

Synthesis and Structural Analysis of Visible Light Photocatalyst, ZnBiGaO_4 for Photocatalytic Solar Hydrogen Production

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ABSTRACT: In this paper, we are reporting a novel spinel metal oxide photocatalyst, ZnBiGaO_4 for the photocatalytic decomposition of hydrogen sulfide (H_2S) to generate hydrogen. ZnBiGaO_4 was prepared by two different methods. One is usual solid state route and another is hydrothermal route which is the first time we are reporting ZnBiGaO_4 synthesized by this route. The newly prepared ZnBiGaO_4 was characterized for its crystal structure and microstructure by using XRD and Field Emission Scanning Electron Microscopy (FESEM) respectively. XRD analysis revealed that the structure of ZnBiGaO_4 is cubic spinel structure. The photocatalyst was also characterized by using UV-Visible diffuse reflectance spectroscopy to determine its band gap and estimated to 2.8eV. Our prima facie observations revealed that the formation of single-phase cubic spinel ZnBiGaO_4 with significant photocatalytic activity under visible light irradiations for solar hydrogen generation from H_2S .

Keywords: Photocatalyst, ZnBiGaO_4 , H_2S splitting, Hydrothermal synthesis, Hydrogen

1. INTRODUCTION

The hydrogen generation by photocatalytic decomposition of hydrogen sulfide (H_2S) is one of the considerable interest due to environmental hazardness of H_2S . Photocatalytic decomposition of H_2S using oxide photocatalysts provides a good method for the generation of hydrogen and

the removal of the pollutant, hydrogen sulfide and leads to the production of hydrogen, which is a clean fuel and a starting material for many industries. H_2S is considered to be a potential source of hydrogen in the future hydrogen energy economy. An ubiquitous Claus process is currently used for the decomposition of hydrogen sulfide.¹ This conventional Claus process comprises the synproportionation

reaction between H_2S and SO_2 yielding elemental sulfur and water vapor. If, hydrogen can be recovered from H_2S , instead of oxidizing it into H_2O (Claus process), immense amount of hydrogen can be produced.² Photocatalytic splitting of H_2S to H_2 using solar energy is a challenging, interesting and an eminent topic of research with the potential to provide clean and renewable alternate energy to the mankind. This process requires less energy compared to photocatalytic decomposition of water. In this connection, generation of H_2 from H_2S has attracted more attention due to economically viable route and protection of environment. Extensive research work was carried out in the development of ultraviolet driven photocatalysts for water and H_2S splitting. However, there is a demand for highly efficient photocatalyst for photocatalytic production of hydrogen under visible light irradiation. Consequently, development of an active photocatalyst under visible light region has attained immense importance and has become an imperative topic in photocatalysis research today. Unfortunately, the photocatalysts investigated under visible region is still limited.³ It is very essential to control the band structure of the materials for the development of efficient photocatalyst to absorb visible light. The approach for the design of photocatalyst is classified in three ways. Approach (a) is the doping of foreign transition metal ions into active photocatalysts.⁴ Especially, Ni and Cu-doped ZnS photocatalysts show activity for H_2 evolution under visible-light irradiation even without hydrogen evolving Pt metal catalyst. But the activity of photocatalysts still low and needs improvement. Many reports including our work are available of doping method for CdS, ZnS, VS, VS_4 , WO_3 .^{5,6} Approach (b) is to explore materials that have a stable conduction band in a more negative position than the conduction band of conventional metal oxide photocatalysts. The nitrides (Ta_3N_5), oxynitrides (TaON ,

