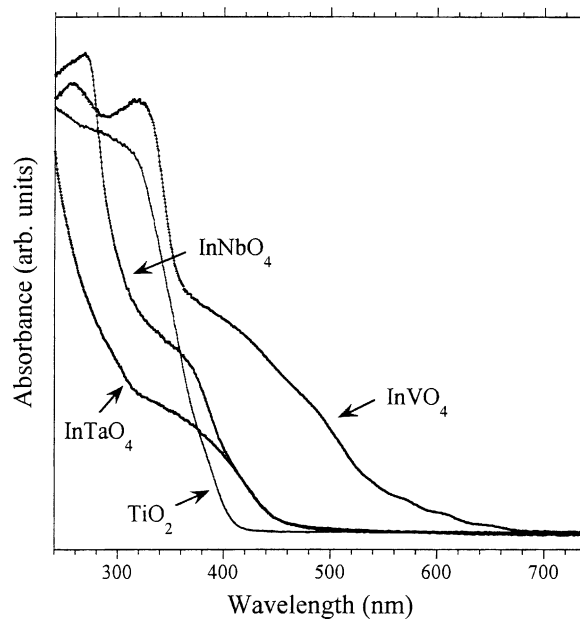


Fig. 4. Diffuse reflection spectra of the InVO₄, InNbO₄ and InTaO₄ photocatalysts. As a comparison, spectrum of TiO₂ is shown together.

the new photocatalysts. In contrast to the well known TiO₂ whose absorption edge is about 400 nm, all the three InMO₄ compounds showed absorption in visible light region. This means that InMO₄ (M = V, Nb, Ta) have ability to respond to visible light, in good agreement with the observed photocatalytic activity as reported for InTaO₄, InNbO₄ [7] and that shown in Fig. 1 for InVO₄. The visible light responding behavior becomes extremely clear in InVO₄, where the bandgap was estimated to be 1.9 eV, much narrower than those in InNbO₄ and InTaO₄ (2.5 and 2.6 eV, respectively).

The process for photocatalysis of semiconductors is considered as the direct absorption of a photon by bandgap of the materials and generates electron–hole pairs in the semiconductor particles. The excitation of an electron from the valence band to the conduction band is initiated by light absorption with energy equal to or greater than the bandgap of the semiconductor. If the conduction band potential level of a semiconductor is more negative than that of hydrogen evolution, and the valence band potential level is more positive than that of oxygen evolution, decomposition of water can occur even without applying electric power [1].

The band structure of oxides is generally defined by d-level and O 2p-level, as confirmed by our theoretical calculations based on the first principles method for TiO₂ and InTaO₄ photocatalysts. In Fig. 5, the left (a) and middle panels (b) show the energy structure and density of states (DOS) of the TiO₂ photocatalyst in rutile structure, and the right panel (c) shows the DOS of the new photocatalyst InTaO₄. The electronic structures were calculated using density functional theory (DFT) within the local density approximation (LDA) approach. The common feature of the two oxide semiconductors is that the conduction band

