

Photocatalytic behavior of a new series of $\text{In}_{0.8}\text{M}_{0.2}\text{TaO}_4$ ($\text{M} = \text{Ni}, \text{Cu}, \text{Fe}$) photocatalysts in aqueous solutions

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A new series of photocatalysts, $\text{In}_{0.8}\text{M}_{0.2}\text{TaO}_4$ ($\text{M} = \text{Ni}, \text{Cu}, \text{Fe}$), were synthesized by a solid-state reaction and characterized by powder X-ray diffraction and Rietveld structure refinement. No apparent structural variation has been recognized with the change of doping atoms. However, the rate of H_2 evolution from $\text{Pt}/\text{CH}_3\text{OH}/\text{H}_2\text{O}$ solution under UV irradiation significantly changed with the change of doping atoms. $\text{In}_{0.8}\text{Ni}_{0.2}\text{TaO}_4$ showed much higher activity than the non-doped InTaO_4 photocatalyst. Furthermore, we found that under visible light irradiation ($\lambda > 420 \text{ nm}$) $\text{In}_{0.8}\text{Ni}_{0.2}\text{TaO}_4$ exhibited also higher activity than the non-doped InTaO_4 photocatalyst.

KEY WORDS: $\text{In}_{0.8}\text{M}_{0.2}\text{TaO}_4$ ($\text{M} = \text{Ni}, \text{Cu}, \text{Fe}$); decomposition of water; visible light irradiation

1. Introduction

The photocatalytic splitting of water using an oxide semiconductor under visible light irradiation attracts increasing interest because the attempt is aimed not only at producing hydrogen of clean-energy from water utilizing solar energy, but also at finding methods of making use of the photosynthetic process as green plants for direct production [1–3]. The discovery of photocatalytic splitting of water on TiO_2 electrodes exhibited that decomposition of water should be possible under visible light [4].

Very recently, we found that InTaO_4 could evolve H_2 from pure water under visible light irradiation, but activity is very low [5]. InTaO_4 belongs to the family of the ABO_4 compounds with the $\text{A}^{3+}\text{B}^{5+}\text{O}_4$ wolframite structure. There are two kinds of octahedron in a unit cell, TaO_6 and InO_6 . The TaO_6 and InO_6 octahedra form the layers by sharing the corner as shown in figure 1. Oxygen planes are formed in parallel with (001) plane. The structure is built up forming infinite corner-sharing TaO_6 octahedron formed $[\text{TaO}_3]_\infty$ chains along [001]. The zigzag chains are connected through InO_6 octahedron to form a network. We considered that M ($\text{M} = \text{Ni}, \text{Cu}, \text{Fe}$) doping of the A^{3+} site in $\text{A}^{3+}\text{B}^{5+}\text{O}_4$ might cause a slight modification of crystal structure, resulting in a change in photocatalytic property. It is known that a slight modification of structure to semiconductor has a dramatic effect on the physical properties [6]. Here we report firstly the synthesis, photocatalytic and structural characterizations of these new photocatalysts, $\text{In}_{0.8}\text{M}_{0.2}\text{TaO}_4$ ($\text{M} = \text{Ni}, \text{Cu}, \text{Fe}$).

2. Experimental

Polycrystalline samples of $\text{In}_{0.8}\text{M}_{0.2}\text{TaO}_4$ ($\text{M} = \text{Ni}, \text{Cu}, \text{Fe}$) were synthesized by a solid-state reaction method. The pre-dried In_2O_3 , Ta_2O_5 , Fe_2O_3 , NiO and CuO with purity of 99.99% were used as starting materials. Stoichiometric amounts of the precursors were mixed and pressed into small columns. The columns were reacted in an aluminum crucible in air for two days at 1100°C . The same procedure was performed three times for the samples.

