

Research Article

Photocatalytic Water Splitting for Hydrogen Production with Novel M_2YbSbO_7 ($M = In, Gd, Y$) by Using Visible Light Photoenergy

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Novel photocatalysts M_2YbSbO_7 ($M = In, Gd, Y$) were synthesized by solid state reaction method for the first time. A comparative study on the structural and photocatalytic properties of M_2YbSbO_7 ($M = In, Gd, Y$) was reported. The results showed that In_2YbSbO_7 , Gd_2YbSbO_7 , and Y_2YbSbO_7 crystallized with the pyrochlore-type structure, cubic crystal system and space group $Fd\bar{3}m$. For the photocatalytic water splitting reaction, H_2 or O_2 evolution was observed from pure water with In_2YbSbO_7 , Gd_2YbSbO_7 , or Y_2YbSbO_7 as the photocatalyst under visible light irradiation. (wavelength > 420 nm). Moreover, under visible light irradiation ($\lambda > 420$ nm), H_2 and O_2 were also evolved by using In_2YbSbO_7 , Gd_2YbSbO_7 , or Y_2YbSbO_7 as catalyst from CH_3OH/H_2O and $AgNO_3/H_2O$ solutions respectively. The In_2YbSbO_7 photocatalyst showed the highest activity compared with Gd_2YbSbO_7 or Y_2YbSbO_7 . At the same time, The Y_2YbSbO_7 photocatalyst showed higher activity compared with Gd_2YbSbO_7 . The photocatalytic activities were further improved under visible light irradiation with In_2YbSbO_7 , Gd_2YbSbO_7 , or Y_2YbSbO_7 being loaded by Pt, NiO, or RuO_2 . The effect of Pt was better than that of NiO or RuO_2 for improving the photocatalytic activity of In_2YbSbO_7 , Gd_2YbSbO_7 , or Y_2YbSbO_7 .

1. Introduction

Since water splitting catalyzed by TiO_2 was discovered in 1972 [1], photocatalysis has attracted far-ranging attention from both academic and industrial organizations [2–6]. In particular, water splitting by the photocatalytic approach has been considered as a highly promising process to obtain clean and renewable H_2 source [5–13]. Presently, TiO_2 was known as the most common photocatalyst for water splitting. However, TiO_2 could only split water under ultraviolet light irradiation which only occupy less than 5% of the whole sunlight. Moreover, ultraviolet light only occupied 4% of sunlight, which was a restrained factor for photocatalysis technology with TiO_2 as catalyst. Therefore, some efficient catalysts which could generate electron-hole pairs under visible light irradiation should be developed because visible light occupied 43% of sunlight.

Fortunately, $A_2B_2O_7$ compounds were often considered to own better photocatalytic properties under visible light

irradiation [14, 15]. In our previous work [14], we had found that Bi_2GaVO_7 crystallized with the tetragonal crystal system and could split pure water into hydrogen under ultraviolet light irradiation and seemed to have potential for improvement of photocatalytic activity by modification of its structure. According to above analysis, we could assume that the substitution of Bi^{3+} by In^{3+} , Gd^{3+} or Y^{3+} , and the substitution of Ga^{3+} by Yb^{3+} , and the substitution of V^{3+} by Sb^{5+} in Bi_2GaVO_7 might increase carriers concentration. As a result, a change and improvement of the electrical transportation and photophysical properties could be found in the novel In_2YbSbO_7 , Gd_2YbSbO_7 , or Y_2YbSbO_7 compound which might own advanced photocatalytic properties.

In_2YbSbO_7 , Gd_2YbSbO_7 , or Y_2YbSbO_7 had never been produced and the data about their structural and photophysical properties such as space group and lattice constants had not been found previously. In addition, the photocatalytic properties of In_2YbSbO_7 , Gd_2YbSbO_7 , or Y_2YbSbO_7 have not been studied by other investigators. The molecular

composition of $\text{In}_2\text{YbSbO}_7$, $\text{Gd}_2\text{YbSbO}_7$, or Y_2YbSbO_7 was very similar with other $\text{A}_2\text{B}_2\text{O}_7$ compounds. Thus the resemblance suggested that $\text{In}_2\text{YbSbO}_7$, $\text{Gd}_2\text{YbSbO}_7$, or Y_2YbSbO_7 might possess photocatalytic properties under visible light irradiation, which was similar with those other members in $\text{A}_2\text{B}_2\text{O}_7$ family. $\text{In}_2\text{YbSbO}_7$, $\text{Gd}_2\text{YbSbO}_7$, or Y_2YbSbO_7 also seemed to have potential for improvement of photocatalytic activity by modification of its structure because it had been proved that a slight modification of a semiconductor structure would result in a remarkable change in photocatalytic properties [16].