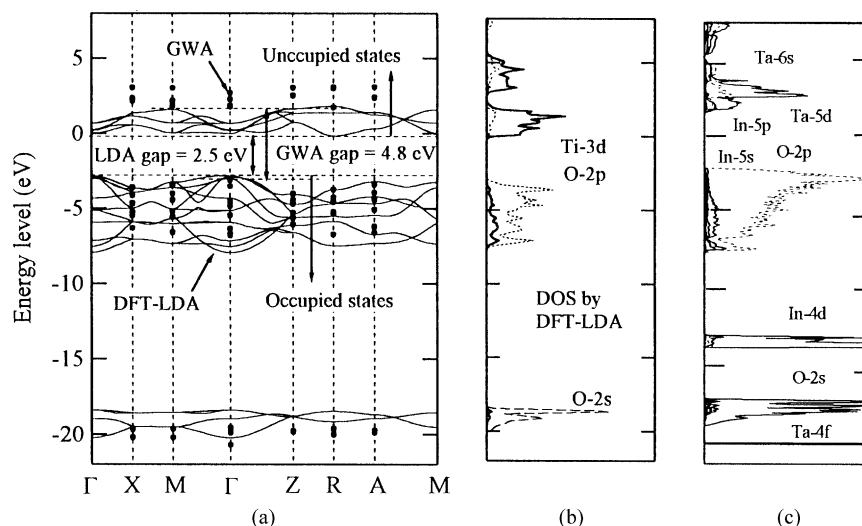


Fig. 5. A comparison of the electronic structures of TiO₂ and InTaO₄: (a) electronic structure of bulk TiO₂ in the rutile structure; (b) DOS of TiO₂ in DFT-LDA; (c) DOS of InTaO₄ in DFT-LDA.

consists of mainly d orbital of the transition metal (3d of titanium in TiO₂ and 5d of tantalum in InTaO₄), and the valence band is spanned dominantly by 2p orbital of oxygen, which is shown with a dotted line.

For oxides with partly filled d-levels, the relationship between the flat band potential and the bandgap can be described as $V_{fb}(SHE) = 2.94 - E_g$, where V_{fb} is the flat band potential and E_g the bandgap. Scaife [10] examined the band structure of the oxide SrNb₂O₆, which contains the NbO₆ octahedra, using the above rule. The valence band energy is at 2.94 (SHE), and the conduction band is at -0.7 (SHE) detected by the empty Nb d-levels. However, for oxides containing two kinds of octahedra such as NiNb₂O₆,

Scaife found that the valence band energy should be assumed from both O 2p-levels of the NiO₆ and NbO₆ octahedra, and showed a value about 1.0 eV negative than 2.94 (SHE) of O 2p-levels. The conduction band was determined at -0.7 eV by d-levels of NbO₆, the lowest empty band. We speculate that the same case takes place in our newly developed InMO₄ (M = V, Nb, Ta) compounds since all these compounds contain two kinds of polyhedra, InO₆ and NbO₆ (TaO₆) or VO₄. From the observed parameters, it appears that InNbO₄ has $E_g = 2.5$ eV, and conduction band is -0.7 eV. Then the valence band energy could be expected to be 1.8 (SHE), about 1.1 eV negative than that of the O 2p-levels. If we assume that the valence bands in the three

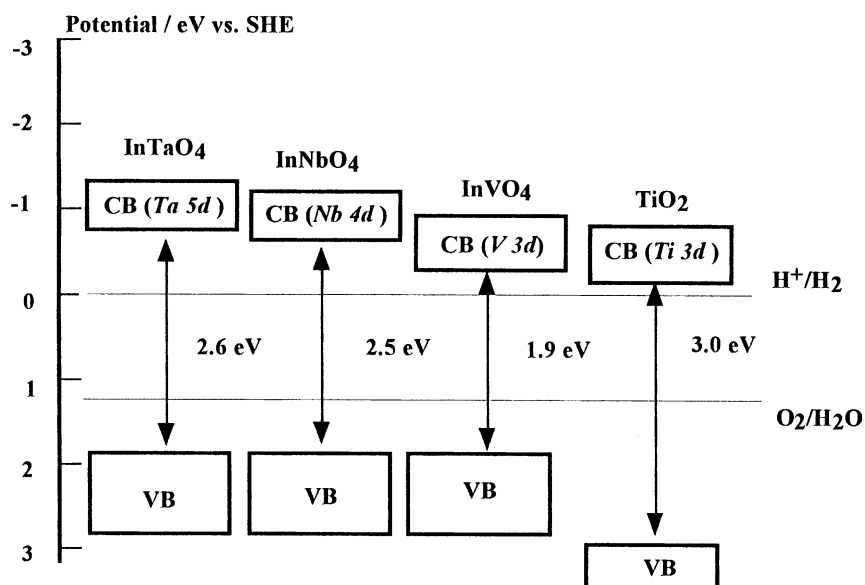


Fig. 6. Suggested band structures of InTaO₄, InNbO₄, InVO₄ and TiO₂.