The chemical composition of the samples before and after photocatalytic reaction was determined by scanning electron microscope–X-ray energy dispersion spectrum (SEM-EDS) with accelerating voltage of 25 kV. The crystal structure of

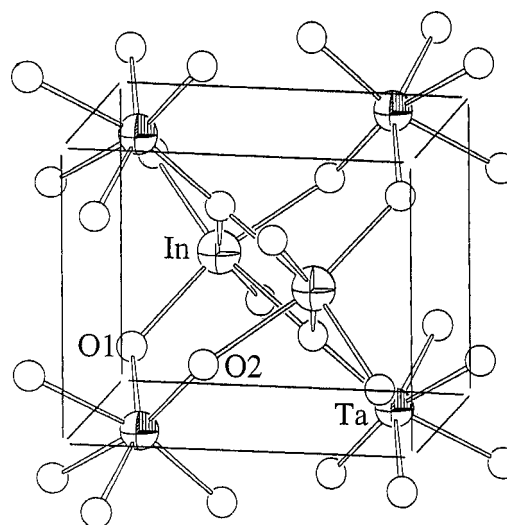


Figure 1. Schematic structure of InTaO_4 with the wolframite type.

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the samples was determined by powder X-ray diffraction method using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). UV-vis diffuse reflectance spectrum of $\text{In}_{0.8}\text{M}_{0.2}\text{TaO}_4$ ($\text{M} = \text{Ni}, \text{Cu}, \text{Fe}$) was measured by using an UV-vis spectrometer (MPS-2000). The surface area was determined by BET measurement (Micromeritics, Shimadzu, Flow-Prep 060).

Photocatalytic reaction was carried out in a closed gas circulation system. The gases evolved were determined with a TCD gas chromatograph, which was connected to a gas circulating line [5]. In order to obtain high activity, it is essential to load a metal or metal oxide on the surface of the photocatalyst, because the addition of noble metals or metal oxides on a semiconductor surface can change the photocatalytic properties by changing the semiconductor surface properties [7]. The Pt was found to be the most effective for TiO_2 photocatalyst [7]. The photocatalytic reaction under UV irradiation was examined using an inner-irradiation type quartz cell with 400 W high-pressure Hg lamp and in an aqueous $\text{Pt}/\text{CH}_3\text{OH}/\text{H}_2\text{O}$ solution (0.5 g powder catalyst, 50 ml CH_3OH , 300 ml H_2O and 0.1 wt% Pt (Pt-loading instead of a H_2PtCl_4)). The photocatalytic reaction under visible light irradiation was examined using a Pyrex glass cell, 300 W Xe arc lamp and in an aqueous $\text{Pt}/\text{CH}_3\text{OH}/\text{H}_2\text{O}$ solution (0.5 g powder catalyst, 50 ml CH_3OH , 200 ml H_2O and 0.1 wt% Pt (Pt-loading instead of a H_2PtCl_4)). The 420 nm cut filter was placed onto the window face of the Pyrex glass cell.

3. Results and discussion

The chemical composition of the photocatalysts before and after photocatalytic reaction was determined using characteristic X-rays of $\text{M L}\alpha$ ($\text{M} = \text{In}, \text{Ni}, \text{Cu}, \text{Fe}$) and $\text{Ta L}\alpha$. The composition content was determined using the ZAF (Z – element number (“Z” number) correction, A – absorption correction, F – fluorescence correction) quantification method [6]. The SEM-EDS analysis showed that the photocatalysts have a homogeneous atomic distribution with no other additional elements. The chemical composition of these samples after reaction is also the same as that of the samples before reaction.

The crystal structure of the photocatalysts before and after photocatalytic reactions was investigated using X-ray powder diffraction. The result is shown in figure 2. The powder X-ray diffraction analysis showed that all samples are the single phases. We can see that the Bragg peak distributions of the $\text{In}_{0.8}\text{M}_{0.2}\text{TaO}_4$ ($\text{M} = \text{Ni}, \text{Cu}, \text{Fe}$) photocatalysts remain unchanged. Full-profile structure refinement of the collected powder diffraction data was performed using the Rietveld program REITAN [8]. Positional parameters and isotropic thermal parameters of samples were refined. The result of refinement shows that all samples crystallize in the same wolframite structural type, monoclinic with space group $\text{P2}_1/\text{c}$.