LaTiO_2N) and oxysulfides ($\text{Sm}_2\text{Ti}_2\text{S}_2\text{O}_5$) have been reported as active photocatalysts.^{7, 9} The preparation methods of the oxynitrides and oxysulfides are quite complicated and perilous. Approach (c) is the control of band structure by making solid solutions between metal oxides having wide and narrow band gaps. The photophysical properties and photovoltaic efficiencies of $\text{Nb}_2\text{O}_5\text{-Bi}_2\text{O}_3$, $\text{Ga}_2\text{O}_3\text{-In}_2\text{O}_3$, SrNb_2O_7 , $\text{Sr}_2\text{Ta}_2\text{O}_7$, $\text{SnO}_2\text{-TiO}_2$, ZnS-CdS , CdS-CdSe and $(\text{AgIn})_x\text{Zn}_{2-x}\text{S}_2$ have been studied extensively.¹⁰⁻¹³ Several nanocrystalline photocatalysts have been reviewed by Beydoun et al.¹⁴ for the effect of nanoparticles on photocatalytic activity. Recently, CdS-TiO_2 nanocomposite film has been used for the photodecomposition of H_2S .¹⁵ The stable and suitable metal oxide support is lacking in this field of research. Most of the previous research works are focusing on the photocatalytic decomposition of H_2S by using chalcogenide semiconductor photocatalysts, which are unstable due to photocorrosion during irradiation.¹⁶ So, there is essential to explore stable, economical and efficient new metal oxide photocatalyst for hydrogen production from photocatalytic decomposition of H_2S .

In this paper, we are reporting first time the photocatalytic decomposition of H_2S by using novel spinel oxide photocatalyst, ZnBiGaO_4 . We have synthesised this photocatalyst by solid-state and hydrothermal methods and characterizing its crystalline property and surface morphology by using XRD and FESEM. This paper also describes the novelty in synthesis of new product, its characterization and evaluated for the photocatalytic decomposition of hydrogen sulfide to generate hydrogen under visible light irradiations.

2. EXPERIMENTAL SECTION

2.1 Materials

In our studies, ZnBiGaO_4 was prepared by two methods. One is the solid-state

reactions between stoichiometric amounts of ZnO, Bi₂O₃ and Ga₂O₃ (all are Aldrich grade). Initially, the mixture was ground in a mortar thoroughly to homogeneous and then calcined at 750°C for 24h in static air and re-calcined at 825°C for 12h. Another method is the hydrothermal method. In this method, a stoichiometric amounts of Zn(NO₃)₂ · 5H₂O, Bi(NO₃)₃ · 6H₂O, Ga(NO₃)₃ · xH₂O and urea were taken in teflon lined hydrothermal reactor (100ml). The reactor was filled with water (80% of the volume) and heated at 180°C for 60h. The resulting as-synthesized product was washed several times with water and ethanol and then decomposed to get desired final product at 350°C in air for 5 h. After sintering, the sample was cooled to room temperature slowly, ground to fine powder and stored in light proof vials. Hereafter the ZnBiGaO₄ prepared by solid - state route is termed as ZnBiGaO₄ (s-s) and hydrothermal route is termed as ZnBiGaO₄ (h-t).

2.2 Characterization of photocatalysts

The crystal structure of the photocatalysts has been elucidated by X-ray diffraction measurements using computer-controlled XRD units (Rigaku-D/MaX-2200V X-ray diffractometer with CuK_α radiation of wavelength, $\lambda = 1.5405\text{\AA}$ with Ni as the filter). In order to get the absorbance of the photocatalysts, a Shimadzu spectrophotometer (Model UV-2450) equipped with an integrating sphere was used to record the diffuse reflectance spectra of both ZnBiGaO₄ (s-s) and ZnBiGaO₄ (h-t). The baseline correction was done using a calibrated sample of BaSO₄ from wavelength 200 to 800 nm.

2.3 Photocatalytic studies under visible irradiations

In all experiments, 500 mg of the photocatalyst was dispersed in 250ml of 0.50M of KOH with the H₂S flow (2.5ml/min.) in a Pyrex glass photoreactor with a water-cooled quartz immersion well and thermostated water jacket. The excess

hydrogen sulfide was trapped in NaOH solution. The solution mixture was thermostated at 25°C and vigorously stirred and the dispersion was purged with argon gas for 1h and then hydrogen sulfide (H₂S) was bubbled through the dispersion solution mixture for about 1h. The dispersion solution mixture was irradiated with 450 W xenon-arc lamp (Oriel) in the case of visible light irradiation which produces a line-free continuum from 350 to 2500 nm. The IR radiation and UV radiation were filtered by a water jacket IR filter and 420nm cut-off light filter(Oriel) respectively. The amount of evolved hydrogen was measured using graduated gas burette and the collected gas was detected as hydrogen by GC (Model Shimadzu GC-14B, MS-5Å column, TCD) by using argon as the carrier gas.

