

모노클리닉 ZnBiVO₄: 수소제조용 신규 광촉매

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Monoclinic ZnBiVO₄: A photocatalyst for photohydrogen production

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ABSTRACT

Zn, Bi 와 V 금속이온 전구체를 사용하여 모노클리닉 결정구조를 갖는 신규 ZnBiVO₄ 광촉매를 손쉽게 합성 할 수 있는 방법을 개발하였다. 합성된 ZnBiVO₄ 광촉매는 XRD 과 FESEM등을 이용하여 미세구조를 분석하였으며, 분석결과 본 삼성분계 금속산화물 반도체 광촉매는 모노클리닉 결정구조를 갖는 것을 알 수 있었다. 저온 수용액방법에 의해 손쉽게 나노 구조를 갖는 ZnBiVO₄가 제조 되었으며, 그 광촉매의 최소 입자크기는 20-30 nm 이다. ZnBiVO₄ 광촉매는 UV-visible DRS (diffuse reflectance spectroscopy)로 그 띠허격(band gap)을 측정하였으며, FT-IR을 사용하여 구조 및 물질 상의 순도를 확인하였다. 그리고 H₂S를 광분해하여 수소를 발생하는(122ml/hr · g) 우수한 광촉매 활성을 보여 주었다.

주요기술용어 : Photocatalyst(광촉매), ZnBiVO₄, hydrogen sulfide(황화수소), metal oxide(금속산화물), photodecomposition(광분해)

1. Introduction

Plenty of H₂S is obtained from refineries and all hydrometallurgy plants which is creating serious environmental pollution problem. To curtail this pollution

problem, it is necessary to utilize hydrogen sulfide into some valuable compounds. In this connection, efforts have been attempted to develop an economical process for hydrogen production from hydrogen sulfide. The conventional Claus process involves the synproportionation reaction between H₂S and SO₂ yielding elemental sulfur and

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water vapor. If hydrogen can be recovered from H_2S , instead of oxidizing it into H_2O (Claus process), an enormous amount of hydrogen can be produced¹⁾. Photodecomposition of the H_2S to H_2 by semiconductor particle photocatalyst is a process that ultimately converts solar energy into fuels. This process requires less energy compared to photodecomposition of water. In this connection, recuperation of H_2 from H_2S has attracted more attention because of its economic and environmental advantages. Extensive work has been 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 photoproduction of hydrogen. It is indispensable to control the band structure of photocatalyst for the development of efficient photocatalyst materials. Substantial work was carried out in the development of photocatalyst by doping method. Doping of foreign transition elements into an active existing photocatalysts was studied extensively²⁻⁵⁾. Especially, Ni and Cu-doped ZnS photocatalysts show activity for H_2 evolution under visible-light irradiation even without Pt catalyst. Many researchers have reported the doping method for CdS, ZnS, VS, VS_4 , WO_3 .⁽⁶⁻¹¹⁾ The nitrides (Ta_3N_5), oxynitrides ($TaON$, $LaTiO_2N$) and oxysulfides ($Sm_2Ti_2S_2O_5$) have been reported as active photocatalysts¹²⁻¹⁷⁾. The photophysical properties and photovoltaic efficiencies of $Nb_2O_5-Bi_2O_3$, $Ga_2O_3-In_2O_3$, $SrNb_2O_7$, $Sr_2Ta_2O_7$, SnO_2-TiO_2 , ZnS-CdS, CdS-CdSe and $(AgIn)_xZn_2(1-x)S_2$ have

been studied extensively¹⁸⁻²²⁾. Several nanocrystalline photocatalysts have been reviewed by Beydoun et al²³⁾, where he has described the effect of nanoparticles on photocatalytic activity. Recently, CdS-TiO₂ nanocomposite film²⁴⁾ has been used for the photodecomposition of H_2S . The stable and suitable metal oxide support is lacking in this work. In past, the research for the photodecomposition of H_2S was focused on sulfide semiconductor photocatalysts, which are unstable due to photocorrosion of the catalyst. The structural and morphological characteristics of photocatalyst are very important in the photocatalysis. In view of this, we synthesized monoclinic $ZnBiVO_4$ for photodecomposition of H_2S .