The InTaO_4 photocatalyst has two kinds of octahedron in a unit cell, TaO_6 and InO_6 [5]. The volume of the InO_6

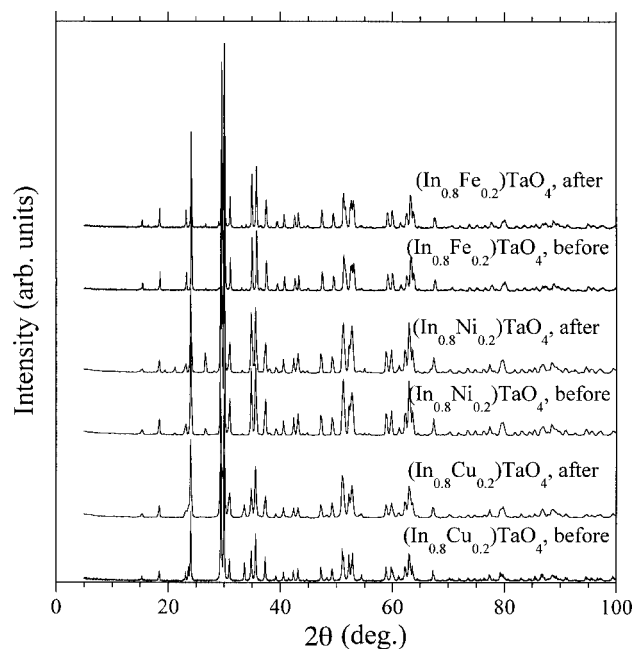


Figure 2. X-ray powder diffraction patterns of photocatalysts before and after photocatalytic reaction.

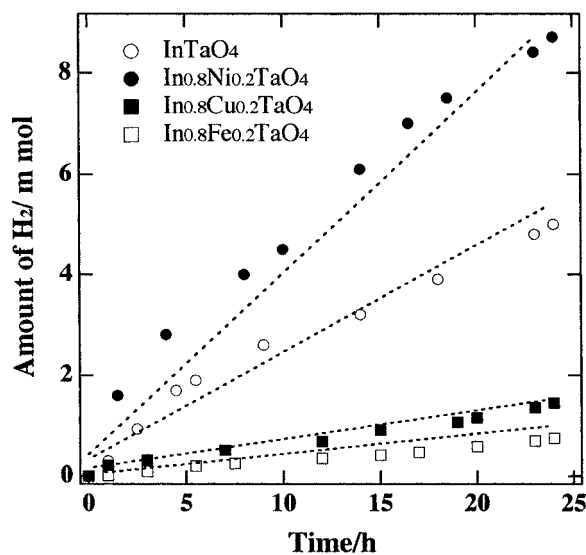


Figure 3. Photocatalytic H_2 evolution on the $\text{In}_{0.8}\text{M}_{0.2}\text{TaO}_4$ ($\text{M} = \text{Ni}, \text{Cu}, \text{Fe}$) compound from $\text{Pt}/\text{CH}_3\text{OH}/\text{H}_2\text{O}$ solution under UV irradiation.

octahedron in InTaO_4 is 13.601 \AA^3 . However, the volume of TaO_6 is 10.648 \AA^3 . This means that the volume of the InO_6 octahedron was changed when In was being doped by Ni, Cu and Fe because of the change of the M atomic radius, but crystal structure could not change. The change of the InO_6 volume suggests to lead to a change of the lattice parameters in the doped InTaO_4 system. The details of the investigations on structure will be published elsewhere [9]. We confirmed that the photocatalysts have changed neither the crystal structure nor the chemical composition after photocatalytic reaction.

Figure 3 shows the H_2 evolution from $\text{Pt}/\text{CH}_3\text{OH}/\text{H}_2\text{O}$ solution under UV irradiation. The formation rates of H_2

Table 1
Rates of gas evolution and physical properties of the photocatalysts.