3. RESULTS AND DISCUSSION

ZnBiGaO₄ has been synthesized by using solid-state route and hydrothermal route as per the procedure mentioned in experimental part. In general, urea is used for the hydrothermal synthesis to control crystallite size of metal oxides. The change in crystal size depend of urea concentration was mainly explained on the effect of concentrations of hydroxide ions, generated by decomposition of urea, on the supply the solute by diffusion and amount of nucleation.¹⁷ We have stoichiometrically synthesized ZnBiGaO₄ using hydrothermal reaction where urea is used as templating agent. The composition of the final product was determined by using XRD and EDS analyses.

3.1 XRD analysis for crystal structure

Powder XRD patterns for ZnBiGaO₄ (s-s) and ZnBiGaO₄ (h-t) are shown in fig. 1(a) and fig.1(b). The XRD patterns of ZnBiGaO₄ (s-s) and ZnBiGaO₄ (h-t) contain peaks at 24.7°, 27.7° and 32° and these peaks matches with the theoretical values.¹⁸ The major peak at 27.7° shows the

formation of ZnBiGaO_4 . XRD results of ZnBiGaO_4 shows that it is cubic spinel structure.

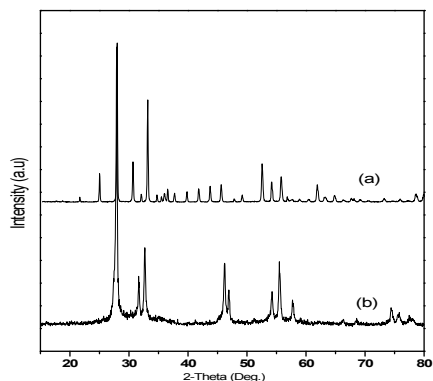


Figure 1: XRD pattern of (a) ZnBiGaO_4 (s-s) and (b) ZnBiGaO_4 (h-t)

The XRD patterns with intense peaks shows high degree of crystallinity. There is no other phases of impurities. DRS of the above material confirms the single phase of ZnBiGaO_4 . The XRD patterns of ZnBiGaO_4 (h-t) shows more widening of peaks due to the nano sized particles. While comparing XRD of ZnBiGaO_4 data with the XRD data of raw materials and their intermediate compounds, there is no impurity of final products.

3.2 Microscopic analysis of photocatalyst powder

Fig.2a and fig.2b depict the FESEM micrographs of ZnBiGaO_4 (s-s) and ZnBiGaO_4 (h-t).

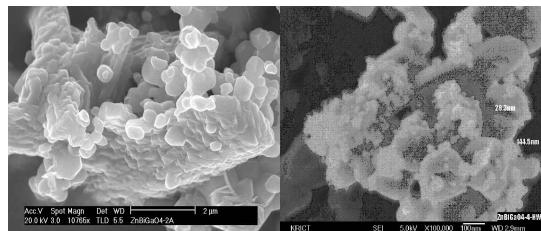


Figure 2: FESEM image of (a) ZnBiGaO_4 (s-s) and (b) ZnBiGaO_4 (h-t)

SEM micrograph of ZnBiGaO_4 (s-s) shows the unique layered structure. The aggregation of particles was observed which suggests the homogeneity of the solid solution with fairly good crystallinity. The very hard nature of the products suggests that there may be formation of highly crystalline glass ceramics having the particle size in the range of 0.2-1.0 μ . ZnBiGaO_4 (h-t) shows little different morphology with layered structure having the particle size in the range 50-150nm which is smaller than ZnBiGaO_4 (s-s) due to low processing temperature.

3.3 Diffused reflectance spectroscopic analysis

Fig.3 shows the UV-vis diffused reflectance spectra of (a) ZnBiGaO_4 (s-s) and (b) ZnBiGaO_4 (h-t). The absorption edge of wavelengths for ZnBiGaO_4 (s-s) and ZnBiGaO_4 (h-t) was 440nm. ZnBiGaO_4 (s-s) has a sharp absorption cut-off as compared to ZnBiGaO_4 (h-t). This implies that ZnBiGaO_4 (s-s) is more crystalline with uniform particles whereas ZnBiGaO_4 (h-t) has mixed crystallites with irregular shape and morphology. These observations are in good agreement with the FESEM results.