In this paper, newly synthesized semiconductor compound $\text{In}_2\text{YbSbO}_7$, $\text{Gd}_2\text{YbSbO}_7$, or Y_2YbSbO_7 was used as photocatalyst for split water into hydrogen under visible light irradiation. The structural, photophysical, and photocatalytic properties of $\text{In}_2\text{YbSbO}_7$, $\text{Gd}_2\text{YbSbO}_7$, or Y_2YbSbO_7 were investigated in detail

2. Experimental

The novel photocatalysts were synthesized by a solid-state reaction method. Yb_2O_3 , In_2O_3 , Gd_2O_3 , Y_2O_3 , and Sb_2O_5 with purity of 99.99% (Sinopharm Group Chemical Reagent Co., Ltd., Shanghai, China) were utilized as starting materials. All powders were dried at 200°C for 4 h before synthesis. In order to synthesize $\text{In}_2\text{YbSbO}_7$, $\text{Gd}_2\text{YbSbO}_7$, or Y_2YbSbO_7 , the precursors were stoichiometrically mixed, then pressed into small columns and put into an alumina crucible (Shenyang Crucible Co., Ltd., China). Finally, calcination was carried out at 1320°C for 65 h in an electric furnace (KSL 1700X, Hefei Kejing Materials Technology Co., Ltd., China). The crystal structure of $\text{In}_2\text{YbSbO}_7$, $\text{Gd}_2\text{YbSbO}_7$, or Y_2YbSbO_7 was analyzed by the powder X-ray diffraction method (D/MAX-RB, Rigaku Corporation, Japan) with $\text{CuK}\alpha$ radiation ($\lambda = 1.54056$). The data were collected at 295 K with a step-scan procedure in the range of $2\theta = 10\text{--}100^\circ$. The step interval was 0.02° and the time per step was 1.2 s. The chemical composition of $\text{In}_2\text{YbSbO}_7$, $\text{Gd}_2\text{YbSbO}_7$, or Y_2YbSbO_7 was determined by scanning electron microscope-X-ray energy dispersion spectrum (SEM-EDS, LEO 1530VP, LEO Corporation, Germany) and X-ray fluorescence spectrometer (XFS, ARL-9800, ARL Corporation, Switzerland). The optical absorption of $\text{In}_2\text{YbSbO}_7$, $\text{Gd}_2\text{YbSbO}_7$, or Y_2YbSbO_7 was analyzed with a UV-visible spectrophotometer (Lambda 40, Perkin-Elmer Corporation, USA). The surface area of $\text{In}_2\text{YbSbO}_7$, $\text{Gd}_2\text{YbSbO}_7$, or Y_2YbSbO_7 was measured by the Brunauer-Emmett-Teller (BET) method (MS-21, Quantachrome Instruments Corporation, USA) with N_2 adsorption at liquid nitrogen temperature.

The photocatalytic water splitting was conducted under visible light irradiation in a gas closed circulation system with an inner-irradiation-type reactor (quartz cell). A light source (300 W Xe arc lamp, Beijing Dongsheng Glass Light Source Factory, China) with the incident photon flux I_0 of $0.056176 \text{ umol cm}^{-2} \text{ s}^{-1}$ was focused through a shutter window and a 420 nm cutoff filter onto the window face of the cell. The gases evolved were determined with a TCD gas

chromatograph (6890 N, Agilent Technologies, USA), which was connected to the gas closed circulation system. Before reaction, the closed gas circulation system and the reaction cell were degassed until O_2 and N_2 could not be detected. Then about 35 Torr of argon was charged into the system. H_2 evolution reaction was carried out in $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ solution (50 mL CH_3OH , 300 mL H_2O) with Pt-, NiO-, or RuO_2 -loaded powder (1.0 g) as the catalyst which was suspended in $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ solution under stirring.

For H_2 evolution reaction, Pt, NiO, or RuO_2 which was loaded on the surface of the catalysts was prepared. Pt was loaded on the catalyst surface by an in situ photodeposition method by using aqueous H_2PtCl_6 solution (Shanghai Chemical Reagent Research Institute, China) as the Pt source. NiO or RuO_2 which was loaded on the surface of the catalysts were prepared by the impregnation method by using $\text{Ni}(\text{NO}_3)_2$ or RuCl_3 solution (Sinopharm Group Chemical Reagent Co., Ltd., Shanghai, China), separately.

3. Results and Discussion

3.1. Characterization. The mean particle size was 98 nm for Y_2YbSbO_7 and 35 nm for $\text{In}_2\text{YbSbO}_7$. Y_2YbSbO_7 , $\text{In}_2\text{YbSbO}_7$, and $\text{Gd}_2\text{YbSbO}_7$ were nanosized particles and irregular shapes. It could be seen from the results that the average particle size of $\text{In}_2\text{YbSbO}_7$ was smaller than that of $\text{Gd}_2\text{YbSbO}_7$ or Y_2YbSbO_7 . SEM-EDS spectrum which was taken from the prepared $\text{In}_2\text{YbSbO}_7$ displayed the presence of indium, ytterbium, antimony, and oxygen. Similarly, SEM-EDS spectrum that was taken from the prepared $\text{Gd}_2\text{YbSbO}_7$ also indicated the presence of gadolinium, ytterbium, antimony, and oxygen. SEM-EDS spectrum that was taken from the prepared Y_2YbSbO_7 also indicated the presence of yttrium, ytterbium, antimony, and oxygen. Other elements could not be identified from Y_2YbSbO_7 , $\text{In}_2\text{YbSbO}_7$, or $\text{Gd}_2\text{YbSbO}_7$.