Photocatalyst	Surface area ($\text{m}^2 \text{g}^{-1}$)	UV irradiation, rate of evolution ($\mu\text{mol h}^{-1}$)		Visible light irradiation, $\lambda > 420 \text{ nm}$, rate of evolution ($\mu\text{mol h}^{-1}$)	
		Pt/CH ₃ OH/H ₂ O		Pt/CH ₃ OH/H ₂ O	AgNO ₃ /H ₂ O
		H ₂	CO	H ₂	O ₂
InTaO ₄	1.35	270	15	0.6	0.8
In _{0.8} Ni _{0.2} TaO ₄	0.97	470	30	1.5	1.1
In _{0.8} Cu _{0.2} TaO ₄	0.81	100	5	Non	Non
In _{0.8} Fe _{0.2} TaO ₄	0.82	80	4	Non	Non

were estimated to be 0.47, 0.1 and 0.08 (mmol h^{-1}) in the first 10 h for Ni, Cu and Fe. The amount of evolved H₂ (mol) exceeded the amount of catalyst (1.38 mmol) at 24 h, indicating that the reaction seems to occur catalytically. The reaction stopped when the light was turned off in this experiment, showing the obvious light response. The result shows that the photocatalytic reaction is induced by the absorption of UV irradiation. The formation rate of H₂ on In_{0.8}Ni_{0.2}TaO₄ is about 180% of that of non-doped InTaO₄, while formation rates on the Cu and Fe doped InTaO₄ photocatalysts are much lower. This means that the activity increases on Ni-doped InTaO₄. However, the activity decreases on Cu- and Fe-doped InTaO₄. The CO evolutions were observed in this reaction from Pt/CH₃OH/H₂O solution as the oxidation product. The result is shown in table 1. The CO evolution increases with illumination time, as does H₂ evolution. However, the rate of CO evolutions is much lower than that of H₂ evolution. The CO originates probably from decomposition of the formaldehyde, which decomposes slower than methanol dehydrogenates. On the other hand, the ratios of non-stationary and non-stoichiometry evolutions between H₂ and CO might result from generation of CO₂ and other evolutions. It is well known that when CH₃OH is added to a Pt/TiO₂ aqueous suspension, sustained H₂ production is observed under UV irradiation and the alcohol molecules are oxidized to final productions of CO₂, CO, CH₄, etc. [14]. The presence of oxygen vacancy defects strongly enhances such interaction due to electron back-donation from surface Ti³⁺ into the π^* orbital of molecular CO [14]. The formation rate of CO changed with the variation of doping atoms, showing the same tendency as observed in H₂ evolution.

It is often observed that doping transition metals into photocatalysts such as TiO₂ decreases significantly the photocatalytic activities [10]. The Cu- and Fe-doped InTaO₄ showed similar result as doped TiO₂. However, such a suppression effect by doping was not predominant in the Ni-doped InTaO₄ photocatalyst. Kudo *et al.* [10] found a similar phenomenon [11]. The photocatalytic activity on Ni-doped ZnS was much higher than on non-doped ZnS, while that on Cu-doped ZnS was lower [11]. Although the origin is unknown yet, the band structure of NiO has been investigated [12]. The band structure of oxides is generally defined by d-level and O 2p-level of the oxides. However, the band structure of NiO is assigned to Ni 3d⁸ and Ni 3d⁹ [12]. This means that the Ni 3d level in the Ni-doped InTaO₄ photocatalyst may

form a new energy level in the band structure of InTaO₄. The light absorption properties of the InTaO₄ and In_{0.8}Ni_{0.2}TaO₄ photocatalysts were investigated. The onset of diffuse reflection spectra showed an obvious shift to high wavelength with In being doped by Ni in InTaO₄. The band gaps of InTaO₄ and In_{0.8}Ni_{0.2}TaO₄ were estimated to be 2.6 and 2.4 eV from the diffuse reflection spectra. This means that the Ni-doped InTaO₄ photocatalyst can utilize a wider spectral region of light irradiation than non-doped InTaO₄.

