Photocatalytic Water Splitting for Hydrogen Production with Gd$_2$MSbO$_7$ (M = Fe, In, Y) Photocatalysts under Visible Light Irradiation

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Abstract: Novel photocatalysts Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ and Gd$_2$YSbO$_7$ were synthesized by the solid state reaction method for the first time. A comparative study about the structural and photocatalytic properties of Gd$_2$MSbO$_7$ (M = Fe, In, Y) was reported. The results showed that Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ and Gd$_2$YSbO$_7$ crystallized with the pyrochlore-type structure, cubic crystal system and space group Fd3m. The lattice parameter $a$ for Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$ was 10.276026 Å, 10.449546 Å or 10.653651 Å. The band gap of Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$ was estimated to be 2.151 eV, 2.897 eV or 2.396 eV. For the photocatalytic water-splitting reaction, H$_2$ or O$_2$ evolution was observed from pure water with Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$ as catalyst under visible light irradiation (wavelength $>$ 420 nm). Moreover, H$_2$ or O$_2$ also split by using Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$ as catalyst from CH$_3$OH/H$_2$O or AgNO$_3$/H$_2$O solutions under visible light irradiation ($\lambda$ $>$ 420 nm). Gd$_2$FeSbO$_7$ showed the highest activity compared with Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$. At the same time, Gd$_2$InSbO$_7$ showed higher activity compared with Gd$_2$YSbO$_7$. The photocatalytic activities were further improved under visible light irradiation with Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$ 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 Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$. 
**Keywords:** Gd$_2$MSbO$_7$ (M = Fe; In; Y); photocatalytic water splitting; visible light irradiation; photocatalytic property

1. Introduction

Since water splitting reaction with TiO$_2$ as catalyst was discovered in 1972 [1], photocatalysis, as one energy-conserving and green emerging technology, has been studied massively and in detail for producing renewable hydrogen. However, early photocatalysts were applied conditionally for their ultraviolet light response. In order to make good use of exhaustless solar energy, plenty of endeavors were made to develop visible light responsive photocatalysts. By summarizing recent research achievements, there were mainly two approaches to obtain visible light responsive photocatalysts. The first approach was to modify TiO$_2$, such as by ion doping [2–4] or forming heterojunction [5–7], which was studied most repeatedly due to its non-toxic performance, excellent stability and low cost. The second approach was to develop new photocatalysts, which had also achieved great progress [8–14]. Especially, the reported CdS photocatalyst [15], with Pt and PdS together as cocatalysts, realized a high quantum efficiency up to 93% in photocatalytic H$_2$ production, which had aroused wide attention across the world. It was known that TiO$_2$ could not be used in the visible light region and could only split water under ultraviolet light irradiation. Moreover, ultraviolet light only occupied 4% of sunlight, which was a limitative factor for photocatalytic technology with TiO$_2$ as the catalyst. Thus, the efficient photocatalysts which could produce electron–hole pairs under visible light irradiation should be developed because visible light occupied 43% of sunlight.

Bi$_2$MNBIO$_7$ (M = Fe$^{3+}$, In$^{3+}$) [16] photocatalysts, as one remarkable representation of A$_2$B$_2$O$_7$ compound family, were first found to realize H$_2$ evolution which was obtained from pure H$_2$O during ultraviolet light irradiation. Thereafter, our research group found that Y$_2$GaSbO$_7$ or Y$_2$GdSbO$_7$ [17] compound also successfully realized photocatalytic water splitting for hydrogen production under visible light irradiation. Therefore, we could reasonably deduce that the substitution of metallic element in A$_2$B$_2$O$_7$ compounds by another suitable metallic element might provide a way to find new photocatalysts which could efficiently catalyze water splitting reaction even under visible light irradiation. In addition, the substitution might result in the lattice O$^{2-}$ and O$^-$ ionsorbed on the surface, which created another way to generate hydroxyl radicals and the highly reactive atomic oxygen species and thus could enhance the photocatalytic activity of solid-solution photocatalysts [18]. Moreover, the substitution of metal ion in A$_2$B$_2$O$_7$ compounds would probably affect the energy level and narrow the band gap of the A$_2$B$_2$O$_7$ compound. As a result, some impurity energy levels or narrow band gaps which had low band gap energy would promote carrier concentration, and thus led to huge change in photocatalytic properties of photocatalysts [19]. Therefore, we speculated Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$ catalyst might have phocatalytic potential for water splitting reaction, of which we were more convinced when we found that above novel photocatalysts successfully realized degrading rhodamine B under visible light irradiation [20,21].

