

Visible Light Driven ZnFe₂Ta₂O₉ Catalyzed Decomposition of H₂S for Solar Hydrogen Production[†]

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Received May 31, 2007

Tantalum-containing metal oxides, well known for their efficiency in water splitting and H₂ production, have never been used in visible light driven photodecomposition of H₂S and H₂ production. The present work is an attempt in this direction and investigates their efficiency. A mixed metal oxide, ZnFe₂Ta₂O₉, with the inclusion of Fe₂O₃ to impart color, was prepared by the conventional ceramic route in single- and double-calcinations (represented as ZnFe₂Ta₂O₉-SC and ZnFe₂Ta₂O₉-DC respectively). The XRD characterization shows that both have identical patterns and reveals tetragonal structure to a major extent and a minor contribution of orthorhombic crystalline system. The UV-visible diffuse reflection spectra demonstrate the intense, coherent and wide absorption of visible light by both the catalysts, with absorption edge at 650 nm, giving rise to a band gap of 1.9 eV. Between the two catalysts, however, ZnFe₂Ta₂O₉-DC has greater absorption in almost the entire wavelength region, which accounts for its strong brown coloration than ZnFe₂Ta₂O₉-SC when viewed by the naked eye. In photocatalysis, both catalysts decompose H₂S under visible light irradiation ($\lambda \geq 420$ nm) and produce solar H₂ at a much higher rate than previously reported catalysts. Nevertheless, ZnFe₂Ta₂O₉-DC distinguishes itself from ZnFe₂Ta₂O₉-SC by exhibiting a higher efficiency because of its greater light absorption. Altogether, the tantalum-containing mixed metal oxide proves its efficient catalytic role in H₂S decomposition and H₂ production process also.

Key Words : ZnFe₂Ta₂O₉, Photocatalyst, H₂S decomposition, Solar hydrogen

Introduction

Visible light mediated photohydrogen production is the best form of conversion of solar energy, because H₂ is the environmentally-clean and ideal source of energy.¹ Ever since the first attempt by Fujishima and Honda,² in photohydrogen production under UV radiation, extensive efforts have been invested in developing visible light active photocatalysts. Visible light is less energetic than UV but is more abundant (about 46%) in the solar spectrum on earth. Among the different categories of semiconductor photocatalysts, the metal oxide materials find a prominent place. Because they have certain intrinsic advantages like stability, simple preparation, modification of the properties through non-stoichiometry, and reactivity with high oxidation potentials etc. Choi *et al.*³ have recently reported the photocatalytic decomposition of ammonia by nanosized TiO₂, V-TiO₂ and Pt/V-TiO₂. Kim *et al.*,⁴ have demonstrated UV light induced photocatalytic degradation of cyanides in aqueous solution over transition metal ion doped TiO₂. The development of new alkali and alkaline earth tantalum oxide materials has been made by Kudo⁵ for water splitting and H₂ production under UV irradiation.

Metal oxides possess suitable and flexible crystalline

structure so that any chemical modification (cationic or anionic doping or a mixture of colored oxide materials) narrows their large band gaps to visible region and makes them visible active photocatalysts. This phenomenon has led to a keen interest on metal oxides. Solar hydrogen production from H₂S decomposition is less energetic than from water splitting and is also environmentally advantageous. Because H₂S is a noxious toxic gas component and is plentifully available in millions of tons of quantities in petroleum refineries⁶ and in natural gas fields (about 30% output⁷). Hence, H₂S is certainly a huge utilizable energy resource. However, as a waste byproduct, H₂S is unwantably decomposed and detoxified in every industry and gas field with the expense of energy. Therefore, it becomes obvious that the solar hydrogen, the fuel of future¹ when produced from H₂S, brings forth the twin benefits of sustainable energy resource and environmental pollution control. The Trari group has been doing systematic studies on solar H₂ production from aqueous alkaline solution containing S²⁻, SO₃²⁻ and S₂O₃²⁻ ions over colored delafossite metal oxides, CuMnO₂⁸, p-type CuYO₂⁹ and CuCrO₂.¹⁰ A novel photocatalyst ZnBiVO₄ with monoclinic crystalline structure from ceramic route and nanocrystalline from solution route, was prepared and examined for H₂S decomposition. In relation to its structure; it was found that the solution route nanomaterial was more effective than the other.¹¹ A recent communication from our laboratory reports that self-

