Substitution Effects of the Trivalent Cations M^{3+} on the Photophysical and Photocatalytic Properties of $\text{In}_{12}\text{NiM}_2\text{Ti}_{10}\text{O}_{42}$ ($M = \text{Al}, \text{Cr}, \text{Ga}$)

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A new series of visible-light-driven photocatalysts $\text{In}_{12}\text{NiM}_2\text{Ti}_{10}\text{O}_{42}$ ($M = \text{Al}, \text{Cr}, \text{Ga}$) with a pyrochlore-related layered structure were synthesized by the conventional solid-state reaction method. The substitution effects of trivalent cations M^{3+} on the electronic structure, photophysical and photocatalytic properties were investigated. It was found that although the three materials were all crystallized in a monoclinic symmetry with the same space group $P2_1/a$, their photocatalytic activities of H_2 evolution were quite different. In comparison with $\text{In}_{12}\text{NiAl}_2\text{Ti}_{10}\text{O}_{42}$ and $\text{In}_{12}\text{NiGa}_2\text{Ti}_{10}\text{O}_{42}$, $\text{In}_{12}\text{NiCr}_2\text{Ti}_{10}\text{O}_{42}$ showed the narrowest band gap and highest activity, which could be ascribed to the formation of broadly dispersed continuous conduction and valence bands due to the involvement of partially filled Cr 3d orbitals in addition to Ni 3d orbitals. The present study suggests a promising method for developing visible-light-driven photocatalysts with tailored properties via transition-metal(s)-mediated band structure engineering.

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Keywords: $\text{In}_{12}\text{NiM}_2\text{Ti}_{10}\text{O}_{42}$ ($M = \text{Al}, \text{Cr}, \text{Ga}$), substitution, electronic structure, electronic state, ionic radius, visible light, photocatalytic H_2 evolution

1. Introduction

Development of visible-light-driven semiconductor photocatalysts for water splitting has attracted increasing attention in recent years in view of efficient solar energy conversion.^{1–7)} Some titanium oxides such as the well-known TiO_2 ^{1,8–10)} and SrTiO_3 ,¹¹⁾ and various indium oxides such as $\text{In}_2\text{O}_3(\text{ZnO})_m$,¹²⁾ MIn_2O_4 ($M = \text{Ca}, \text{Sr}, \text{Ba}$),^{13,14)} LnInO_3 ($\text{Ln} = \text{La}, \text{Nd}$) and $\text{Sr}_{1-x}\text{M}_x\text{In}_2\text{O}_4$ ($M = \text{Ca}, \text{Ba}$)¹⁵⁾ have been reported as photocatalysts for water splitting. However, most Ti^{4+} - and/or In^{3+} -containing compounds, except for those containing lower or mixed valence of Ti cation,¹⁶⁾ only respond to UV light or little amount of visible light. Other transition metal oxides such as Cr_2O_3 , Fe_2O_3 , CuO and PbO etc. are able to absorb visible light. However, the potential levels of conduction band bottoms are less negative than that for reduction of H_2O to produce H_2 .⁶⁾ One of the methods for developing visible-light-driven photocatalyst is to introduce transition metal(s) into an oxide semiconductor of large band gap to create an electron donor level above O 2p. Suppose that the conduction band bottom of the host semiconductor is suitable for reduction of H_2O , electrons excited from the donor level to the conduction band of host semiconductor under visible light irradiation can thus be used for reduction of H_2O into H_2 . For examples, photocatalytic H_2 evolution under visible light irradiation have ever been reported over the transition metal(s)-introduced oxides such as Ni-doped InTaO_4 ,²⁾ Cr-doped TiO_2 and SrTiO_3 ,^{17–21)} Sb/Nb/Ta and Cr-codoped SrTiO_3 ,²²⁾ and M-doped $\text{La}_2\text{Ti}_2\text{O}_7$ ($M = \text{Cr}, \text{Fe}$).²³⁾ Since the 3d orbitals of transition metals show versatile features in constructing the band structure of a semiconductor material depending on the crystal structure, the type of M–O polyhedra (tetrahedron, octahedron etc.) and the transition metal(s) used, visible-light-driven photocatalysts with suitable band structures and tailored photophysical

and photocatalytic properties might be expected by incorporation of appropriate transition metals.