In this experiment, we synthesized aforementioned photocatalysts Gd$_2$MSbO$_7$ (M = Fe, In, Y) again by a solid-state reaction method. Different from previous studies, Gd$_2$MSbO$_7$ (M = Fe, In, Y), herein,
served as photocatalysts for splitting water into hydrogen under visible light irradiation. Meanwhile, the structural, photophysical and photocatalytic properties of photocatalysts Gd$_2$MSbO$_7$ (M = Fe, In, Y) were also analyzed more comprehensively.

2. Experimental Section

The novel photocatalysts were synthesized by a solid-state reaction method. Gd$_2$O$_3$, In$_2$O$_3$, Y$_2$O$_3$, Fe$_2$O$_3$ and Sb$_2$O$_3$ with purity of 99.99% (Sinopharm Group Chemical Reagent Co., Ltd., Shanghai, China) were used as starting materials. All powders were dried at 200 °C for 4 h before synthesis. In order to synthesize Gd$_2$YSbO$_7$, the precursors were stoichiometrically mixed, then pressed into small columns and put into an alumina crucible (Shenyang Crucible Co., Ltd., Shenyang, China). Finally, calcination was carried out at 1320 °C for 50 h in an electric furnace (KSL 1700X, Hefei Kejing Materials Technology Co., Ltd., Hefei, China). For the sake of preparing Gd$_2$FeSbO$_7$, the precursors were stoichiometrically churred up, subsequently pressed into small columns and put into an alumina crucible. Eventually, calcination was performed at 1250 °C for 65 h in an electric furnace. Similarly, Gd$_2$InSbO$_7$ was prepared by calcination at 1320 °C for 65 h. The heating rate of calcination was 0.24 °C/s. The crystal structure of Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$ was analyzed by the powder X-ray diffraction method (D/MAX-RB, Rigaku Corporation, Tokyo, Japan) with CuKα radiation (λ = 1.54056 Å). The voltage was 40.0 kV and current was 30.0 mA. The data were collected at 295 K with a step-scan procedure in the range of 2θ = 10°–100°. The step interval was 0.02° for Gd$_2$FeSbO$_7$ or Gd$_2$YSbO$_7$ and the time per step was 1.2 s. The step interval was 0.01° for Gd$_2$InSbO$_7$ and the time per step was 1.0 s. The chemical composition of Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$ was determined by scanning electron microscope-X-ray energy dispersion spectrum (SEM-EDS, LEO 1530VP, LEO Corporation, Krefeld, Germany). The scanning accelerating voltage was 20 kV and linked with an Oxford Instruments X-ray analysis system (Oxford, UK) and X-ray fluorescence spectrometer (XFS, ARL-9800, ARL Corporation, Geneva, Switzerland). The diffuse reflectance spectra of Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$ was analyzed with an UV-visible spectrophotometer (Lambda 40, Perkin-Elmer Corporation, Waltham, MA, USA) in a UV-Vis diffuse reflectance experiment by the dry-pressed disk samples and BaSO$_4$ was used as the reference material. The surface area of Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$ was measured by the Brunauer-Emmett-Teller (BET) method (MS-21, Quantachrome Instruments Corporation, Boynton Beach, FL, USA) with N$_2$ adsorption at liquid nitrogen temperature. All the samples were degassed at 180 °C for 8 h prior to nitrogen adsorption measurements. The BET surface area was determined by a multipoint BET method using the adsorption data in the relative pressure (P/P$_0$) range of 0.05–0.3. A desorption isotherm was used to determine the pore size distribution by the Barret-Joyner-Halender (BJH) method, assuming a cylindrical pore model. The nitrogen adsorption volume at the relative pressure (P/P$_0$) of 0.994 was used to determine the pore volume and average pore size.

The photocatalytic water splitting was carried out 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, Beijing, China) with the incident photon flux $I_0$ of 0.056176 µmol cm$^{-2}$ s$^{-1}$ or 0.078245 µmol cm$^{-2}$ s$^{-1}$ was focused through a shutter window and a 420 nm or 390 nm cut-off filter onto the window face of the cell. The incident photon flux $I_0$ was
determined by a Ray virtual radiation actinometer (FU 100, silicon ray detector, Thorlabs Corporation, Newton, NJ, USA). According to the measured $I_0$ values with 420 nm and 390 nm cut-off filter, the percentage of UV light passing 390 nm cut-off filter was estimated to be 28.2%. The gas which evolved was determined with a thermal conductivity detector TCD-based gas chromatograph (6890 N, Agilent Technologies, Tempe, AZ, USA), which was connected to the gas closed circulation system. One gram of catalyst was suspended in 300 mL H$_2$O under stirrer. 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 CH$_3$OH/H$_2$O solution (50 mL CH$_3$OH, 300 mL H$_2$O) with Pt, NiO or RuO$_2$-loaded powder as the catalyst.