Figure 1 shows the X-ray powder diffraction patterns of $\text{In}_2\text{YbSbO}_7$, $\text{Gd}_2\text{YbSbO}_7$, and Y_2YbSbO_7 . It could be seen from Figure 1 that Y_2YbSbO_7 , $\text{In}_2\text{YbSbO}_7$, or $\text{Gd}_2\text{YbSbO}_7$ was a single phase. According to the Rietveld analysis, Y_2YbSbO_7 , $\text{In}_2\text{YbSbO}_7$, or $\text{Gd}_2\text{YbSbO}_7$ owned the pyrochlore-type structure and a cubic crystal system which had a space group $Fd\bar{3}m$. The lattice parameter for $\text{In}_2\text{YbSbO}_7$ was 10.340277 \AA . The lattice parameter for $\text{Gd}_2\text{YbSbO}_7$ was 10.639527 \AA and that for Y_2YbSbO_7 was 10.499778 \AA . Moreover, the XRD results showed that 2 theta angles of each reflection of $\text{In}_2\text{YbSbO}_7$ changed with In^{3+} being substituted by Y^{3+} or Gd^{3+} . The lattice parameter α increased from $\alpha = 10.340277 \text{ \AA}$ for $\text{In}_2\text{YbSbO}_7$ to $\alpha = 10.499778 \text{ \AA}$ for Y_2YbSbO_7 , and from $\alpha = 10.499778 \text{ \AA}$ for Y_2YbSbO_7 to $\alpha = 10.639527 \text{ \AA}$ for $\text{Gd}_2\text{YbSbO}_7$, which indicated a increase in lattice parameter of the photocatalyst with increase of the M ionic radii ($\text{In}^{3+} (0.92 \text{ \AA}) < \text{Y}^{3+} (1.019 \text{ \AA}) < \text{Gd}^{3+} (1.053 \text{ \AA})$).

Figure 2 represents the absorption spectra of Y_2YbSbO_7 , $\text{In}_2\text{YbSbO}_7$, and $\text{Gd}_2\text{YbSbO}_7$. Compared with well-known photocatalyst TiO_2 whose absorption edge was only 380 nm, the absorption edge of $\text{In}_2\text{YbSbO}_7$ was found to be at 525 nm, that of $\text{Gd}_2\text{YbSbO}_7$ was found to be at 502 nm, and that of

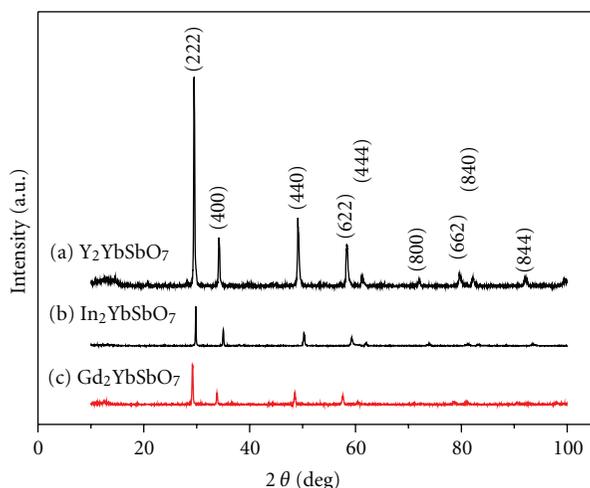


FIGURE 1: X-ray powder diffraction patterns of $\text{In}_2\text{YbSbO}_7$, $\text{Gd}_2\text{YbSbO}_7$, or Y_2YbSbO_7 prepared by a solid-state reaction method at 1320°C .

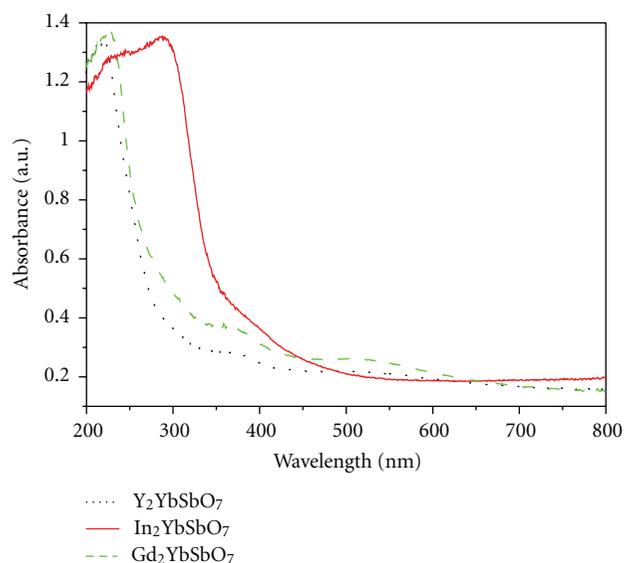


FIGURE 2: The diffuse reflectance absorption spectra of $\text{In}_2\text{YbSbO}_7$, $\text{Gd}_2\text{YbSbO}_7$, and Y_2YbSbO_7 .