[†]This paper is dedicated to Professor Sang Chul Shim on the occasion of his honorable retirement.

assembled hexagonal prismatic Cu doped ZnO wurtzite nanoparticles function as active photocatalyst for H₂ production from H₂S.¹² The studies are, however, limited as shown above. Especially, to the best of our knowledge, no tantalum metal oxide catalyst has so far been studied for photocatalytic decomposition of H₂S and H₂ production. In water splitting, however, tantalum oxides are well known.^{5,13,14} Furthermore, there is a continuous strive to find better efficiency catalyst. In this context, our present work with the catalyst ZnFe₂Ta₂O₉ assumes significance.

The present work is an investigation of visible light driven ($\lambda \geq 420$ nm) decomposition of H₂S in aqueous medium and the resultant solar H₂ production using the catalyst ZnFe₂Ta₂O₉. The mere tantalum oxide or in combination with ZnO does not absorb visible light. Hence Fe₂O₃ was incorporated, which imparted brown color and visible activity. Prepared by the conventional ceramic route, the present visible photocatalyst ZnFe₂Ta₂O₉ exhibits a higher efficiency in decomposition of H₂S and production of solar H₂. Also the effect of times of calcinations, i.e., single- or double-calcinations of the oxide precursors at the identical conditions, is investigated with an application of point of view.

Experimental Section

Materials. The metal oxides, Fe₂O₃ (> 98% purity), ZnO (99.9%) and Ta₂O₅ (99.9%) were purchased from Yakuri, Japan, Sigma-Aldrich and Strem, USA, respectively. H₂S was of 99.9% purity. Ultra-pure water was used throughout the experiment. All other chemicals used were of reagent grade. All chemical items were used without further purification.

Preparation of catalysts. The present photocatalyst was prepared by the conventional solid state reaction method.¹¹ In a single-calcination process, the oxide precursors in appropriate quantities were ground thoroughly in a mortar and pestle until they became homogeneous and the mixture was then calcined in static air at 1165 °C for 15 h in a single step. After cooling, the sample was collected, ground well and stored. In the double-calcination process, the single-calcined catalyst was calcined again under identical condition in a second time and the catalyst was ground well as above and stored.

Characterizations. Crystal structure was elucidated by XRD measurements (Rigaku-D/MaX-2200 V X-ray diffractometer, 40 kV/40 mA, CuK_α radiation, $\lambda = 1.5405$ Å, graphite filter) in the 2θ range of 10–90°. The specific surface area of the powder samples was determined by the BET and Langmuir nitrogen adsorption/desorption method in Micromeritics TriStar 3000 apparatus. Diffuse reflectance spectra of the catalysts were recorded with a Shimadzu spectrophotometer (model UV-2450), with BaSO₄ reference and were converted to absorbance instrumentally by the Kubelka-Munk method.

Photocatalytic decomposition of H₂S. Photocatalytic decomposition of H₂S was carried out in cylindrical Pyrex

outer-irradiation type photochemical reactor equipped with a quartz window and a thermostated water jacket. The light source was a 450 W xenon lamp (Oriel) with a cut-off filter for UV radiation ($\lambda \geq 420$ nm) and a water jacket filter for IR radiation. In a typical experiment, initially 250 mL of 0.5 M aqueous KOH solution vigorously stirred and thermostated at 25 ± 1 °C, was purged with argon for 1 h and then with bubbling H₂S gas for 1 h. 0.5 g of the catalyst was then dispersed and H₂S was passed at a flow rate of 2.5 mL/min with excess gas being trapped in NaOH solution. Under this condition, the aqueous slurry was irradiated with visible light. H₂ evolved was determined by GC (Shimadzu 14B, MS-5 Å column, TCD detector and Ar carrier gas) and the gas was collected in a graduated burette.