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$_2$PtCl$_6$ solution (Shanghai Chemical Reagent Research Institute, Shanghai, China) as the Pt source. A typical synthesis procedure was as follows: 1 g catalyst powder and a calculated amount of (0.2 wt%) H$_2$PtCl$_6$ solution were mixed in 150 mL deionized water, and the suspension was then irradiated by a 300 W Xe lamp ($\lambda > 420$ nm) under continuous stirring. After 5 h photo-deposition, the suspension was filtered, washed with de-ionized water for 4 times, and finally dried in vacuum at 60 °C for 12 h. NiO or RuO$_2$ which was loaded on the surface of the catalysts, was prepared by the impregnation method by using Ni(NO$_3$)$_2$ or RuCl$_3$ solution (Sinopharm Group Chemical Reagent Co., Ltd., Shanghai, China), separately. Normally, 1 g catalyst powder was ultrasonically dispersed in 20 mL deionized water, and then a calculated amount of metal precursors (1.0 wt%) Ni(NO$_3$)$_2$ or RuCl$_3$ solution was added to the catalyst powder dispersed water. After magnetically stirring for 1 h, the mixed solution was boiled at 100 °C, and next dried at 60 °C for 12 h. Lastly, the as obtained sample was put into an electric furnace to calcine for 4 h at 450 °C in moving air.

3. Results and Discussion

3.1. Characterization

Figure 1 shows the X-ray powder diffraction patterns of Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ and Gd$_2$YSbO$_7$. It could be seen from Figure 1 that Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$ was a single phase. The calculations of lattice parameters were performed with the program of Cambridge serial total energy package (CASTEP) and first-principles simulation. The CASTEP package was provided by Materials Studio software and the CASTEP calculation was composed of the plane-wave pseudopotential total energy method according to the density functional theory. Thus, our calculations were based on the plane-wave-based density functional theory (DFT) in generalized gradient approximations (GGA) with Perdew–Burke–Ernzerh of (PBE) exchange-correlation potential.

In order to obtain the crystal lattice parameters, Rietveld refinement from X-Ray Diffraction (XRD) data was performed with DBWS software, experimental XRD data and simulation XRD data. The uncertainty of the refined lattice parameters lay in the estimated standard deviation (e.s.d.), calculated by the full pattern fitting program. However, e.s.d. was a measure of precision rather than of accuracy, and these two terms must not be confused. For a sound estimation of the measurement uncertainty of lattice parameters that were refined from XRD data, more information was needed than just the e.s.d.
that was provided by the Rietveld refinement of the diffraction pattern of the sample. The outcome of refinements for Gd2InSbO7 generated the unweighted R factors, \( R_p = 12.13\% \) with space group Fd3m. As for Gd2YSbO7, \( R_p \) was 12.16\% with space group Fd3m. As for Gd2FeSbO7, \( R_p \) was 16.20\% with space group Fd3m. According to the Rietveld analysis, Gd2FeSbO7, Gd2InSbO7 or Gd2YSbO7 had the pyrochlore-type structure and a cubic crystal system which owned a space group Fd3m. The atomic coordinates and structural parameters of Gd2FeSbO7, Gd2InSbO7 and Gd2YSbO7 are listed in Tables 1–3, respectively. The lattice parameter \( a \) for Gd2FeSbO7, Gd2InSbO7 or Gd2YSbO7 was 10.276026 Å, 10.449546 Å or 10.653651 Å. Moreover, the XRD results showed that two theta angles of each reflection of Gd2FeSbO7 changed with Fe3+ being substituted by In3+ or Y3+. The lattice parameter \( a \) increased from \( a = 10.276026 \) Å for Gd2FeSbO7 to \( a = 10.449546 \) Å for Gd2InSbO7, which indicated a decrease in the lattice parameter of the photocatalyst with a decrease of the M ionic radii, Fe3+ (0.78 Å) < In3+ (0.92 Å). The lattice parameter \( a \) also increased from \( a = 10.276026 \) Å for Gd2FeSbO7 to \( a = 10.653651 \) Å for Gd2YSbO7, which indicated a decrease in lattice parameter of the photocatalyst with decrease of the M ionic radii, Fe3+ (0.78 Å) < Y3+ (1.019 Å). Meanwhile, The lattice parameter \( a \) also increased from \( a = 10.449546 \) Å for Gd2InSbO7 to \( a = 10.653651 \) Å for Gd2YSbO7, which indicated a decrease in lattice parameter of the photocatalyst with a decrease of the M ionic radii, In3+ (0.92 Å) < Y3+ (1.019 Å).