Y_2YbSbO_7 was found to be at 419 nm, which belonged to the visible region of the spectrum. Clearly, the obvious absorption (defined hereby as 1-transmission) did not result from reflection and scattering. Consequently, the apparent absorbance at subbandgap wavelengths (520 to 800 nm for $\text{In}_2\text{YbSbO}_7$, 530 to 800 nm for $\text{Gd}_2\text{YbSbO}_7$, and 428 to 800 nm for Y_2YbSbO_7) was higher than zero.

For a crystalline semiconductor, the optical absorption near the band edge followed the equation: $\alpha h\nu = A(h\nu - E_g)^n$ [17, 18]. Here, A , α , E_g , and ν were proportional constant, absorption coefficient, bandgap, and light frequency, respectively. Within this equation, n determined the character of the transition in a semiconductor. E_g and n could be calculated by the following steps: (i) plotting

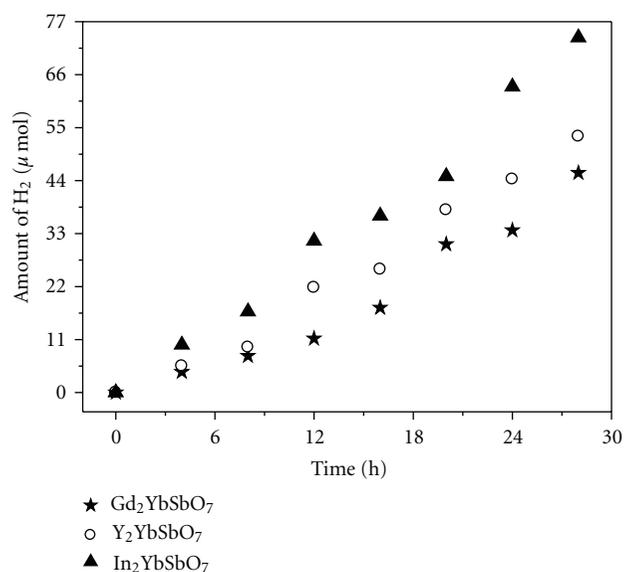


FIGURE 3: Photocatalytic H_2 evolution from aqueous methanol solution with Y_2YbSbO_7 , $\text{In}_2\text{YbSbO}_7$, or $\text{Gd}_2\text{YbSbO}_7$ as catalyst under visible light irradiation ($\lambda > 420\text{ nm}$, 0.5 g 0.1 wt% Pt-loaded powder sample, 50 mL methanol solution, 200 mL pure water). Light source: 300 W Xe lamp.

$\ln(\alpha h\nu)$ versus $\ln(h\nu - E_g)$ by assuming an approximate value of E_g , (ii) deducing the value of n according to the slope in this graph and (iii) refining the value of E_g by plotting $(\alpha h\nu)^{1/n}$ versus $h\nu$ and extrapolating the plot to $(\alpha h\nu)^{1/n} = 0$. According to this method, the bandgap of $\text{In}_2\text{YbSbO}_7$ was estimated to be 2.361 eV. The bandgap of $\text{Gd}_2\text{YbSbO}_7$ was 2.469 eV and that of Y_2YbSbO_7 was 2.521 eV.

3.2. Photocatalytic Activity of Y_2YbSbO_7 , $\text{In}_2\text{YbSbO}_7$, and $\text{Gd}_2\text{YbSbO}_7$. Generally speaking, the semiconductor photocatalysis started from the direct absorption of suprabandgap photons and the generation of electron-hole pairs in the semiconductor particles. Subsequently, the diffusion of the charge carriers to the surface of the semiconductor particle was followed. Under visible light irradiation, we measured H_2 and O_2 evolution rate by using $\text{In}_2\text{YbSbO}_7$, $\text{Gd}_2\text{YbSbO}_7$, and Y_2YbSbO_7 as photocatalysts from $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ and $\text{AgNO}_3/\text{H}_2\text{O}$ solutions, respectively. Wavelengths (λ) dependence of the photocatalytic activity under light irradiation from full arc up to $\lambda = 420\text{ nm}$ was measured by using different cutoff filters.

Figure 3 shows the photocatalytic H_2 evolution from aqueous methanol solution with Y_2YbSbO_7 , $\text{In}_2\text{YbSbO}_7$, or $\text{Gd}_2\text{YbSbO}_7$ as catalyst under visible light irradiation ($\lambda > 420\text{ nm}$, 0.5 g 0.1 wt% Pt-loaded powder sample, 50 mL methanol solution, 200 mL pure water). It could be found from Figure 3 that under visible light irradiation, the rate of H_2 evolution in the first 28 h with $\text{In}_2\text{YbSbO}_7$ as catalyst was $5.264\ \mu\text{mol h}^{-1}\text{ g}^{-1}$, that with Y_2YbSbO_7 as catalyst was $3.800\ \mu\text{mol h}^{-1}\text{ g}^{-1}$, that with $\text{Gd}_2\text{YbSbO}_7$ as catalyst was $3.257\ \mu\text{mol h}^{-1}\text{ g}^{-1}$, indicating that the photocatalytic activity of the $\text{In}_2\text{YbSbO}_7$ photocatalyst was much higher