In the present investigation, we have synthesized the monoclinic $ZnBiVO_4$ using simple solution method. The structural and morphological study was carried out using XRD and FESEM. The nanosize, $ZnBiVO_4$ was obtained using the solution route. Photodecomposition of H_2S was carried out and fairly good photocatalytic activity has been obtained.

2. Experimental Procedure

2.1 Materials

To prepare $ZnBiVO_4$ by solution route, a stoichiometric amount of $Zn(NO_3)_2 \cdot 5H_2O$, $Bi(NO_3)_3 \cdot 6H_2O$, and ammonium metavanadate (NH_4VO_3) were dissolved in water and heated slowly at 70°C till evaporation. The powder obtained was calcined at 180°C for 12h. The resulting product was washed several times with

water and ethanol and then dried at 120°C for 5h.

2.2 Characterization

Powder X-ray Diffractograms were recorded with a Model Rigaku-D/MaX-2200V X-ray Diffractometer with CuK α radiation with Ni filter. The surface morphology and particle size were determined using a Field Emission Scanning Electron Microscope (FESEM Model JEOL-JSM6700F). Spectroscopic study of the catalyst was carried out using UV-visible (Model SHIMADZU UV-2450 diffuse reflectance mode) Spectrophotometer and a Fourier Transform Infra Red Spectrophotometer (Model, JASCO 610-FTIR). Specific surface area measurements were performed using a BET Surface Area Analyzer (Model BET-MICROMERITICS ASAP-2400).

2.3 Photodecomposition of H₂S

The photocatalyst was introduced as a suspension into cylindrical pyrex photochemical reactor with a water-cooled quartz immersion well and a thermostated water-jacket. A high-pressure mercury lamp (Hanovia) source of intensity 450 watt with pyrex cut off filter was used. At a constant temperature 25 \pm 1°C, the vigorously stirred suspension was purged with argon for 1h and then hydrogen sulfide (H₂S) was bubbled through the solution for about 1h.

Each experiment was carried out using 1g of catalyst in 500ml distilled water

with the H₂S flow, 10ml/min. The excess hydrogen sulfide was trapped in NaOH solution. The amount of evolved hydrogen was measured using graduated gas burette and gas chromatograph (Model Shimadzu GC-14B, MS-5A column, TCD, Ar carrier).

3. Results and Discussion

Zinc nitrate, bismuth nitrate and ammonium metavanadate were taken in stoichiometric quantities in aqueous medium and evaporated slowly at 70°C till dryness. The dried powder was crushed, homogenized and calcined at 180°C for 12h. Ammonium vanadate is soluble in water and forms H₃VO₄ as per the following reaction:



During the slow evaporation, Zn and Bi ions in water are reacted with H₃VO₄ and formed ZnBiVO₄. The formation of ZnBiVO₄ is critical and temperature sensitive. XRD, UV-Vis (DRS) and IR spectroscopy confirmed the phase purity of the product.

3.1 X-ray analysis

Baeg et al. has synthesized ZnBiVO₄ by solid-state method and it has been compared with ZnBiVO₄ prepared by solution method. Powder XRD patterns of ZnBiVO₄, prepared by solid-state²⁵⁾ and solution route are shown in Fig.1. The difference in XRD pattern of ZnBiVO₄ (solid-state) and ZnBiVO₄ (sol) can be judged by the existence of the peaks at 2θ

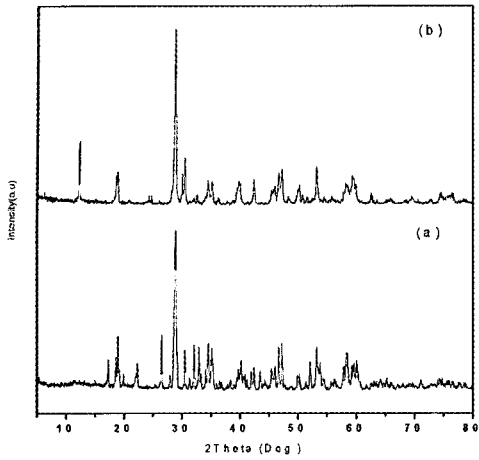


Fig. 1. XRD pattern of (a) ZnBiVO₄ (solid-state) (b) ZnBiVO₄ (sol).