Previous study on the crystal structure, photophysical and photocatalytic properties of $\text{Bi}_2\text{MnNbO}_7$ ($M = \text{Al}, \text{Ga}, \text{In}$) showed that the substitution of M^{3+} cations affected the structure, the carrier concentration and the conduction band edge of the photocatalysts.²⁴⁾ Recently, we reported a new visible-light-driven photocatalyst $\text{In}_{12}\text{NiCr}_2\text{Ti}_{10}\text{O}_{42}$ for H_2 evolution.²⁵⁾ In present paper, the substitution effects of the trivalent cations M^{3+} with different electronic states (Al^{3+} : $2p^6$; Cr^{3+} : $3d^3$; Ga^{3+} : $3d^{10}$) on the electronic structure, photophysical and photocatalytic properties of the isostructural $\text{In}_{12}\text{NiM}_2\text{Ti}_{10}\text{O}_{42}$ ($M = \text{Al}, \text{Cr}, \text{Ga}$) were systematically studied. Our purpose is to provide useful guidelines for designing visible-light-driven photocatalysts with tailored properties by transition-metal(s)-mediated band structure engineering.

2. Experimental

Polycrystalline $\text{In}_{12}\text{NiM}_2\text{Ti}_{10}\text{O}_{42}$ ($M = \text{Al}, \text{Cr}, \text{Ga}$) powder samples were prepared by the conventional solid-state reaction method. Reagent grade oxides In_2O_3 , NiO , TiO_2 and M_2O_3 ($M = \text{Al}, \text{Cr}, \text{Ga}$) (Wako) in the stoichiometric ratio of $\text{In}_{12}\text{NiM}_2\text{Ti}_{10}\text{O}_{42}$ were mixed carefully with addition of ethanol in an agate mortar. The mixtures were heated in alumina crucibles at 1423 K ($M = \text{Ga}$) and 1473 K ($M = \text{Al}, \text{Cr}$), respectively, for 172.8 ks and rapidly cooled to room temperature in air.

Crystal structure was determined by X-ray diffraction (XRD, JEOL JDX-3500) with the Cu $K\alpha$ radiation ($\lambda = 0.154178$ nm). Raman spectroscopy was performed on a laser Raman spectrophotometer (NRS-1000, Jasco) at room temperature. The power of incident laser beam was 100 mW with a monochromatic wavelength of 532 nm. The exposure time was 1 s. Morphological observation and compositional analysis were carried out on a field emission

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scanning electron microscope (FE-SEM, JEOL-JSM 6500F) equipped with an X-ray energy dispersive spectroscopy (EDS). UV–vis diffuse reflectance spectrum was measured with a UV–vis spectrometer (UV-2500, Shimadzu) at room temperature and was converted to absorbance spectrum by the Kubelka-Munk method.²⁶⁾ Surface areas of the powder samples were measured on a Gemini-2360 surface area analyzer (Micromeritics®, Shimadzu) by nitrogen absorption at 77 K using the Brunauer–Emmett–Teller (BET) method.

Photocatalytic reaction for H₂ evolution was carried out in an outer irradiation Pyrex glass cell connected to a closed gas circulation system. The light source was a 300 W xenon arc lamp (ILC Technology, CERMAX LX-300), which was operated at 200 W and focused on the side window of the reaction cell through a long-pass cut-off filter ($\lambda \geq 420$ nm, HOYA; L42). By using a magnetic stirrer, the Pt (0.2 mass%)/In₁₂NiM₂Ti₁₀O₄₂ (M = Al, Cr, Ga) powder catalyst was dispersed in an aqueous methanol solution (50×10^{-3} dm³ of CH₃OH + 220×10^{-3} dm³ of H₂O) in the reaction cell. The cocatalyst Pt (0.2 mass%) was loaded by an *in situ* photodeposition method: under light irradiation, an equivalent molar amount of H₂PtCl₆ in solution was reduced to metallic Pt state and was deposited onto the catalyst surface, forming the Pt-loaded catalyst. Before reaction, the closed gas circulation system and the cell containing reaction solution were well evacuated and then introduced into ~ 2.5 kPa of argon gas as carrier. Upon light irradiation, the gases evolved were *in situ* analyzed with an online TCD gas chromatograph (Shimadzu GC-8AIT).