The difference in the surface area of the photocatalysts can generally lead to the difference in photocatalytic activity since an efficient photocatalytic reaction process occurs on the photocatalyst surface. However, the surface area of the photocatalysts is similar, as shown in table 1. It is hard to consider that the differences in the surface area of the photocatalysts led to the differences in the photocatalytic activity. In order to clear the origin of different photocatalytic activity between the Ni-doped and Cu- and Fe-doped InTaO₄ photocatalysts, further band structure analyses seem to be necessary.

It is interesting to note that under visible light irradiation ($\lambda > 420 \text{ nm}$) H₂ and O₂ were evolved using the In_{0.8}Ni_{0.2}TaO₄ photocatalyst from Pt/CH₃OH/H₂O and AgNO₃/H₂O solutions, respectively. However, the Cu- and Fe-doped InTaO₄ photocatalysts cannot work under these conditions. Figure 4(a) shows the H₂ evolution from Pt/CH₃OH/H₂O solution under visible light irradiation using the In_{0.8}Ni_{0.2}TaO₄ and InTaO₄ photocatalysts. The H₂ evolution increases with illumination time. The formation rate of H₂ on Ni-doped InTaO₄ is much higher than that of the non-doped InTaO₄ photocatalyst, as does H₂ evolution under UV irradiation. The effect of visible light irradiation was investigated by dark experiment. The H₂ evolution stopped when light irradiation was terminated, showing the obvious visible light response.

O₂ evolution reaction was performed in an aqueous silver nitrate solution under visible light irradiation ($\lambda > 420 \text{ nm}$) and the following stoichiometric reaction takes place: $4\text{Ag}^+ + 2\text{H}_2\text{O} \rightarrow 4\text{Ag}^0 + \text{O}_2 + 4\text{H}^+$ [13]. Figure 4(b) shows the O₂ evolution under visible light irradiation. This result shows that both In_{0.8}Ni_{0.2}TaO₄ and InTaO₄ have potential for O₂ evolution from aqueous solution. However, the rate of O₂ evolution increases with In being doped by Ni in the InTaO₄ photocatalyst. The rate of O₂ evolution on In_{0.8}Ni_{0.2}TaO₄ is 1.1 $\mu\text{mol h}^{-1}$. The activity increased to about 140% of that of non-doped InTaO₄ (see table 1).