Figure 1. X-ray powder diffraction pattern of Gd2FeSbO7, Gd2InSbO7 or Gd2YSbO7 prepared by a solid-state reaction method at 1250 °C, 1320 °C or 1320 °C.

Table 1. Structural parameters of Gd2YSbO7 prepared by solid-state reaction method. \( x, y \) and \( z \) refer to the position coordinates of different atoms in one unit cell, respectively.

| Atom   | \( x \)   | \( y \)   | \( z \)   | Occupation Factor |
|--------|-----------|-----------|-----------|------------------|
| Gd     | 0.00000   | 0.00000   | 0.00000   | 1.0              |
| Y      | 0.50000   | 0.50000   | 0.50000   | 0.5              |
| Sb     | 0.50000   | 0.50000   | 0.50000   | 0.5              |
| O(1)   | -0.16519  | 0.12500   | 0.12500   | 1.0              |
| O(2)   | 0.12500   | 0.12500   | 0.12500   | 1.0              |
Table 2. Structural parameters of Gd$_2$BiSbO$_7$ prepared by solid-state reaction method. $x, y$ and $z$ refer to the position coordinates of different atoms in one unit cell, respectively.

| Atom | $x$     | $y$     | $z$     | Occupation Factor |
|------|---------|---------|---------|-------------------|
| Gd   | 0.00000 | 0.00000 | 0.00000 | 1.0               |
| Bi   | 0.50000 | 0.50000 | 0.50000 | 0.5               |
| Sb   | 0.50000 | 0.50000 | 0.50000 | 0.5               |
| O(1) | −0.14538| 0.12500 | 0.12500 | 1.0               |
| O(2) | 0.12500 | 0.12500 | 0.12500 | 1.0               |

Table 3. Structural parameters of Gd$_2$FeSbO$_7$ prepared by solid-state reaction method. $x, y$ and $z$ refer to the position coordinates of different atoms in one unit cell, respectively.

| Atom | $x$     | $y$     | $z$     | Occupation Factor |
|------|---------|---------|---------|-------------------|
| Gd   | 0.00000 | 0.00000 | 0.00000 | 1.0               |
| Fe   | 0.50000 | 0.50000 | 0.50000 | 0.5               |
| Sb   | 0.50000 | 0.50000 | 0.50000 | 0.5               |
| O(1) | −0.20249| 0.12500 | 0.12500 | 1.0               |
| O(2) | 0.12500 | 0.12500 | 0.12500 | 1.0               |

Figure 2 represents the diffuse reflection spectra of Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ and Gd$_2$YSbO$_7$. Compared with well-known photocatalyst TiO$_2$ whose absorption edge was only 380 nm, the absorption band edge of Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$ was found to be 586 nm, 428 nm or 479 nm. Clearly, the obvious absorption did not result from reflection and scattering. Consequently, the apparent absorbance at sub-band gap wavelengths (600–800 nm for Gd$_2$FeSbO$_7$, and 425–800 nm for Gd$_2$InSbO$_7$, and 490–700 nm for Gd$_2$YSbO$_7$) was higher than zero.

Figure 2. The diffuse reflection spectrum of Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$.

For a crystalline semiconductor, the optical absorption near the band edge followed the equation: $ahv = A (hv - E_g)^n$ [22,23]. Here, $A$, $\alpha$, $E_g$ and $v$ were proportional constant, absorption coefficient, band gap and light frequency, respectively. $E_g$ and $n$ could be calculated by the following steps: (i) plotting $\ln(ahv)$ vs. $\ln(hv - E_g)$ by assuming an approximate value of $E_g$; (ii) deducing the value of $n$ according to the slope in this graph; (iii) refining the value of $E_g$ by plotting $(ahv)^{1/n}$ vs. $hv$ and...
extrapolating the plot to \((ahv)^{1/n} = 0\). According to the above method, the band gap of Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$ was estimated to be 2.151 eV, 2.897 eV or 2.396 eV.