The quantum yield was measured using a 450 W Xe lamp (Oriel) attached with an IR filter (Oriel), an interference filter (500 ± 5 nm; Oriel) and a cut off filter ($\lambda \geq 420$ nm; Oriel). The number of incident photons was measured using a silicon photodiode with integrating sphere (Oriel). The quantum yield (%) is calculated by the following equation:⁶

$$\text{Quantum Yield (\%)} = \frac{[\text{Number of H}_2 \text{ molecules evolved} \times 2]}{[\text{Number of incident photons}]} \times 100$$

Results and Discussion

The single- and double-calcined catalysts, designated respectively as ZnFe₂Ta₂O₉-SC and ZnFe₂Ta₂O₉-DC were characterized structurally and employed in visible light driven photocatalytic decomposition of H₂S and H₂ production. The material characteristics and the remarkable catalytic role of the photocatalysts are described below.

Structural characterization. The XRD patterns of both the catalysts are shown in Figure 1. The pattern exhibits four major high intense sharp peaks and several less intense small peaks. Obviously, the patterns reveal that the catalyst samples are of crystalline nature. However, the two patterns look alike and there is no observable difference. Hence, it can be concluded that (i) the single- and double-calcined catalysts must have the same crystalline structure and (ii) the times of calcination do not have any influence on crystallinity. Many major high intense peaks at $2\theta = 26.8, 34.9$ and 52.8° together with small peaks are assignable to tetragonal structure while only one major peak at $2\theta = 30.4^\circ$ and several minor peaks are attributable to the orthorhombic structure. Thus, a mixed crystalline form has arisen. Perhaps, this is due to the fact that among the three precursor oxides, Ta₂O₅ (JCPDS file # 77-2305) and iron tantalum oxide (JCPDS file # 71-0932) (yielding more major peaks) have tetragonal structure while zinc tantalum oxide (JCPDS file # 39-1484) and iron tantalum oxide (JCPDS file # 25-1401) (yielding only small peaks) have orthorhombic structure, the latter having polymorphism with a major contribution from tetragonal system. Hence, the observed XRD pattern and the peak assignment clearly demonstrate that the photocatalyst

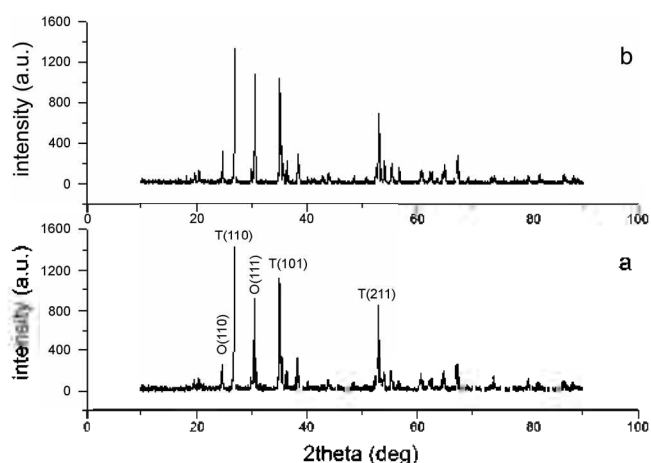


Figure 1. XRD patterns of (a) ZnFe₂Ta₂O₉-SC and (b) ZnFe₂Ta₂O₉-DC; O and T near the (hkl) plane representation refer to orthorhombic and tetragonal crystal systems.

ZnFe₂Ta₂O₉ possesses a mixed crystalline form, qualitatively the tetragonal being in larger proportion. Such a polycrystalline nature is quite possible and in fact, in our previous work,¹¹ we observed tetragonal (major) and monoclinic structural systems for ZnBiVO₄.

The BET and Langmuir surface areas, representatively for the double-calcined catalyst were determined by N₂ adsorption/desorption method. The values are 0.6245 and 1.0266 m²/g, respectively and are only moderate.