new photocatalysts are similar, then the band structures of InMO_4 ($M = \text{V}, \text{Nb}, \text{Ta}$) as well as TiO_2 could be shown schematically in Fig. 6. The conduction bands of InNbO_4 and InTaO_4 consist of Nb 4d, and Ta 5d, respectively, while that of InVO_4 is V 3d. The difference of bandgaps among InVO_4 , InNbO_4 and InTaO_4 might be due to the difference in their conduction bands. This is consistent with the observation of their photocatalytic activities. In any case, the potentials of conduction band of InVO_4 , InNbO_4 and InTaO_4 are more negative than that of the hydrogen evolution, leading to H_2 evolution from pure water.

Oxygen evolution was not observed from pure water in this experiment under visible light irradiation, although the potential levels of valence band in the new photocatalysts are more positive than that of oxygen evolution. We consider that the phenomenon might be contributed to behavior of holes on surface of the photocatalysts. Amy et al. [11] also found a similar result in TiO_2 photocatalyst that the oxygen produced can be photoabsorbed on the surface of the photocatalyst under UV irradiation. Although it is not clear whether the O_2 molecule photoadsorbed on surface of the photocatalysts is in a physisorbed and/or chemisorbed molecular state, we speculate that the phenomenon as observed in TiO_2 takes place on the surface of our photocatalysts.

4. Conclusion

In addition to the newly discovered InTaO_4 and InNbO_4 photocatalysts, we have developed another photocatalyst with 3d transition metal V. Although the new photocatalyst

InVO_4 has similar atomic ratio to that of InTaO_4 and InNbO_4 , the crystal structures of three compounds are quite different. In InTaO_4 and InNbO_4 , which crystallize in a wolframite-type structure, there are two kinds of octahedra, InO_6 and NbO_6 (TaO_6), while InVO_4 consists of the InO_6 octahedra and VO_4 tetrahedra. The different conduction bands defined by V 3d, Nb 4d and Ta 5d seem to have led to the difference in their bandgaps and hence photocatalytic activities. All the three new photocatalysts showed obvious visible light responsivity. H_2 evolution was observed from pure water with the native new catalysts. The activity increased remarkably by loading NiO as a co-catalyst, suggesting nickel metal oxide actually modified the photocatalytic properties of the photocatalyst by changing the distribution of electrons.

References

- [1] K. Honda, A. Fujishima, Nature 238 (1972) 37.
- [2] Y.V. Pleskov, Y.Y. Gurevich, in: P.N. Bartlett (Ed.), Semiconductor Photochemistry, Plenum Press, New York, 1986.
- [3] J. Yoshimure, Y. Ebina, J. Kondo, K. Domen, J. Phys. Chem. 97 (1993) 1970.
- [4] A. Kudo, I. Mikami, Chem. Lett. (1998) 1027.
- [5] A. Kudo, K. Ueda, H. Kato, I. Mikami, Catal. Lett. 53 (1998) 229.
- [6] A. Kudo, K. Omiori, H. Kato, J. Am. Chem. Soc. 121 (1999) 11459.
- [7] Z. Zou, J. Ye, H. Arakawa, Chem. Phys. Lett. 332 (2000) 271.
- [8] P.M. Touboul, P. Toledano, Acta Cryst. B 36 (1980) 240.
- [9] J. Ye, H. Horiuchi, T. Shishido, N. Toyota, K. Ukei, T. Sasaki, T. Fukuda, J. Cryst. Growth 99 (1990) 969.
- [10] D.E. Scaife, Solar Energy 25 (1980) 41.
- [11] L.L. Amy, L. Guangqan, T. John, Yates Jr., Chem. Rev. 95 (1995) 435.