3.2. Photocatalytic Activity of Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ and Gd$_2$YSbO$_7$

Generally speaking, the semiconductor photocatalysis started from the direct absorption of supra-band gap 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$_2$ or O$_2$ evolution rate by using Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$ as photocatalyst from CH$_3$OH/H$_2$O or AgNO$_3$/H$_2$O solution, respectively. The wavelength (\(\lambda\)) dependence on the photocatalytic activity under light irradiation from full arc up to \(\lambda = 420\) nm was measured by using different cut-off filters.

Figure 3a shows the photocatalytic H$_2$ evolution from pure water with Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$ as catalyst under visible light irradiation (\(\lambda > 420\) nm, 0.5 g power sample, 250 mL pure water). It could be found from Figure 3a that under visible light irradiation, the rate of H$_2$ evolution in the first 28 h with Gd$_2$FeSbO$_7$ as catalyst was 6.329 \(\mu\)mol h$^{-1}$ g$^{-1}$, and that with Gd$_2$InSbO$_7$ as catalyst was 5.157 \(\mu\)mol h$^{-1}$ g$^{-1}$, and that with Gd$_2$YSbO$_7$ as catalyst was 4.314 \(\mu\)mol h$^{-1}$ g$^{-1}$. Besides, under dark condition, no H$_2$ evolution was detected from pure water with above three catalysts, which reflected the photocatalytic H$_2$ evolution activities from pure water of three synthesized catalysts. The reason that water could be split for H$_2$ evolution from pure water with Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$ as catalyst under visible light irradiation (\(\lambda > 420\) nm) was as following: Water could be split at a wavelength higher than 420 nm. However, the wavelength was not cut in exactly at 420 nm, in fact, the wavelength was cut by +50 or −50 nm, which meant that the wavelength up to 370 nm was probably absorbed by Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$, which could split water to provide tiny amounts of hydrogen generation in our experiment. The recycling experiments were performed three times with the same experimental conditions of Figure 3a, and the results were almost the same as the above results in Figure 3a. It could be seen that the photocatalysts we had produced had good stability and were thus desirably recyclable.

Figure 3b shows the photocatalytic O$_2$ evolution from pure water with Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$ as catalyst under visible light irradiation (\(\lambda > 420\) nm, 0.5 g powder sample, 250 mL pure water). It could be found from Figure 3b that under visible light irradiation, the rate of O$_2$ evolution in the first 28 h with Gd$_2$FeSbO$_7$ as catalyst was 3.158 \(\mu\)mol h$^{-1}$ g$^{-1}$, and that with Gd$_2$InSbO$_7$ as catalyst was 2.574 \(\mu\)mol h$^{-1}$ g$^{-1}$, and that with Gd$_2$YSbO$_7$ as catalyst was 2.149 \(\mu\)mol h$^{-1}$ g$^{-1}$.

Figure 3c shows the photocatalytic H$_2$ evolution from aqueous methanol solution with Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$ as catalyst under visible light irradiation (\(\lambda > 420\) 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 3c that under visible light irradiation, the rate of H$_2$ evolution in the first 28 h with Gd$_2$FeSbO$_7$ as catalyst was 18.271 \(\mu\)mol h$^{-1}$ g$^{-1}$, and that with Gd$_2$InSbO$_7$ as catalyst was 12.479 \(\mu\)mol h$^{-1}$ g$^{-1}$, and that with Gd$_2$YSbO$_7$ as catalyst was 10.986 \(\mu\)mol h$^{-1}$ g$^{-1}$, indicating that the photocatalytic activity of Gd$_2$FeSbO$_7$ was much higher than that of Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$.
We would estimate apparent quantum yield in this paper because scattering effects were assumed to be the same for all the photocatalysts and our system was a suspension rather than a homogeneous solution. The apparent quantum yield for hydrogen evolution at 420 nm with Gd$_2$FeSbO$_7$ as catalyst was 0.446%, and that with Gd$_2$InSbO$_7$ as catalyst was 0.305% and that with Gd$_2$YSbO$_7$ as catalyst was 0.268% under visible light irradiation. Moreover, Gd$_2$InSbO$_7$ showed higher photocatalytic activity than Gd$_2$YSbO$_7$. This also proved that the conduction band level of Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$ was more negative than the reduction potential of H$_2$O for forming H$_2$. The formation rate of H$_2$ increased with decreasing the M ionic radii within Gd$_2$MSbO$_7$ (M = Fe, In, Y), Fe$^{3+}$ (0.78 Å) < In$^{3+}$ (0.92 Å) < Y$^{3+}$ (1.019 Å). The reason was that the surface area of the photocatalyst increased with decreasing the M ionic radii, and the creation of more active sites was realized. As a result, the hydrogen generation rate increased. Moreover, the decrease of the M ionic radii would result
in a decrease for the migration distance of photogenerated electrons and holes to reach the reaction site on the photocatalyst surface. Thus, the photogenerated electrons and holes could get to the photocatalyst surface more quickly. Above factors would suppress the electron–hole recombination, therefore, the photocatalytic activity would be enhanced. Such results were in good agreement with the optical absorption property of Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$ (see Figure 2). The rate of H$_2$ evolution also increased with increasing illumination time. The photocatalytic activity of Gd$_2$FeSbO$_7$ increased by about 166% than that of Gd$_2$YSbO$_7$.