Spectral characterization. The UV-visible diffuse absorbance spectra are displayed in Figure 2. The spectra are broad, almost smooth and continuous. These features suggest that on irradiation the electronic transition occurs only from VB to CB and not between any intermediate/impurity levels. Although from XRD, a small degree of

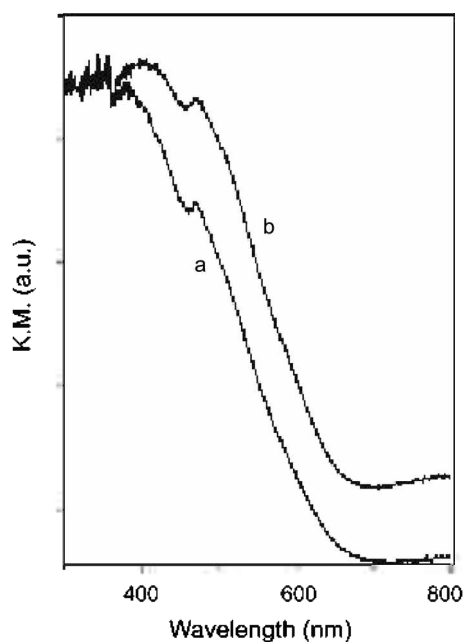


Figure 2. UV-visible diffuse reflectance spectra of (a) ZnFe₂Ta₂O₉-SC and (b) ZnFe₂Ta₂O₉-DC.

orthorhombic system is inferred co-existing in to the major tetragonal crystalline system, the smooth UV-visible spectra indicate that either the orthorhombic system is quantitatively very small or the two systems are so integrated as to lead to single electronic transition. The spectra have a similar absorption edge at about 650 nm, pointing out a band gap of 1.9 eV. The relatively less band gap implies a wide absorption of visible light. All the above-said features are common to both the spectra and are, therefore, applicable to both the single- and double-calcined catalysts. The only differential feature is that the spectrum for double-calcined catalyst, *i.e.*, ZnFe₂Ta₂O₉-DC has greater intensity almost in the entire wavelength region than that for ZnFe₂Ta₂O₉-SC. That means, the former has greater visible light absorption and this observation substantiates the strong and light brown colorations of the two catalysts when viewed by the naked eye. The single and double calcined catalysts are chemically and structurally similar (same XRD pattern). Therefore, the greater absorption of ZnFe₂Ta₂O₉-DC could be attributable only to its absorption coefficient. This parameter is dependent on the electronic transition probability and the magnitude of transition moment integral for the ground and excited electronic state wavefunctions. ZnFe₂Ta₂O₉-DC might have greater transition moment integral value than the single calcined catalyst ZnFe₂Ta₂O₉-SC. Basically this characteristic originates from ordered and coherent molecular structure in ZnFe₂Ta₂O₉-DC relative to ZnFe₂Ta₂O₉-SC, resulting in a greater degree of molecular orbitals overlap and hence a higher transition moment integral value in former.

Photocatalysis. Photocatalytic decomposition of H₂S by the two catalysts, ZnFe₂Ta₂O₉-SC and ZnFe₂Ta₂O₉-DC was carried out in 0.5 M aqueous KOH solution under visible light irradiation of $\lambda \geq 420$ nm. Table 1 presents the H₂ evolution data and the quantum yield. The rates of H₂ evolution per hour for the two catalysts are 1657 μ mol and 2320 μ mol, respectively. This difference leads to about 40% higher efficiency for the latter. It is clear that ZnFe₂Ta₂O₉-DC, the double-calcined catalyst has more activity than ZnFe₂Ta₂O₉-SC. Obviously, the greater efficiency of the double-calcined catalyst arises due to its greater visible light absorption noticed and discussed in the previous section. In conformation to the experimental conditions and the results obtained, the following mechanism is offered for the entire process.

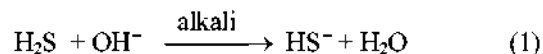
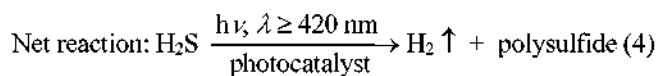
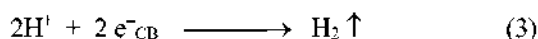
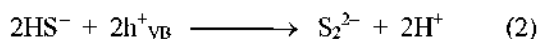


Table 1. Rates of H₂ evolution and quantum yields of the two photocatalysts^a

Catalyst	H ₂ evolution (μ mol/h)	Quantum yield (%)
ZnFe ₂ Ta ₂ O ₉ -SC	1657	8.1
ZnFe ₂ Ta ₂ O ₉ -DC	2320	11.4

^aCatalyst 0.5 g; 250 mL 0.5 M aqueous KOH; H₂S flow 2.5 mL/min; 450 W Xe lamp (Oriol) with cut off filter ($\lambda \geq 420$ nm)



In alkaline medium, H_2S undergoes deprotonation forming hydrosulfide ion, HS^- . h^+_{VB} generated upon band-gap excitation, oxidatively decomposes HS^- ion into H^+ and disulfide ion; e^-_{CB} reduces H^+ and ultimately yields H_2 .