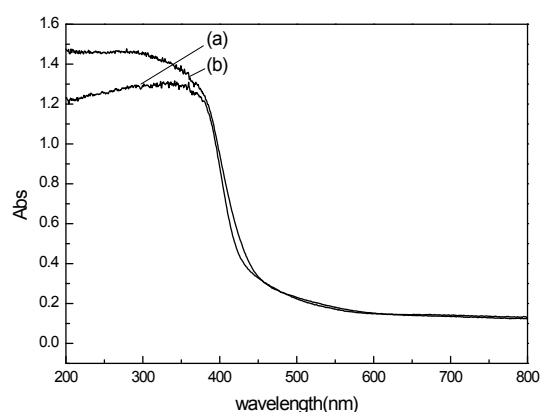


Figure 3: UV-vis diffuse reflectance spectra of (a) ZnBiGaO_4 (s-s) and (b) ZnBiGaO_4 (h-t)

From the DRS spectra, the band gap energies for ZnBiGaO_4 (s-s) and ZnBiGaO_4

(h-t) are same i.e, 2.80 eV. The steep shape of band edge in visible region and strong absorption in the same region also reveals that absorption band of ZnBiGaO₄ is due to the transition between the valence band to the conduction band but not to the transition between the metal impurity level to the conduction band.

3.4 Photocatalytic Studies of ZnBiGaO₄

The efficiency of prepared photocatalysts was evaluated by photocatalytic decomposition of H₂S and generation of hydrogen. Photocatalytic decomposition of H₂S on semiconductor particles is the direct conversion of solar radiation into storable form of hydrogen and solar detoxification of pollutants. Under bandgap excitation, metal oxide semiconductor particles behave as short-circuited electrodes, with both oxidation and reduction processes occurring on their surfaces. Thus two critical processes determine the overall quantum efficiency for interfacial charge transfer. These are the competition between the recombination and the trapping of the charge carriers. It has been shown that in heterogeneous photocatalytic reactions involving proton reduction, the efficiency can be enhanced by the loading of electron transfer catalysts, like Ni or the noble metals on the surface of the semiconductor particles. This affects the dynamics of electron-hole recombination and interfacial charge transfer.

In this paper, the photocatalytic decomposition of hydrogen sulfide by using ZnBiGaO₄ as photocatalyst is presented. Different series of experiments were carried out using photocatalysts of ZnBiGaO₄ (s-s) and ZnBiGaO₄ (h-t). By using ZnBiGaO₄ as new photocatalyst, we have studied the photocatalytic activity under visible light of radiation. Table 1 presents the photocatalytic decomposition of H₂S of ZnBiGaO₄ (s-s) and ZnBiGaO₄ (h-t) under visible light irradiation.

From the table 1, we understand that the both photocatalysts having more or less

similar photocatalytic activities. This implies that there is no effect of size of particle on the photocatalytic activity. ZnBiGaO₄ (s-s) seems to be more crystalline than the ZnBiGaO₄ (h-t) which also observed in XRD and SEM which reflects in the photocatalytic activity. From the above studies, we concluded that the photocatalytic activity is more dependent on crystallinity and good microstructure than the smaller particle size and high surface area.¹⁴ Low light absorption and unsatisfactory stability in time are, unfortunately, typical for smaller particle sized(nanoparticles) photocatalysts.

Table I: Photocatalytic decomposition of H₂S by using ZnBiGaO₄ for H₂ evolution under visible light irradiation

Photocatalyst	Band gap energy(eV)	H ₂ evolution rate(μ mol/h) ^a
ZnBiGaO ₄ (s-s)	2.80	3030
ZnBiGaO ₄ (h-t)	2.80	3022

^a Catalyst 0.5 g; 250 ml 0.5 M aqueous KOH; H₂S flow 2.5 ml/min; 450 W Xe lamp (Oriel) with cut off filter ($\lambda \geq 420$ nm).