Figure 4 shows the photocatalytic O$_2$ evolution from AgNO$_3$ solution with Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$ as catalyst under visible light irradiation ($\lambda > 420$ nm, 0.5 g photocatalyst, 1 mmol AgNO$_3$, 270 mL pure water). It could be seen from Figure 4 that under visible light irradiation, the rate of O$_2$ evolution in the first 28 h with Gd$_2$FeSbO$_7$ as catalyst was 34.329 μmol h$^{-1}$ g$^{-1}$, and that with Gd$_2$InSbO$_7$ as catalyst was 23.264 μmol h$^{-1}$ g$^{-1}$, and that with Gd$_2$YSbO$_7$ as catalyst was 17.200 μmol h$^{-1}$g$^{-1}$, indicating that the valence band level of Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$ was more positive than the oxidation potential of H$_2$O for forming O$_2$. The formation rate of O$_2$ increased with decreasing the M ionic radii within Gd$_2$MnSbO$_7$ (M = Fe, In, Y), Fe$^{3+}$ (0.78 Å) < In$^{3+}$ (0.92 Å) < Y$^{3+}$ (1.019 Å). The apparent quantum yield for the oxygen evolution at 420 nm with Gd$_2$FeSbO$_7$ as catalyst was 1.677%, and that with Gd$_2$InSbO$_7$ as catalyst was 1.136%, and that with Gd$_2$YSbO$_7$ as catalyst is 0.840% under visible light irradiation.

![Figure 4](image-url)

**Figure 4.** Photocatalytic O$_2$ evolution from AgNO$_3$ solution with Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$ as catalyst under visible light irradiation ($\lambda > 420$ nm, 0.5 g photocatalyst, 1 mmol AgNO$_3$, 270 mL pure water). Light source: 300 W Xe lamp.

Figure 5 shows the photocatalytic H$_2$ evolution from aqueous methanol solution with Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$ as catalyst under light irradiation (390 nm cut-off filter, 0.5 g 0.1 wt% Pt-loaded powder sample, 50 mL CH$_3$OH, 200 mL pure water). It was depicted in Figure 5 that under light irradiation (390 nm cut-off filter), the rate of H$_2$ evolution in the first 28 h with Gd$_2$FeSbO$_7$ as catalyst was 49.707 μmol h$^{-1}$ g$^{-1}$, and that with Gd$_2$InSbO$_7$ as catalyst was 35.900 μmol h$^{-1}$ g$^{-1}$, and that with Gd$_2$YSbO$_7$ as catalyst was 29.457 μmol h$^{-1}$ g$^{-1}$, indicating that the effect of wavelength ($\lambda$) dependence on the photocatalytic activity was very important. The apparent quantum yield for hydrogen evolution at 390 nm with Gd$_2$FeSbO$_7$ as catalyst was 0.871%, and that with Gd$_2$InSbO$_7$ as
catalyst was 0.629% and that with Gd$_2$YSbO$_7$ as catalyst was 0.516% under light irradiation (390 nm cut-off filter).