It is of interest to have a comparison of H_2 production activity of $\text{ZnFe}_2\text{Ta}_2\text{O}_9$ -DC with those of previously reported catalysts. Over CuCrO_2 delafossite oxide, Saadi *et al.*¹⁰ have photoelectrochemically produced a maximum H_2 yield of only 2.05 mL/h. However, the present catalyst yields H_2 in a much higher rate (2320 $\mu\text{mol/h}$). Also there is a continuous evolution without any decomposition or degradation of the catalyst.

Conclusions

Tantalum containing mixed metal oxide catalyst in single- and double-calcination was prepared. Both catalysts were found to have tetragonal structure to a larger extent and orthorhombic in smaller degree from XRD characterization. The UV-visible absorption spectra demonstrate their wide visible light absorption with a band gap of 1.9 eV. The stronger absorption of the double-calcined catalyst explains its intense brown coloration. In photocatalysis, both exhibit a greater efficiency than the previously reported catalysts. Between the two, however, the double-calcined catalyst displays a higher activity than the single-calcined catalyst. This effect has origin on the intense light absorption of the

former. Altogether, the tantalum containing mixed metal oxide proves its efficient catalytic role in visible light driven H_2S -decomposition- H_2 -production process also.

Acknowledgement. This research (paper) was performed for the Hydrogen Energy R&D Center, that is one of the 21st Century Frontier R&D Programs funded by the Ministry of Science and Technology, Republic of Korea. The authors thank the authorities concerned for the award of Brain Pool Scheme to our laboratory. This paper is dedicated to professor Sang Chul Shim.

References

1. Nowotny, J.; Sorrell, C.; Sheppard, L. R.; Bak, T. *Int. J. Hydrogen Energy* **2005**, *30*, 521.
2. Fujishima, A.; Honda, K. *Nature* **1972**, *238*, 37.
3. Choi, H. J.; Kim, J. S.; Kang, M. *Bull. Korean Chem. Soc.* **2007**, *28*, 581.
4. Kim, H. J.; Lu, L.; Kim, J. H.; Lee, C. H.; Hyeon, T.; Choi, W.; Lee, H. I. *Bull. Korean Chem. Soc.* **2001**, *22*, 1371.
5. Kudo, A. *Int. J. Hydrogen Energy* **2006**, *31*, 197.
6. Kale, B. B.; Baeg, J. O.; Lee, S. M.; Chang, H.; Moon, S. J.; Lee, C. W. *Adv. Funct. Mater.* **2006**, *16*, 1349.
7. Bessekhoud, Y.; Mohammed, M.; Trari, M. *Sol. Energy Mater. Sol. Cells* **2002**, *73*, 339.
8. Bessekhoud, Y.; Trari, M.; Doumerc, J. P. *Int. J. Hydrogen Energy* **2003**, *28*, 43.
9. Trari, M.; Bouguelia, A.; Bessekhoud, Y. *Solar Energy Mater. Solar Cells* **2006**, *90*, 190.
10. Saadi, S.; Bouguelia, A.; Trari, M. *Solar Energy* **2006**, *80*, 272.
11. Kale, B. B.; Baeg, J. O.; Yoo, J. S.; Lee, S. M.; Lee, C. W.; Moon, S. J.; Chang, H. *Can. J. Chem.* **2005**, *83*, 527.
12. Kanade, K. G.; Kale, B. B.; Baeg, J. O.; Lee, S. M.; Lee, C. W.; Moon, S. J.; Chang, H. *Mater. Chem. Phys.* **2007**, *102*, 98.
13. Hitoki, G.; Takata, T.; Kondo, J. N.; Michikazu, H.; Kobayashi, H.; Domen, K. *Chem. Commun.* **2002**, 1698.
14. Zou, Z.; Ye, J.; Sayama, K.; Arakawa, H. *Nature* **2001**, *414*, 625.