=13.0° and splitting peaks at $2\theta = 18.5^\circ, 35.0^\circ$ and 46.0° . The main (100% relative intensity) peak was obtained at $2\theta = 28.8^\circ$, shows the existence of ZnBiVO₄ phase. From the XRD, sharp peaks observed at $2\theta = 13.0^\circ$ and 18.8° reveals the existence of mixture of tetragonal and monoclinic crystal system in ZnBiVO₄ (sol). The XRD pattern of ZnBiVO₄ (solid-state) shows a few unknown weak peaks, which may be originated from the raw materials.

However, peaks pertaining to impurities or the intermediate were not observed in XRD pattern of ZnBiVO₄ (sol). Comparison of the present XRD data with the XRD data of raw materials and their related compounds, showed

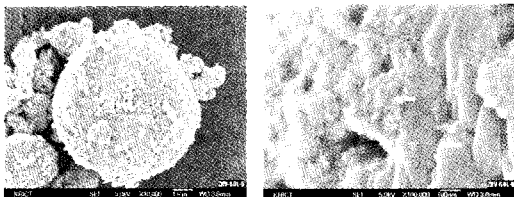


Fig. 2. FESEM micrographs of ZnBiVO₄ (Sol).

the absence of their corresponding peaks. The monoclinic crystal system was observed in ZnBiVO₄, the details parameters needs more experimentation.

3.2 Powder Morphology

Fig. 2(a) and (b) reveals the FESEM micrographs of the ZnBiVO₄ (sol) at low and higher magnification. The particle shapes were observed to be spherical. Some of the crystals possessed plate-like morphology with about 28–200nm of plate diameter. The minimum size of the crystallite was observed in the range of 20–30nm.

In fact, some of the crystals were less than 20nm, which could not be measured by FESEM. Since the synthesis was carried out at a low temperature, nanocrystalline ZnBiVO₄ has been obtained. The SEM observations are thus in agreement with our XRD results.

3.3 Spectroscopic study

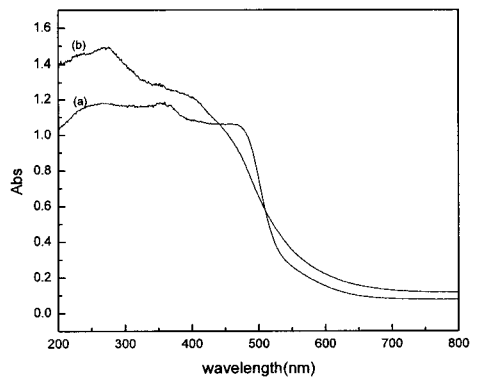


Fig. 3. UV - vis diffuse reflectance spectra of (a) ZnBiVO₄ (s-s) and (b) ZnBiVO₄(sol).

Fig. 3 represent the UV - vis diffuse reflectance ZnBiVO₄ (sol).

The absorption edge cut off of ZnBiVO₄ (sol) was observed at 560nm. The nature of the broad steepness of UV-visible DRS cut off shows nanocrystalline nature of the particle with agglomeration.

Non-uniformity in particle size and shape is also one of the reasons for broad UV cut off of ZnBiVO₄. From the spectra, estimated band gap energy (Table.1) was observed 2.21 eV for ZnBiVO₄ (sol) which is in agreement with the reported value²⁵⁾.

The IR spectrums of ZnBiVO₄ (sol), which represents a typical pattern built up by VO₄ tetrahedra²⁷⁾.

The absorption bands were characterized as follows: 1 (VO₄) and 3 (VO₄) 500-900cm⁻¹ and 4(VO₄) = 578cm⁻¹. Accordingly, bands were assigned as shown in Fig.4. This vibrational band centered at 743cm⁻¹ is the characteristic of ZnBiVO₄. A band centered at 1356cm⁻¹, 1384cm⁻¹ is the characteristics of nitrates presents in the ZnBiVO₄ (sol) which

originate from the starting materials. A weak broad band at 3436cm⁻¹ is the characteristics of O-H. This O-H stretching was observed due to the adsorbed water present in the product.