3. Results and Discussion

The XRD patterns of In₁₂NiM₂Ti₁₀O₄₂ (M = Al, Cr, Ga) powder samples taken at room temperature are shown in Fig. 1. The materials were all crystallized in a monoclinic system with the same space group P2₁/a, and the lattice constants calculated by the least square method were summarized in Table 1. These results are consistent with those reported by Brown *et al.*²⁷⁾ In fact, the formula In₁₂NiM₂Ti₁₀O₄₂ can be rewritten as (InTi_x)(Ti_{1-x-y}Ni_{2x-M_y})O_{4(1-x-y/2)} ($x = 1/24$, $y = 1/6$), in which two metal

Table 1 Crystal structures and lattice parameters of In₁₂NiM₂Ti₁₀O₄₂ (M = Al, Cr, Ga).

Photocatalysts	Crystal symmetry	Space group	Lattice parameters (nm)
In ₁₂ NiAl ₂ Ti ₁₀ O ₄₂	monoclinic	P2 ₁ /a	a = 0.5886(4) b = 1.0092(1) c = 0.6353(4) $\beta = 108.02(3)$
In ₁₂ NiCr ₂ Ti ₁₀ O ₄₂	monoclinic	P2 ₁ /a	a = 0.5932(2) b = 1.0098(1) c = 0.6358(2) $\beta = 108.12(2)$
In ₁₂ NiGa ₂ Ti ₁₀ O ₄₂	monoclinic	P2 ₁ /a	a = 0.5916(9) b = 1.0134(3) c = 0.6362(8) $\beta = 108.05(7)$

positions are involved: M1, occupied primarily by In and very few Ti; and M2, by Ti, Ni and M = Al, Cr, Ga. In the pyrochlore-related layered structure of In₁₂NiM₂Ti₁₀O₄₂ (M = Al, Cr, Ga) as described previously,^{25,28)} two layers are alternately stacked along the *c* axis: one is an edge-shared M1O₆ octahedral sheet with the coordination number CN = 6 with oxygen and the other M2–O is surrounded by three or four oxygen ions on the plane and two additional ones along the axis *c*. For simplicity, the M2–O can be considered as a pseudo-octahedron with oxygen vacancies.

Raman spectroscopy is known to be more sensitive than XRD to local atomic arrangements in the crystal lattice.²⁹⁾ As shown in Fig. 1, the XRD patterns of In₁₂NiM₂Ti₁₀O₄₂ (M = Al, Cr, Ga) are almost same, except for subtle changes in the lattice parameters due to different ionic radii of M³⁺ (Al³⁺: 0.0535 nm; Cr³⁺: 0.0615 nm; Ga³⁺: 0.062 nm).³⁰⁾ However, the Raman spectra of In₁₂NiM₂Ti₁₀O₄₂ (M = Al, Cr, Ga) powder samples as shown in Fig. 2 are apparently different. As a consequence, the three compounds might show different photophysical and photocatalytic properties associated with the lattice vibration of a crystal.

From the SEM morphologies of In₁₂NiM₂Ti₁₀O₄₂ (M = Al, Cr, Ga) powder samples as shown in Fig. 3, we can see

Fig. 1 X-ray diffraction patterns of In₁₂NiM₂Ti₁₀O₄₂ (M = Al, Cr, Ga) powder samples at room temperature.

Fig. 2 Raman spectra of In₁₂NiM₂Ti₁₀O₄₂ (M = Al, Cr, Ga) powder samples at room temperature.