The photocatalytic H$_2$ evolution from aqueous methanol solution with Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$ as catalyst under light irradiation (No cut-off filter, 0.5 g 0.1 wt% Pt-loaded powder sample, 50 mL CH$_3$OH, 200 mL pure water) are shown in Figure 6. It could be found from Figure 6 that under light irradiation without using any filters, the rate of H$_2$ evolution in the first 28 h with Gd$_2$FeSbO$_7$ as catalyst was 94.614 μmol h$^{-1}$ g$^{-1}$, and that with Gd$_2$InSbO$_7$ as catalyst was 70.893 μmol h$^{-1}$ g$^{-1}$, and that with Gd$_2$YSbO$_7$ as catalyst was 57.100 μmol h$^{-1}$ g$^{-1}$, indicating that Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$ shows high photocatalytic activity under full arc irradiation. The apparent quantum yield for hydrogen evolution at 420 nm with Gd$_2$FeSbO$_7$ as catalyst was 2.311%, and that with Gd$_2$InSbO$_7$ as catalyst was 1.731%, and that with Gd$_2$YSbO$_7$ as catalyst was 1.394% under light irradiation without using any filters. The photocatalytic activity decreased with increasing incident wavelength λ. As to Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$, the turnover number—the ratio of total amount of gas evolves to catalyst—exceeded 1 for Gd$_2$FeSbO$_7$ after 46 h reaction time, exceeded 1 for Gd$_2$InSbO$_7$ after 57 h reaction time, and exceeded 1 for Gd$_2$YSbO$_7$ after 66 h reaction time under visible light irradiation (λ > 420 nm). Under the condition of full arc irradiation, after 28 h of reaction time, the turnover number exceeded 1.60 for Gd$_2$FeSbO$_7$, and the turnover number exceeded 1.32 for Gd$_2$InSbO$_7$, and the turnover number exceeded 1.02 as to Gd$_2$YSbO$_7$. 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.

**Figure 5.** Photocatalytic H$_2$ evolution from aqueous methanol solution with Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$ as catalyst under light irradiation (390 nm cut-off filter, 0.5 g 0.1 wt% Pt-loaded powder sample, 50 mL CH$_3$OH, 200 mL pure water). Light source: 300 W Xe lamp.
It was known that TiO$_2$ has very high photocatalytic activity under ultraviolet light irradiation. By contrast, the photocatalytic activity was not obtained with Pt/TiO$_2$ as catalyst under visible light irradiation (λ > 420 nm), while an obvious photocatalytic activity was observed with Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$ as catalyst, showing that Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$ could respond to visible light irradiation. The formation rate of H$_2$ evolution with Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$ as catalyst was much larger than that with TiO$_2$ as catalyst under visible light irradiation. This indicated that the photocatalytic activity of Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$ for decomposing CH$_3$OH/H$_2$O solution was higher than that of TiO$_2$. The structure of Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$ after photocatalytic reaction was also checked by using X-ray diffraction method, and no change in their structures was observed during this reaction, which indicated that the H$_2$ evolution was induced from the photocatalytic reaction of H$_2$O.

Figure 7 shows the effect of Pt, NiO and RuO$_2$ co-catalysts on the photoactivity of Gd$_2$FeSbO$_7$ under visible light irradiation (λ > 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 co-catalyst particles and the recombination of the photoinduced electrons with the photoinduced holes was therefore markedly suppressed. It could be found from Figure 7 that in the first 28 h under visible light irradiation, the rate of H$_2$ evolution was estimated to be 41.471 μmol h$^{-1}$ g$^{-1}$ with 0.2 wt%-Pt/Gd$_2$FeSbO$_7$ as catalyst, and that was estimated to be 32.064 μmol h$^{-1}$ g$^{-1}$ with 1.0 wt%-NiO/Gd$_2$FeSbO$_7$ as catalyst, and that was estimated to be 24.114 μmol h$^{-1}$ g$^{-1}$ with 1.0 wt%-RuO$_2$/Gd$_2$FeSbO$_7$ as catalyst, indicating that the photocatalytic activities could be further improved under visible light irradiation with Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$ being loaded by Pt, NiO or RuO$_2$. The apparent quantum yield for hydrogen evolution at 420 nm with 0.2 wt%-Pt/Gd$_2$FeSbO$_7$ as catalyst was 1.013%, and that with 1.0 wt%-NiO/Gd$_2$FeSbO$_7$ as catalyst was 0.783%, and that with 1.0 wt%-RuO$_2$/Gd$_2$FeSbO$_7$ as catalyst was 0.589% under visible light irradiation (λ > 420 nm). The effect of Pt was better than that of NiO or RuO$_2$ for improving the photocatalytic activity of Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$. 

**Figure 6.** Photocatalytic H$_2$ evolution from aqueous methanol solution with Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YSbO$_7$ as catalyst under light irradiation (No cut-off filter, 0.5 g 0.1 wt% Pt-loaded powder sample, 50 mL CH$_3$OH, 200 mL pure water). Light source: 300 W Xe lamp.
It was known that the process for photocatalysis of semiconductors was the direct absorption of photon by band gap 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 band gap of the semiconductor. Upon excitation of photon, the separated electron and hole could follow the solid surface. This suggested that the narrow band gap could more easily 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 H$_2$ evolution, and the valence band potential level was more positive than that of O$_2$ evolution, decomposition of water could occur even without applying electric power [1]. According to the above analysis, the photon absorption of Gd$_2$FeSbO$_7$ was much easier than that of the Gd$_2$InSbO$_7$ or Gd$_2$YbO$_7$, which resulted in higher photocatalytic activity of Gd$_2$FeSbO$_7$.