The UV-VIS absorption spectra for ZnBiGaO₄ revealed that main light absorption edge at 440nm. This absorption wavelength was increased by 160nm compared to the ZnGa₂O₄ (280nm).³⁴ The band gap for ZnBiGaO₄ is 2.80 eV which is much smaller than the band gap of ZnGa₂O₄, i.e, 4.3 eV. For ZnBiGaO₄, Bismuth is responsible for the reduction of the band gap energy. Recently, ZnGa₂O₄ electronic structure has been discussed thoroughly wherein it was concluded that p-d repulsion is responsible for narrower band gap.¹⁹ Since ZnBiGaO₄ has two 3d bands of Zn and Ga elements and additionally one 5d band of Bi. So, it might be further accelerating the p-d repulsion. This may be one of the reasons

for reduction in the band gap of ZnBiGaO_4 . The other possibility is the conduction band position. The bottom of the conduction band is composed of the $\text{Zn}3d$, $\text{Bi}6s$ and $\text{Ga}4s$ atomic orbitals. Most probably, the strong mixing of Zn , Ga and Bi orbitals in the conduction band of ZnBiGaO_4 are also responsible for the narrow band gap. The large dispersion in DOS indicates the above observations. Thus, the characteristic feature of ZnBiGaO_4 is that the diffuse $4s$ and $4p$ orbitals and $6s$ and $6p$ contribute as an electron acceptor to photocatalysis. So, it confirms that the diffused orbitals of Gallium ($4s$ and $4p$) are responsible for photocatalytic activity under ultraviolet light¹⁷ and diffused orbitals of Bismuth ($6s$ and $6p$) are responsible for the photocatalytic activity under visible light irradiations. Overall, Gallium and Bismuth both are responsible for the photocatalytic activity of ZnBiGaO_4 . Solid photocatalysts so far investigated have been composed of the octahedrally co-ordinated d^{10} transition metals comprises Ti , Zr , Nb and Ta as well as p -block elements like In , Sn , and Sb with d^{10} configuration.^{20, 21} The present study equivocally showed that naked ZnBiGaO_4 comprises Ga^{3+} and Bi^{3+} with d^{10} configuration has the excellent photocatalytic activity. The presence of Gallium in the crystal structure of ZnBiGaO_4 make this photocatalyst thermally, chemically and catalytically more stable. If the novel ZnBiGaO_4 spinel photocatalyst overcoated with RuO_2 and Pt , it will have excellent photocatalytic activity. The further research work on this novel photocatalyst for better performance is on progress.

The reaction mechanisms for the photocatalytic decomposition of H_2S in presence of photocatalyst are proposed.²²

It is known that, in alkaline medium, the photocatalytic decomposition of aqueous sulfide leads to the formation of disulfide ions and no sulfur precipitation is observed.²³

However, hydrogen and sulfur are produced in acidic solutions with a small quantum yield. In the present study, the colorless aqueous sulfide solution turns yellow after prolonged photocatalytic decomposition, indicating the formation of disulfide and polysulfide ions which can be electrochemically and spectrophotometrically detected. Thus in this investigation, as the photocatalytic reaction is carried out in alkaline medium (pH 12-13), only the formation of disulfides and polysulfides is observed. No sulfur precipitation is detected. The yellow disulfides and polysulfides thus formed compete with the light absorption by photocatalyst acting as internal filters. Hence the formation of disulfides and polysulfides decreases the efficiency of the reaction.

The hydrosulfide ion produced by dissociation of H_2S in alkaline medium. The photogenerated holes on the surface of the photocatalyst oxidize hydrosulfide ion to give disulfide ion. Finally, the hydrogen is formed by the reduction of protons by the photogenerated electrons. The overall process corresponds to the cleavage of H_2S by two photons of light which require the Gibbs energy 7.892 kcal/mol.²⁴

4. CONCLUSION

A novel ZnBiGaO_4 spinel oxide material used first time as a visible light photocatalyst after synthesized by solid-state route and achieved single phase nano-sized ZnBiGaO_4 by simple hydrothermal method. The product obtained by solid-state method i.e. $\text{ZnBiGaO}_4(\text{s-s})$ and $\text{ZnBiGaO}_4(\text{h-t})$ exhibits cubic spinel structure with band gap energy of 2.80 eV. The photocatalytic decomposition of hydrogen sulfide for production of hydrogen using ZnBiGaO_4 implies that the significant photocatalytic activity was observed under visible light irradiations. The photocatalytic activity observed under visible light irradiation is attributed due to the metal ions, Ga^{3+} and Bi^{3+} having of d^{10}

configurations. If ZnBiGaO_4 spinel photocatalyst doping with RuO_2 and Pt, it will have excellent photocatalytic activity.

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