Fig. 3 SEM images of $\text{In}_{12}\text{NiM}_2\text{Ti}_{10}\text{O}_{42}$ ($M = \text{Al}, \text{Cr}, \text{Ga}$) powder samples at room temperature.

clearly that the different particle sizes were in the following order: $\text{In}_{12}\text{NiAl}_2\text{Ti}_{10}\text{O}_{42} \sim \text{In}_{12}\text{NiCr}_2\text{Ti}_{10}\text{O}_{42} > \text{In}_{12}\text{NiGa}_2\text{Ti}_{10}\text{O}_{42}$. Consistently, the BET surface areas of $\text{In}_{12}\text{NiAl}_2\text{Ti}_{10}\text{O}_{42}$, $\text{In}_{12}\text{NiCr}_2\text{Ti}_{10}\text{O}_{42}$, and $\text{In}_{12}\text{NiGa}_2\text{Ti}_{10}\text{O}_{42}$ powder samples were measured to be 0.53, 0.44, and 0.79 m^2/g , respectively.

Figure 4 shows the UV–vis diffuse reflectance spectra of $\text{In}_{12}\text{NiM}_2\text{Ti}_{10}\text{O}_{42}$ ($M = \text{Al}, \text{Cr}, \text{Ga}$) powder samples at room temperature. From the main absorption edges, the band gap

Fig. 4 UV–vis diffuse reflectance spectra of $\text{In}_{12}\text{NiM}_2\text{Ti}_{10}\text{O}_{42}$ ($M = \text{Al}, \text{Cr}, \text{Ga}$) powder samples at room temperature.

energies were estimated to be $\sim 2.63 \text{ eV}^{31)}$ ($M = \text{Al}, \text{Ga}$) and $\sim 2.14 \text{ eV}$ ($M = \text{Cr}$), respectively. Obviously, the electronic state of trivalent cation M^{3+} imposed a significant effect on the band structure of $\text{In}_{12}\text{NiM}_2\text{Ti}_{10}\text{O}_{42}$. It appears that the band gap energies of $\text{In}_{12}\text{NiM}_2\text{Ti}_{10}\text{O}_{42}$ ($M = \text{Al}, \text{Ga}$) are probably related to the divalent cation Ni^{2+} but not related to M^{3+} ($M = \text{Al}, \text{Ga}$) without $3d$ orbitals or with fully filled $3d$ orbitals. On the contrary, the band gap energy of $\text{In}_{12}\text{NiCr}_2\text{Ti}_{10}\text{O}_{42}$ containing Cr^{3+} with partially filled $3d$ orbitals is as small as $\sim 2.14 \text{ eV}$. It means that the band edges of $\text{In}_{12}\text{NiCr}_2\text{Ti}_{10}\text{O}_{42}$ are determined by $\text{Cr } 3d$ rather than $\text{Ni } 3d$. No apparent humps were observed in the absorption spectra, indicating the formation of continuous conduction and valence bands. Further details of the effect of trivalent cations M^{3+} with empty, partially or fully filled $3d$ orbitals on the electronic structures of $\text{In}_{12}\text{NiM}_2\text{Ti}_{10}\text{O}_{42}$ ($M = \text{Al}, \text{Cr}, \text{Ga}$) will be discussed below in combination with the photocatalytic activities.

Photocatalytic H_2 evolution from aqueous methanol solution over Pt (0.2 mass%)/ $\text{In}_{12}\text{NiM}_2\text{Ti}_{10}\text{O}_{42}$ ($M = \text{Al}, \text{Cr}, \text{Ga}$) powder catalyst (0.5 g) under visible light irradiation ($\lambda \geq 420 \text{ nm}$) is shown in Fig. 5. The activities are in the following order: $\text{In}_{12}\text{NiCr}_2\text{Ti}_{10}\text{O}_{42} \gg \text{In}_{12}\text{NiGa}_2\text{Ti}_{10}\text{O}_{42} > \text{In}_{12}\text{NiAl}_2\text{Ti}_{10}\text{O}_{42}$. A dark test with Pt (0.2 mass%)/ $\text{In}_{12}\text{NiCr}_2\text{Ti}_{10}\text{O}_{42}$ showed that almost no H_2 was evolved when the light was turned off, excluding the possibility of H_2 generation from the “mechano-catalytic mechanism”.³⁾ No change of crystal structure was detected with XRD on the samples after aforementioned reaction, indicating the stability of the materials against photo-irradiation. These results confirmed that the H_2 evolution was inherently resulted from photocatalytic reaction.