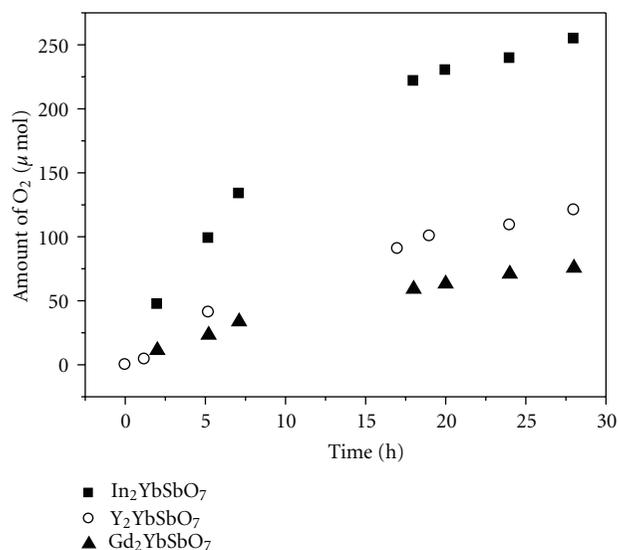


FIGURE 4: Photocatalytic O₂ evolution from AgNO₃ solution with Y₂YbSbO₇, In₂YbSbO₇, or Gd₂YbSbO₇ as catalyst under visible light irradiation ($\lambda > 420$ nm, 0.5 g photocatalyst, 1 mmol AgNO₃, 270 mL pure water). Light source: 300 W Xe lamp.

than that of Y₂YbSbO₇ or Gd₂YbSbO₇. The quantum yield for hydrogen evolution at 420 nm with Gd₂YbSbO₇ as catalyst was 0.0795%, and that with Y₂YbSbO₇ as catalyst was 0.0928%, and that with In₂YbSbO₇ as catalyst was 0.1285% under visible light irradiation. Furthermore, the Y₂YbSbO₇ photocatalyst showed slightly higher photocatalytic activity than the Gd₂YbSbO₇ photocatalyst. This also proved that the conduction band level of Y₂YbSbO₇, In₂YbSbO₇, or Gd₂YbSbO₇ was more negative than the reduction potential of H₂O for forming H₂. Such results were in good agreement with the optical absorption property of Y₂YbSbO₇, In₂YbSbO₇, or Gd₂YbSbO₇ (see Figure 2). The rate of H₂ evolution also increased with increasing illumination time. The photocatalytic activity of the In₂YbSbO₇ photocatalyst increased by about 150% than that of the Gd₂YbSbO₇ photocatalyst.

Figure 4 shows the photocatalytic O₂ evolution from AgNO₃ solution with Y₂YbSbO₇, In₂YbSbO₇, or Gd₂YbSbO₇ as catalyst under visible light irradiation ($\lambda > 420$ nm, 0.5 g photocatalyst, 1 mmol AgNO₃, 270 mL pure water). It could be found from Figure 4 that under visible light irradiation, the rate of O₂ evolution in the first 28 h with In₂YbSbO₇ as catalyst was $18.186 \mu\text{mol h}^{-1} \text{g}^{-1}$, that with Y₂YbSbO₇ as catalyst was $8.628 \mu\text{mol h}^{-1} \text{g}^{-1}$, and that with Gd₂YbSbO₇ as catalyst was $5.404 \mu\text{mol h}^{-1} \text{g}^{-1}$, indicating that the valence band level of In₂YbSbO₇, Y₂YbSbO₇, or Gd₂YbSbO₇ was more positive than the oxidation potential of H₂O for forming O₂. The formation rate of O₂ increased with decreasing the M ionic radii within M₂YbSbO₇ (M = In, Gd, Y), In^{3+} (0.92 Å) < Y^{3+} (1.019 Å) < Gd^{3+} (1.053 Å). The quantum yield for oxygen evolution at 420 nm with Gd₂YbSbO₇ as catalyst was 0.2639%, that with Y₂YbSbO₇ as catalyst was 0.4214%, and that with In₂YbSbO₇ as catalyst was 0.8881% under visible light irradiation.

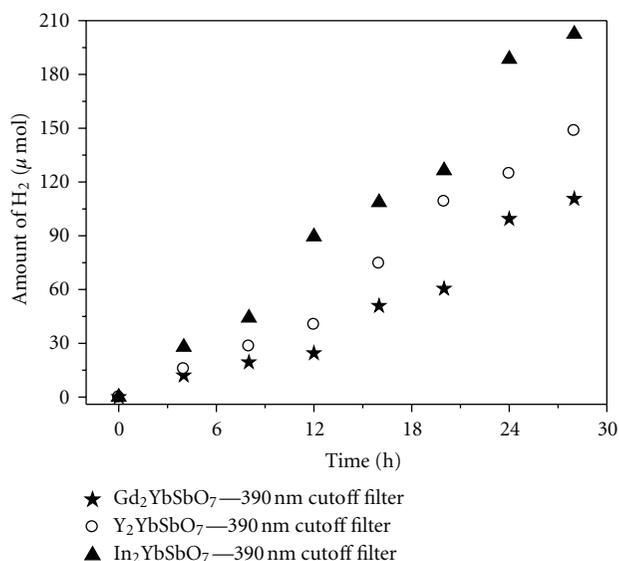


FIGURE 5: Photocatalytic H₂ evolution from aqueous methanol solution with Y₂YbSbO₇, In₂YbSbO₇, or Gd₂YbSbO₇ as catalyst under visible light irradiation (390 nm cut-off filter, 0.5 g 0.1 wt% Pt-loaded powder sample, 50 mL CH₃OH, 200 mL pure water). Light source: 300 W Xe lamp.