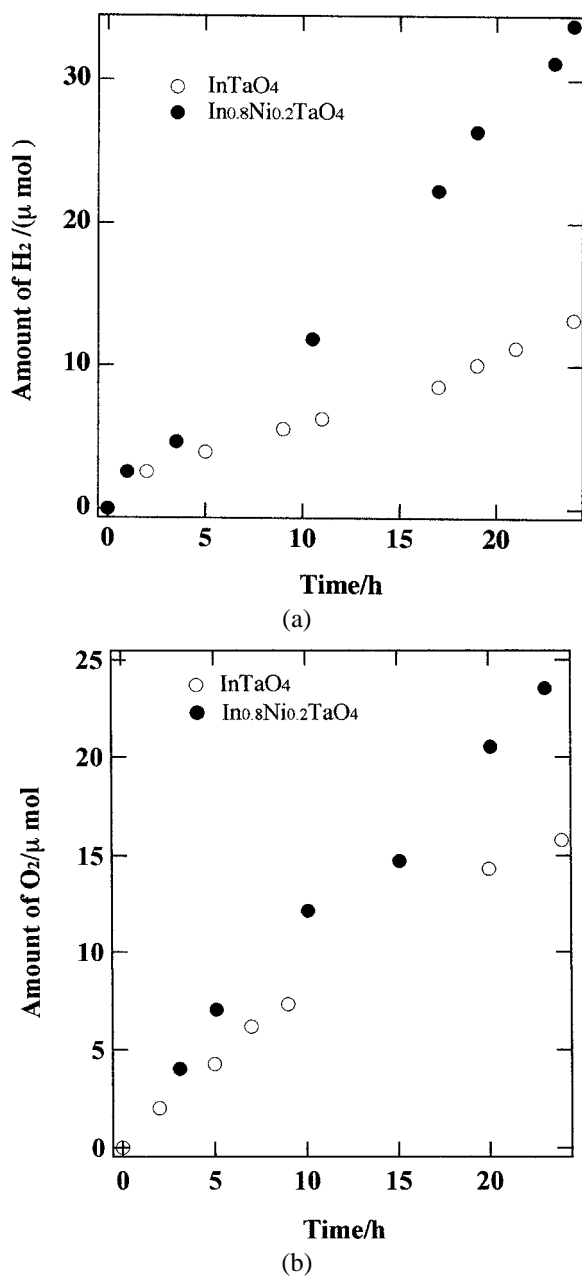


Figure 4. (a) Photocatalytic H_2 evolution from $\text{Pt}/\text{CH}_3\text{OH}/\text{H}_2\text{O}$ solution under visible light irradiation, $\lambda > 420$ nm. (b) Photocatalytic O_2 evolution from an aqueous silver nitrate solution under visible light irradiation, $\lambda > 420$ nm.

The wavelengths (λ) dependence of the photocatalytic activity under the light irradiation from full arc up to $\lambda = 550$ nm was measured using different cut-off filters. The photocatalytic reaction was examined using a Pyrex glass cell, a 300 W Xe arc lamp and in an aqueous $\text{Pt}/\text{CH}_3\text{OH}/\text{H}_2\text{O}$ solution. These results are plotted in figure 5. The photocatalytic activity dependence of λ of light irradiation displays a normal photocatalyst behavior, with increasing λ of light irradiation, the photocatalytic activity decreases rapidly, since the number of incident photons was decreased when a cut-off filter was used. An obvious photocatalytic activity was observed when visible light ($\lambda >$

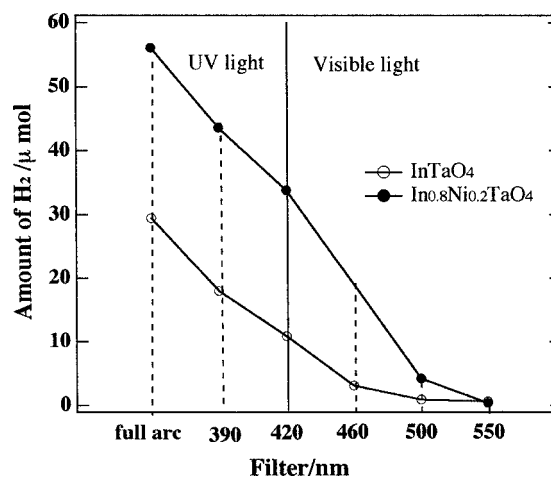


Figure 5. The photocatalytic activity dependence of the wavelengths (λ) from full arc irradiation to $\lambda = 550$ nm; the amount of evolved H_2 at 24 h; a Pyrex glass cell, 300 W Xe arc lamp and in an aqueous $\text{Pt}/\text{CH}_3\text{OH}/\text{H}_2\text{O}$ solution (0.5 g powder catalyst, 50 ml CH_3OH , 200 ml H_2O and 0.1 wt% Pt (Pt-loading instead of a H_2PtCl_4)).

420 nm) was irradiated, showing that both $\text{In}_{0.8}\text{Ni}_{0.2}\text{TaO}_4$ and InTaO_4 can respond visible light irradiation. The photocatalytic activity was also obtained when a cut-off filter of $\lambda > 460$ nm was employed. However, the activity disappeared when λ of light irradiation was larger than 500 nm. This means that light response occurred only at wavelengths shorter than 500 nm.