Previous results showed that the substitution of different trivalent cations M^{3+} gave rise to different photophysical and photocatalytic properties in $\text{In}_{12}\text{NiM}_2\text{Ti}_{10}\text{O}_{42}$ ($M = \text{Al}, \text{Cr}, \text{Ga}$). Therefore, it is important to clarify the behaviour of M^{3+} in the M_2O_6 (M_2 : Ti, Ni and M) pseudo-octahedral field so as to understand the role of M^{3+} in constructing the electronic structure of $\text{In}_{12}\text{NiM}_2\text{Ti}_{10}\text{O}_{42}$ ($M = \text{Al}, \text{Cr}, \text{Ga}$). According to the crystal field theory (CFT),³²⁾ the $\text{Ni } e_g$ orbitals with a

Fig. 5 Photocatalytic H₂ evolution from aqueous methanol solution ($50 \times 10^{-3} \text{ dm}^3$ of CH_3OH + $220 \times 10^{-3} \text{ dm}^3$ of H_2O) over the Pt (0.2 mass%)/ $\text{In}_{12}\text{NiM}_2\text{Ti}_{10}\text{O}_{42}$ ($\text{M} = \text{Al}, \text{Cr}, \text{Ga}$) powder catalysts (0.5 g) under visible light irradiation ($\lambda \geq 420 \text{ nm}$).

high spin state ($S = 1$) will further split into a low energy level b_{1g} and a high energy level b_{2g} : the eight $3d$ electrons of Ni^{2+} will occupy the low energy states t_{2g} and b_{1g} , leaving the higher energy state b_{2g} empty and decreasing the spin state to $S = 0$.²⁵⁾ For $\text{M} = \text{Cr}$, three $3d$ electrons prefer to occupy the lower energy state t_{2g} . In the case of Cr-doped TiO_2 and SrTiO_3 ,^{17–21)} the occupied state t_{2g} is located at a potential level of $\sim 2.2 \text{ eV}$ below the conduction band bottom. Coincidentally, the band gap energy of $\text{In}_{12}\text{NiCr}_2\text{Ti}_{10}\text{O}_{42}$ ($\sim 2.14 \text{ eV}$) is very close to 2.2 eV . It seems that the Cr $3d$ orbitals in $\text{In}_{12}\text{NiCr}_2\text{Ti}_{10}\text{O}_{42}$ behave like those in the Cr-doped TiO_2 and SrTiO_3 although their crystal structures are different. The valence band (VB) top of $\text{In}_{12}\text{NiCr}_2\text{Ti}_{10}\text{O}_{42}$ should be determined by the occupied Cr $3d t_{2g}$ states. The occupied $3d$ orbitals of Ni^{2+} and Cr^{3+} in $\text{In}_{12}\text{NiCr}_2\text{Ti}_{10}\text{O}_{42}$ might connect or even overlap with O $2p$ to form a well-hybridized VB. For $\text{M} = \text{Al}$ or Ga , the band gap energy is as large as $\sim 2.63 \text{ eV}$, implying that the Al $2p$ or Ga $3d$ orbitals are located below the occupied Ni $3d$ states. Previously calculated band structures of $\text{Mg}_3\text{V}_2\text{O}_8$ and $\text{Zn}_3\text{V}_2\text{O}_8$ showed that, in the octahedral field, the Mg $2p$ orbitals located far below the O $2p$ orbitals while the Zn $3d$ orbitals hybridized with the O $2p$ orbitals and located at a lower position.³³⁾ We speculate that the Al $2p$ in $\text{In}_{12}\text{NiAl}_2\text{Ti}_{10}\text{O}_{42}$ behaves like the Mg $2p$ in $\text{Mg}_3\text{V}_2\text{O}_8$; whereas, the Ga $3d$ in $\text{In}_{12}\text{NiGa}_2\text{Ti}_{10}\text{O}_{42}$ behaves like the Zn $3d$ in $\text{Zn}_3\text{V}_2\text{O}_8$. The hybridization of Ga $3d$ and O $2p$ orbitals will favor the mobility of photo-induced holes in the valence band and thus, improve its photocatalytic activity for $\text{M} = \text{Ga}$ in comparison with that for $\text{M} = \text{Al}$. Judging from the UV–vis diffuse reflectance spectra of $\text{In}_{12}\text{NiM}_2\text{Ti}_{10}\text{O}_{42}$ ($\text{M} = \text{Al}, \text{Ga}$) as shown in Fig. 4, the occupied Ni $3d$ orbitals seem to connect with O $2p$ orbitals and determine the VB tops of $\text{In}_{12}\text{NiM}_2\text{Ti}_{10}\text{O}_{42}$ ($\text{M} = \text{Al}, \text{Ga}$). The conduction bands (CBs) of $\text{In}_{12}\text{NiM}_2\text{Ti}_{10}\text{O}_{42}$ ($\text{M} = \text{Al}, \text{Cr}, \text{Ga}$) are constructed primarily by the empty Ti $3d$ and In $5s$ orbitals. For $\text{M} = \text{Al}$ and Ga , the empty Ni $3d (b_{2g})$ orbitals also involve in the CBs and probably overlap with Ti $3d$ and In $5s$. The CB