Figure 5 shows the photocatalytic H₂ evolution from aqueous methanol solution with Y₂YbSbO₇, In₂YbSbO₇, or Gd₂YbSbO₇ as catalyst under visible light irradiation (390 nm cut-off filter, 0.5 g 0.1 wt% Pt-loaded powder sample, 50 mL CH₃OH, 200 mL pure water). It could be found from Figure 5 that under visible light irradiation, the rate of H₂ evolution in the first 28 h with In₂YbSbO₇ as catalyst was $14.464 \mu\text{mol h}^{-1} \text{g}^{-1}$, that with Y₂YbSbO₇ as catalyst was $10.614 \mu\text{mol h}^{-1} \text{g}^{-1}$, and that with Gd₂YbSbO₇ as catalyst was $7.900 \mu\text{mol h}^{-1} \text{g}^{-1}$, indicating that the effect of wavelength (λ) dependence on the photocatalytic activity was very important. The quantum yield for hydrogen evolution at 420 nm with Gd₂YbSbO₇ as catalyst was 0.1929%, that with Y₂YbSbO₇ as catalyst was 0.2592%, and that with In₂YbSbO₇ as catalyst was 0.3532% under visible light irradiation (390 nm cut-off filter). Figure 6 shows the photocatalytic H₂ evolution from aqueous methanol solution with Y₂YbSbO₇, In₂YbSbO₇, or Gd₂YbSbO₇ as catalyst under visible light irradiation (no cut-off filter, 0.5 g 0.1 wt% Pt-loaded powder sample, 50 mL CH₃OH, 200 mL pure water). It could be found from Figure 6 that under visible light irradiation without using any filters, the rate of H₂ evolution in the first 28 h with In₂YbSbO₇ as catalyst was $32.321 \mu\text{mol h}^{-1} \text{g}^{-1}$, that with Y₂YbSbO₇ as catalyst was $24.693 \mu\text{mol h}^{-1} \text{g}^{-1}$, and that with Gd₂YbSbO₇ as catalyst was $22.864 \mu\text{mol h}^{-1} \text{g}^{-1}$, indicating that In₂YbSbO₇, Y₂YbSbO₇, or Gd₂YbSbO₇ showed not only high photocatalytic activity under full arc irradiation but also an activity under visible light irradiation. The quantum yield for hydrogen evolution at 420 nm with Gd₂YbSbO₇ as catalyst was 0.5583%, that with Y₂YbSbO₇ as catalyst was 0.6030%, and that with In₂YbSbO₇ as catalyst was 0.7892% under visible light irradiation without using any filters. The photocatalytic activity decreased

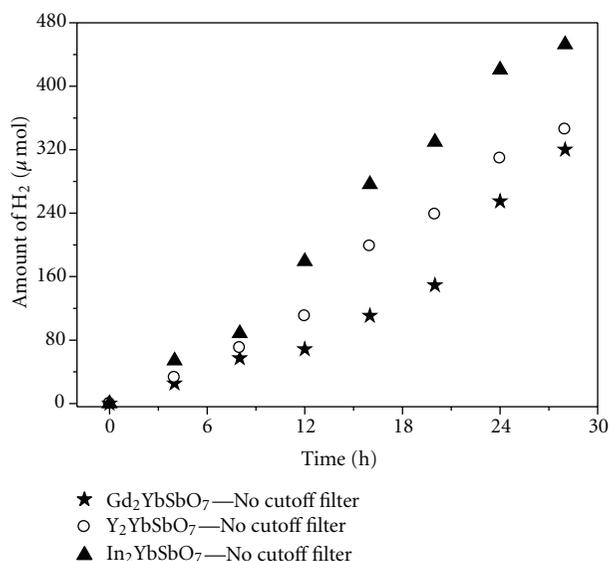


FIGURE 6: Photocatalytic H₂ evolution from aqueous methanol solution with Y₂YbSbO₇, In₂YbSbO₇, or Gd₂YbSbO₇ as catalyst under visible light irradiation (no cut-off filter, 0.5 g 0.1 wt% Pt-loaded powder sample, 50 mL CH₃OH, 200 mL pure water). Light source: 300 W Xe lamp.

with increasing incident wavelength λ . As to In₂YbSbO₇, Y₂YbSbO₇, or Gd₂YbSbO₇, the turnover number—the ratio of total amount of gas evolved to catalyst—exceeded 0.09381 for In₂YbSbO₇, 0.06220 for Y₂YbSbO₇, and 0.06578 for Gd₂YbSbO₇, respectively, after 28 h of reaction time under visible light irradiation ($\lambda > 420$ nm). The turnover number which was in terms of reacted electrons relative to the amount of In₂YbSbO₇ reached 1 at 60 h reaction time. As to Y₂YbSbO₇, the turnover number exceeded 1 after 75 h reaction time. As to Gd₂YbSbO₇, the turnover number exceeded 1 after 72 h reaction time. Under the condition of full arc irradiation, after 28 h of reaction time, the turnover number exceeded 0.576 as to In₂YbSbO₇, and the turnover number exceeded 0.404 as to Y₂YbSbO₇, and the turnover number exceeded 0.462 as to Gd₂YbSbO₇. The above results were enough to prove that the reaction occurred catalytically. The reaction stopped when the light was turned off in this experiment, showing the obvious light response.