The information about the specific surface area, pore volume, average pore size of Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ and Gd$_2$YbO$_7$ are presented in Table 4, from which we could see that the specific surface area of Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YbO$_7$ was measured to be 4.12 m$^2$ g$^{-1}$, 3.26 m$^2$ g$^{-1}$ or 1.28 m$^2$ g$^{-1}$, which was significantly smaller than that of TiO$_2$ photocatalyst (53.8 m$^2$ g$^{-1}$). Above results indicated much higher potential efficiency of Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YbO$_7$. Although the surface area of Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YbO$_7$ was smaller than that of TiO$_2$, but Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YbO$_7$ showed higher photocatalytic activity for H$_2$ evolution under visible light irradiation, which indicated that the high photocatalytic activity of the Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YbO$_7$ was not owing to a big surface area, but rather due to the narrow band gap. It was obvious that further increase in photocatalytic activity might be prospected from increasing the surface area of Gd$_2$FeSbO$_7$, Gd$_2$InSbO$_7$ or Gd$_2$YbO$_7$. Since an efficient photocatalytic reaction process occurred on the photocatalyst surface, the increase of the surface area for the photocatalysts might lead to the increase of their photocatalytic activity.
Table 4. The detailed information about the specific surface area, pore volume, average pore size of Gd₂FeSbO₇, Gd₂InSbO₇ and Gd₂YSbO₇ catalysts.

| Catalyst       | Specific Surface Area (m² g⁻¹) | Pore Volume (cm³ g⁻¹) | Average Pore Size (nm) |
|----------------|-------------------------------|-----------------------|------------------------|
| Gd₂FeSbO₇      | 4.12                          | 0.034                 | 33                     |
| Gd₂InSbO₇      | 3.26                          | 0.033                 | 41                     |
| Gd₂YSbO₇       | 1.28                          | 0.019                 | 59                     |

4. Conclusions

In the present work, we prepared single phase of Gd₂FeSbO₇, Gd₂InSbO₇ or Gd₂YSbO₇ by solid-state reaction method and studied the structural, optical and photocatalytic properties of Gd₂FeSbO₇, Gd₂InSbO₇ or Gd₂YSbO₇. Rietveld structure refinement results revealed that Gd₂FeSbO₇, Gd₂InSbO₇ or Gd₂YSbO₇ crystallized with the pyrochlore-type structure, cubic crystal system and space group Fd3m. The lattice parameter a for Gd₂FeSbO₇, Gd₂InSbO₇ or Gd₂YSbO₇ was 10.276026 Å, 10.449546 Å or 10.653651 Å. The band gap of Gd₂FeSbO₇, Gd₂InSbO₇ or Gd₂YSbO₇ was estimated to be 2.151 eV, 2.897 eV or 2.39 eV. Gd₂FeSbO₇, Gd₂InSbO₇ or Gd₂YSbO₇ showed optical absorption in the visible light region, indicating that above 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 Gd₂FeSbO₇, Gd₂InSbO₇ or Gd₂YSbO₇ as catalyst under visible light irradiation (λ > 420 nm). In addition, under visible light irradiation (λ > 420 nm), H₂ or O₂ was also produced by using Gd₂FeSbO₇, Gd₂InSbO₇ or Gd₂YSbO₇ as catalyst from CH₃OH/H₂O or AgNO₃/H₂O solutions. Gd₂FeSbO₇ showed the highest activity compared with Gd₂InSbO₇ or Gd₂YSbO₇. At the same time, Gd₂InSbO₇ showed higher activity compared with Gd₂YSbO₇. The photocatalytic activities were further improved under visible light irradiation with Gd₂FeSbO₇ 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 Gd₂FeSbO₇. Moreover, the synthesis of Gd₂FeSbO₇, Gd₂InSbO₇ or Gd₂YSbO₇ offered some useful insights for the design of new photocatalysts for the photocatalytic evolution of H₂ or O₂.

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Author Contributions

Jingfei Luan conceived and designed the experiment project. Yanyan Li performed the experiments. Jingfei Luan and Yanyan Li wrote the paper. All authors read and approved the manuscript.
Conflicts of Interest

The authors declare no conflict of interest.

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