Fig. 6 Schematic band structures of $\text{In}_{12}\text{NiM}_2\text{Ti}_{10}\text{O}_{42}$ ($\text{M} = \text{Al}, \text{Cr}, \text{Ga}$).

bottoms are supposed to be determined by the empty Ni $3d (b_{2g})$. For $\text{M} = \text{Cr}$, both the empty Ni- $3d (b_{2g})$ and Cr $3d$ orbitals involve in the CB and overlap with Ti $3d$ and In $5s$, and the CB bottom is determined by the empty Cr $3d$. The schematic band structures of $\text{In}_{12}\text{NiM}_2\text{Ti}_{10}\text{O}_{42}$ ($\text{M} = \text{Al}, \text{Cr}, \text{Ga}$) are shown in Figs. 6(a), (b) and (c), respectively. Obviously, the broadly dispersed conduction and valence bands of $\text{In}_{12}\text{NiCr}_2\text{Ti}_{10}\text{O}_{42}$ with the narrowest band gap could account for the improved photocatalytic activity for $\text{M} = \text{Cr}$ in comparison with those for $\text{M} = \text{Al}, \text{Ga}$. In general, the energy band structures and thus the photocatalytic activities of $\text{In}_{12}\text{NiM}_2\text{Ti}_{10}\text{O}_{42}$ ($\text{M} = \text{Al}, \text{Cr}, \text{Ga}$) are strongly dependent on the trivalent cations M^{3+} with different electronic states.

4. Conclusions

The substitution of trivalent cations M^{3+} with different electronic states imposed significant effects on the electronic structure, photophysical and photocatalytic properties of $\text{In}_{12}\text{NiM}_2\text{Ti}_{10}\text{O}_{42}$ ($\text{M} = \text{Al}, \text{Cr}, \text{Ga}$) crystallized in a monoclinic system with the space group $\text{P}2_1/\text{a}$. For $\text{M} = \text{Cr}$ with partially filled $3d$ orbitals, continuous conduction and valence bands with the smallest band gap energy (e_g) of $\sim 2.14 \text{ eV}$ was formed in combination with the partially filled Ni $3d$ orbitals; for $\text{M} = \text{Al}$ without $3d$ orbitals and $\text{M} = \text{Ga}$ with fully filled $3d$ orbitals, the band gap energies were both $\sim 2.63 \text{ eV}$. As a consequence, the photocatalytic activities for H_2 evolution were remarkably different. Properly incorporating transition metals into a structure with suitable band edges has been proven to be a promising approach to develop visible-light-responsive photocatalyst for water splitting.

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