It was known that the TiO₂ photocatalyst had very high photocatalytic activity under ultraviolet light irradiation. By contrast, the photocatalytic activity was not obtained with Pt/TiO₂ as catalyst under visible light irradiation ($\lambda > 420$ nm), while an obvious photocatalytic activity was observed with In₂YbSbO₇, Y₂YbSbO₇, or Gd₂YbSbO₇ as catalyst, showing that the In₂YbSbO₇, Y₂YbSbO₇, or Gd₂YbSbO₇ could respond to visible light irradiation. The formation rate of H₂ evolution with In₂YbSbO₇, Y₂YbSbO₇, or Gd₂YbSbO₇ as catalyst was much larger than that with TiO₂ as catalyst under visible light irradiation. This indicated that the photocatalytic activity of In₂YbSbO₇, Y₂YbSbO₇, or Gd₂YbSbO₇ for decomposing CH₃OH/H₂O solution was higher than that of TiO₂. The structure of In₂YbSbO₇,

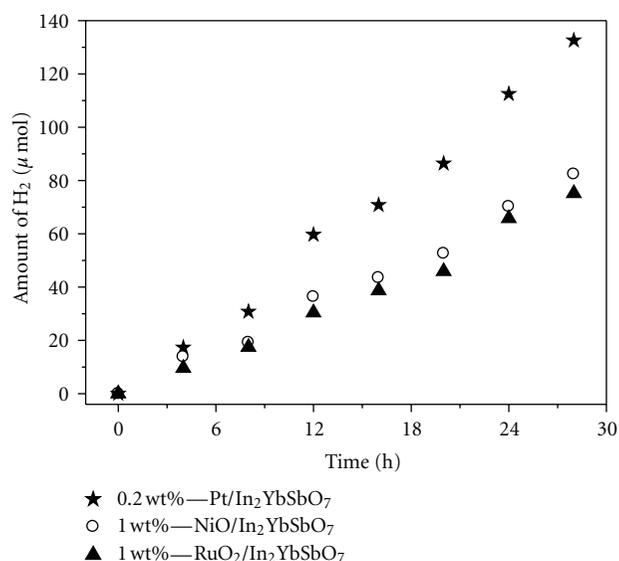


FIGURE 7: Effect of Pt, NiO, and RuO₂ co-catalysts on the photoactivity of In₂YbSbO₇ under visible light irradiation ($\lambda > 420$ nm, 0.5 g powder sample, 50 mL methanol solution, 200 mL pure water). Light source: 300 W Xe lamp.

Y₂YbSbO₇, or Gd₂YbSbO₇ after photocatalytic reaction was also checked by using X-ray diffraction method and no change in their structures were observed during this reaction, which indicated that the H₂ evolution was resulted from the photocatalytic reaction of H₂O. SEM-EDS results also confirmed that the chemical composition of In₂YbSbO₇, Y₂YbSbO₇, or Gd₂YbSbO₇ did not change after reaction.

Figure 7 shows effect of Pt, NiO, and RuO₂ cocatalysts on the photoactivity of In₂YbSbO₇ under visible light irradiation ($\lambda > 420$ nm, 0.5 g powder sample, 50 mL methanol solution, 200 mL pure water). In principle, the photoinduced electrons preferentially enriched on the surface of cocatalyst particles and the recombination of the photoinduced electrons with the photoinduced holes were therefore markedly suppressed. It could be found from Figure 7 that in the first 28 h under visible light irradiation, the rate of H₂ evolution was estimated to be $9.471 \mu\text{mol h}^{-1} \text{g}^{-1}$ with 0.2 wt% Pt/In₂YbSbO₇ as catalyst, and that was estimated to be $5.886 \mu\text{mol h}^{-1} \text{g}^{-1}$ with 1.0 wt% NiO/In₂YbSbO₇ as catalyst, and that was estimated to be $5.371 \mu\text{mol h}^{-1} \text{g}^{-1}$ with 1.0 wt% RuO₂/In₂YbSbO₇ as catalyst, indicating that the photocatalytic activities could be further improved under visible light irradiation with In₂YbSbO₇, Gd₂YbSbO₇, or Y₂YbSbO₇ being loaded by Pt, NiO, or RuO₂. The quantum yield for hydrogen evolution at 420 nm with 0.2 wt% Pt/In₂YbSbO₇ as catalyst was 0.2313%, that with 1.0 wt% NiO/In₂YbSbO₇ as catalyst was 0.1437%, and that with 1.0 wt% RuO₂/In₂YbSbO₇ as catalyst was 0.1312% under visible light irradiation ($\lambda > 420$ nm). The effect of Pt was better than that of NiO or RuO₂ for improving the photocatalytic activity of In₂YbSbO₇, Gd₂YbSbO₇, or Y₂YbSbO₇.