3.4 Photodecomposition of H₂S

Different series of experiments were performed using the ZnBiVO₄ catalyst. Table.1 depicts the rates of hydrogen evolution from hydrogen sulfide using ZnBiVO₄. These results reveal that the photocatalytic activity has been enhanced by almost 100% in ZnBiVO₄ (sol) as compared to ZnBiVO₄ reported by solid state method²⁸⁾.

The enhancement in the catalytic activity for ZnBiVO₄ may be due to nanosize particles (less than 28nm) and high surface area (4.7 m²/gm).

This could be one of the reasons for enhancement of the photocatalytic activity. The photodecomposition carried out at higher pH (Table1) did not show an

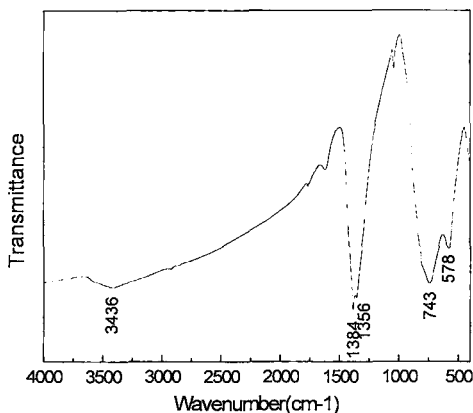


Fig. 4. FTIR spectra of ZnBiVO₄ (sol).

Table 1. Photocatalytic activities of ZnBiVO₄ photocatalyst for H₂ evolution from H₂S.^a

Catalyst	Band gap energy (eV)	BET (m ² /g)	H ₂ evolution rate (mL/h · g)
ZnBiVO ₄ (sol)	2.21	4.70	122
ZnBiVO ₄ (sol)	2.21	4.70	104 ^b
ZnBiVO ₄ (s-s)	2.30	0.27	57

^aCatalyst: 1.0g, 500mL of H₂S saturated H₂O(pH = 4.4), H₂S (10mL/min), 450 W Hg lamp (λ > 325nm). ^bAn aqueous solution of KOH(0.5M) + H₂S(pH = 8.5).

appreciable effect on the photocatalytic activity.

A marginal decrease in activity, attributed to the low concentration of protons at high pH^{23,26}.

Reported data on BiVO₄²⁷⁾ shows that the tetragonal BiVO₄ do not have photocatalytic activity whereas monoclinic BiVO₄ exhibit good photocatalytic activity. The reason quoted is that the monoclinic BiVO₄ is greatly distorted as compared with tetragonal BiVO₄. Similar phenomenon is observed in ZnBiVO₄ where the distortion has been arisen due to 6s² lone pairs of Bi³⁺. The photocatalytic activity has been enhanced significantly in ZnBiVO₄ owing to distortion due to 6s² lone pairs of Bi³⁺. This implies that monoclinic crystallite system and structure of ZnBiVO₄ is responsible for the good photocatalytic activity. Such effects have been reported earlier²⁷⁾ for the similar compound with different crystal structure. This indicates that the distortion of the metal oxygen polyhedron is an important factor affecting the photocatalytic properties. The distortion probably affects the charge separation and dislocation of photogenerated electrons and holes. The high surface area and nanosize particles are also helping to enhance the photocatalytic activity in ZnBiVO₄.

4. Conclusions

A low temperature and ambient pressure aqueous process has been developed for synthesis of ZnBiVO₄. The

product obtained, shows monoclinic crystal system. The size of the crystallites in the product prepared by solution route was observed to be in the range of 20–28nm. Some of the crystals possessed plate-like morphology with about 28–200nm plate diameter. UV-DRS showed a broad absorption edge indicative of the nanocrystalline nature of the ZnBiVO₄. The photocatalytic activity has been enhanced almost 100% in ZnBiVO₄ (sol) as compared to solid-state ZnBiVO₄ reported. This enhancement of photocatalytic activity attributed to high surface area of nanopowder and distortion due to 6s² lone pairs of Bi³⁺ in ZnBiVO₄ (sol). The distortion of the metal oxygen polyhedron is an important factor affecting the photocatalytic properties.

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