The process for photocatalysis over semiconductors is the direct absorption of a photon by the band gap of the materials thereby generating electron-hole pairs in the semiconductor particles. The excitation of an electron from the valence band to the conduction band initiated by light absorption with energy equal to or greater than the band gap of the semiconductor [4]. The diffuse reflectance spectrum of $\text{In}_{0.8}\text{Ni}_{0.2}\text{TaO}_4$ shows a visible light absorption band with the onset around 520 nm, while that of InTaO_4 is around 480 nm. This means that under visible light irradiation ($\lambda > 420$ nm) the Ni-doped InTaO_4 photocatalyst can response in a range of wavelength above 40 nm than that of non-doped InTaO_4 . The difference between the visible light absorption band of $\text{In}_{0.8}\text{Ni}_{0.2}\text{TaO}_4$ and InTaO_4 might lead to the difference in photocatalytic activity. This is consistent with the observation of photocatalytic activity, as shown in figure 4. BET measurement showed that the surface areas of InTaO_4 and $\text{In}_{0.8}\text{Ni}_{0.2}\text{TaO}_4$ are 1.35 and 0.97 $\text{m}^2 \text{g}^{-1}$, respectively, as shown in table 1. This is about 1/50 of the surface area for the TiO_2 photocatalyst (53.8 $\text{m}^2 \text{g}^{-1}$). Since an efficient photocatalytic reaction process occurs on the photocatalyst surface, the increase of the surface area for the photocatalysts might lead to the increase of their photocatalytic activity under visible light irradiation. The study for effects of surface area on photocatalytic activity under visible light irradiation is in progress, which is believed to lead to further understanding of the new photocatalysts.

In summary, under visible light irradiation ($\lambda > 420$ nm) H_2 and O_2 were evolved using both Ni-doped and non-doped

InTaO_4 photocatalyst from $\text{Pt}/\text{CH}_3\text{OH}/\text{H}_2\text{O}$ and $\text{AgNO}_3/\text{H}_2\text{O}$ solutions, respectively. The $\text{In}_{0.8}\text{Ni}_{0.2}\text{TaO}_4$ photocatalyst showed much higher activity than the non-doped InTaO_4 photocatalyst. Ni-doped InTaO_4 has been developed as a new visible light photocatalyst for H_2 and O_2 evolutions from aqueous solutions. The study of doping effects on structural and photocatalytic properties of InTaO_4 solid oxide photocatalyst will provide useful information on the mechanism of the photocatalysts and also on making stable photocatalysts with high activity under visible light irradiation.

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References

- [1] K. Tomoji and S. Tadayoshi, *Nature* 286 (1980) 474.
- [2] B.S. Geoffrey and E.M. Thomas, *J. Phys. Chem. B* 101 (1997) 2508.
- [3] K. Yeong, S. Samer, J.H. Munir and E.M. Thomas, *J. Am. Chem. Soc.* 113 (1991) 9561.
- [4] K. Honda and A. Fujishima, *Nature* 238 (1972) 37.
- [5] Z. Zou, J. Ye and H. Arakawa, *Chem. Phys. Lett.* 332 (2000) 271.
- [6] Z. Zou, J. Ye, K. Oka and Y. Nishihara, *Phys. Rev. Lett.* 80 (1998) 1074.
- [7] H.G. Kim, D.W. Hwang, J. Kim, Y.G. Kim and J. Lee, *Chem. Commun.* (1999) 1077.
- [8] F. Izumi, *J. Crystallogr. Assoc. Jpn.* 27 (1985) 23.
- [9] J. Ye, Z. Zou and H. Arakawa, to be published.
- [10] A. Kudo and M. Sekizawa, *Chem. Commun.* (2000) 1371.
- [11] A. Kudo and M. Sekizawa, *Catal. Lett.* 58 (1999) 241.
- [12] M.P. Dare-Edwards, J.B. Goodenough, A. Hamnett and N.D. Nicholson, *J. Chem. Soc. Faraday Trans. II* 77 (1981) 643.
- [13] H. Tada, A. Hattori, Y. Tokihisa, K. Imai, N. Tohee and S. Ito, *J. Phys. Chem. B* 104 (2000) 4585.
- [14] Z. Zou, J. Ye, R. Abe and H. Arakawa, *Catal. Lett.* 68 (2000) 235.