It was known that the process for photocatalysis of semiconductors was the direct absorption of photon by

bandgap of the materials and generated electron-hole pairs in the semiconductor particles, and the excitation of an electron from the valence band to the conduction band was initiated by light absorption with energy equal to or greater than the bandgap of the semiconductor. Upon excitation of photon the separated electron and hole could follow surface of solid. This suggested that the the narrow bandgap was easier to excite an electron from the valence band to the conduction band. If the conduction band potential level of the semiconductor was more negative than that of H₂ evolution, and the valence band potential level was more positive than that of O₂ evolution, decomposition of water can occur even without applying electric power [1]. Based on above analysis, the photon absorption of In₂YbSbO₇ was much easier than that of the Gd₂YbSbO₇ or Y₂YbSbO₇, which led to higher photocatalytic activity of In₂YbSbO₇.

The specific surface area of In₂YbSbO₇ was measured to be 1.98 m²/g which was about 3.7% of the surface area of the TiO₂ photocatalyst (53.8 m²/g), and the surface area of Gd₂YbSbO₇ was measured to be 1.32 m²/g which was only about 2.5% of the surface area of TiO₂, and the specific surface area of Y₂YbSbO₇ was measured to be 1.70 m²/g which was only about 3.2% of the surface area of TiO₂. It indicated much higher potential efficiency of In₂YbSbO₇, Gd₂YbSbO₇, or Y₂YbSbO₇. Although the surface area of In₂YbSbO₇, Gd₂YbSbO₇, or Y₂YbSbO₇ was smaller than that of TiO₂, In₂YbSbO₇, Gd₂YbSbO₇, or Y₂YbSbO₇ showed higher photocatalytic activity for H₂ evolution under visible light irradiation, which indicated that the high photocatalytic activity of the In₂YbSbO₇, Gd₂YbSbO₇, or Y₂YbSbO₇ was not due to big surface area but due to the narrow bandgap. It was obvious that further increase in photocatalytic activity might be prospected from increasing the surface area of In₂YbSbO₇, Gd₂YbSbO₇, or Y₂YbSbO₇. Since an efficient photocatalytic reaction process occurred on the photocatalyst surface, the increase of the surface area for the photocatalysts might result in the increase of their photocatalytic activity.

4. Conclusion

In the present work we prepared single phase of In₂YbSbO₇, Gd₂YbSbO₇, or Y₂YbSbO₇ by solid-state reaction method and investigated the structural, optical, and photocatalytic properties of In₂YbSbO₇, Gd₂YbSbO₇, or Y₂YbSbO₇. Rietveld structure refinement revealed that In₂YbSbO₇, Gd₂YbSbO₇, or Y₂YbSbO₇ crystallized with the pyrochlore-type structure, cubic crystal system, and space group *Fd3m*. The lattice parameter for In₂YbSbO₇ was 10.340277 Å. The lattice parameter for Gd₂YbSbO₇ was 10.639527 Å, and that for Y₂YbSbO₇ was 10.499778 Å. The bandgap of In₂YbSbO₇ was estimated to be 2.361 eV. The bandgap of Gd₂YbSbO₇ was 2.469 eV and that of Y₂YbSbO₇ was 2.521 eV. In₂YbSbO₇, Gd₂YbSbO₇, or Y₂YbSbO₇ showed optical absorption in the visible light region, indicating the photocatalysts had the ability to respond to the wavelength of visible light region. For the photocatalytic water splitting reaction, H₂ or O₂ evolution was observed from pure water with In₂YbSbO₇, Gd₂YbSbO₇, or Y₂YbSbO₇ as the photocatalyst under visible light irradiation. (Wavelength >

420 nm). Moreover, under visible light irradiation ($\lambda > 420$ nm), H₂ and O₂ were also evolved by using In₂YbSbO₇, Gd₂YbSbO₇, or Y₂YbSbO₇ as catalyst from CH₃OH/H₂O and AgNO₃/H₂O solutions, respectively. The In₂YbSbO₇ photocatalyst showed the highest activity compared with Gd₂YbSbO₇ or Y₂YbSbO₇. At the same time, the Y₂YbSbO₇ photocatalyst showed higher activity compared with Gd₂YbSbO₇. The photocatalytic activities were further improved under visible light irradiation with In₂YbSbO₇, Gd₂YbSbO₇, or Y₂YbSbO₇ being loaded by Pt, NiO, or RuO₂. The effect of Pt was better than that of NiO or RuO₂ for improving the photocatalytic activity of In₂YbSbO₇, Gd₂YbSbO₇, or Y₂YbSbO₇. In addition, the synthesis of In₂YbSbO₇, Gd₂YbSbO₇, or Y₂YbSbO₇ offered some useful insights for the design of new photocatalysts for the photocatalytic H₂ and O₂ evolution.

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