

HYDROTHERMAL SYNTHESIS OF YTTRIUM ORTHOVANADATE (YVO₄) AND ITS APPLICATION IN PHOTO CATALYTIC DEGRADATION OF SEWAGE WATER

J. K. Komal^{1,*}, P. Karimi² and K. S. Hui³

* *kompaddy@yahoo.com*

Received: April 2010

Accepted: August 2010

1 Department of Environmental Science, University of Mysore, Manasagangothri, Mysore, INDIA.

2 Department of Geology, University of Mysore, Manasagangothri, Mysore, INDIA.

3 Department of Manufacturing Engineering & Engineering Management, City University of Hong Kong, Kowloon Tong, HONG KONG.

Abstract: In this paper, YVO₄ powder was successfully synthesized from Vanadium Pentaoxide (V₂O₅), Yttrium Oxide (Y₂O₃) and ethyl acetate as a mineralizer by hydrothermal method at a low temperature (T=.230°C, and P=100bars). The as-prepared powders were characterized by X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), UV-V Spectroscopy and Chemical Oxygen Demand (COD) of the sewage water, respectively. The results show that hydrothermal method can greatly promote the crystallization and growth of YVO₄ phase. XRD pattern clearly indicates the tetragonal structure and crystallinity. An FTIR spectrum of the YVO₄ shows the presence of Y-O and V-O bond, respectively. The presence of these two peaks indicates that yttrium vanadate has been formed. UV-V is absorption spectra suggesting that YVO₄ particles have stronger UV absorption than natural sunlight and subsequent photocatalytic degradation data also confirmed their higher photocatalytic activity.

Keywords: XRD, FTIR, SEM, Hydrothermal Growth, Photocatalysis, COD.

1. INTRODUCTION

Water is one of the primary natural resources and a necessity for sustaining life on earth. Supplying an adequate amount of potable water to the population worldwide for the sake of growing industrial and domestic needs is a gigantic task. The threats of global [1] warming and climate change which aggravate the problem of water shortage, are of particular concern to India as this country largely depends on glaciers and rainfall for water supply.

Water pollution is the contamination [2] of water bodies such as lakes, rivers, oceans and ground water. Water pollution affects organisms and plants that live in these water bodies and, in almost all cases, it damages not only individual species and population but also natural biological communities. It occurs when pollutants are discharged directly or indirectly into water bodies without adequate treatment to remove harmful contaminants.

Environmental contamination, [3] which is growing around the world and in our daily life, is a serious social problem which cannot be

neglected. Examples of such contaminations can be listed as follows:

1. Water pollution by household waste water discharge and industrial discharge.
2. Respiratory diseases caused by air pollutants such as Sox or Nox.
3. Global warming, climate change, glacier melting etc.

The fact is that using energy to eliminate such environmental contamination increases the emission of CO₂ resulting in more global warming. Therefore, it leads to a dilemma of using energy to achieve the anti-pollution goal. Under such circumstances, it can be concluded that a material is needed which can gently [4] harmonize the contaminated environment in order to restore original conditions using natural energy which is a part of the environment and low cost energy which is supplied to the daily life. One solution to this problem which is presented in this research is photo catalysis. YVO₄, an important [5] optical material, has many wonderful characteristics and optical properties. The Yttrium Orthovanadate (YVO₄) as an important metal [6]. Rare earth vanadates

(MVO_4 , where $M=Y, Bi, Fe, In$, etc) has found some wide and practical applications, such as excellent laser host materials in single crystal form, which make it play [7] an important role in almost any devices involving the artificial production [8] of light and display [9] fields, such as excellent [10] polarizer and laser host material. This system has shown an excellent performance in the production [11] of both hydrogen and oxygen in UV and visible light, however its photocatalytic property is poorly understood.

The band gap of YVO_4 is about 3.5eV, [12] which is wider than that of $InVO_4$, though both have a V element in their structure. As heterogeneous Y^{3+} introduced, the crystal structure is modulated to the tetragonal zircon-type consequently. Therefore the electronic structure is also changed and, the band gap is widened.

Hence in this study, an attempt is made to study the photocatalytic application of pure Yttrium Orthovanadate (YVO_4).

2. MATERIALS AND METHOD

For preparing YVO_4 particles, appropriate amounts of Y_2O_3, V_2O_5 in 1:1 molar ratio were dissolved in ethyl acetate as a mineralizer solution, and the entire mixture was stirred in a magnetic stirrer for 15 minutes till a homogeneous solution was obtained and the solution was completely transferred into the Teflon liner of 25ml capacity provided with

general purpose autoclaves of SS316. The use of Teflon liners helps in overcoming the entry of inclusions from the autoclave material into the crystals. The temperature and pressure were kept constant at $T=230^\circ C$ and $P=100$ bars, respectively, and the experimental duration was 6 hr. After the experimental run the autoclave was taken out from the hot air oven and was cooled naturally at room temperature. The, synthesized material from the Teflon liner was collected and washed with distilled water for 3 to 4 times; then it was dried for 1hr at $60^\circ C$ in hot air oven in order to eliminate the moisture content from the obtained material. The obtained materials from the hydrothermal method were characterized using X-ray Diffraction (XRD) analysis, which was performed using a Rigaku miniflex2, copper target, ($\lambda=1.5405\text{\AA}$) and in the scanning range of $10-800$ (2θ), Fourier Transform Infrared Spectroscopy (FTIR 460 plus Jasco) Scanning Electron Microscopy (SEM Hitachi model S-3500N), UV-V spectroscopy (minispectroscop SL171, Elco) and Chemical oxygen demand (COD).

The photocatalytic property of the YVO_4 was tested, at first, 0.1601mg of hydrothermally synthesized YVO_4 powder was dispersed into five beakers, which were filled with 40 ml of sewage waste water separately. Prior to irradiation, the suspension were magnetically stirred in a dark condition for 30 min to establish adsorption/degradation equilibrium. The suspensions were then irradiated under the UV



Fig.1. Shows the XRD pattern of the YVO_4 crystal prepared by hydrothermal method

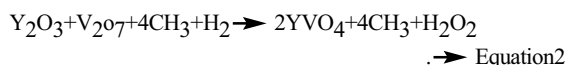
light and sun light. A 400w high-pressure Hg lamp with a maximum emission at about 360 nm was used as a light source.

3. RESULTS AND DISCUSSION

YVO₄ crystal has a zircon type structure and belongs to the tetragonal space group of I4₁/amd with cell dimensions of. a=7.119Å, c=6.289Å [13]. Fig.1 shows the XRD pattern of YVO₄ crystals prepared by hydrothermal method. All the diffraction peaks could be identified as belonging to the tetragonal zircon-type lattice structure of YVO₄. (JCPDS: 17-0341).The tetragonal-phase YVO₄ can be easily obtained even at T- 230°C. Three predominant diffraction peaks of 2θ=24.7, 33.26 and 49.48 belongs to the crystalline YVO₄ were observed clearly which indicate the relative high crystallinity. It can be concluded that YVO₄ single phase was

formed successively by the hydrothermal method.

Figs 2.A.B.andC. shows the FTIR spectra of YVO₄ particle before and after photodegradation. The infrared spectra of the YVO₄ were recorded in the range of 4000-400cm⁻¹, from the FTIR spectra,, It can be observed that a strong peak at 836 cm⁻¹, is apparently associated with the characteristic vibrating modes of the VO₄ group and a weak absorption peak of the Y-O (449.333 cm⁻¹). The presence of these two peaks indicates that yttrium orthovanadate has formed and completed the crystallization of the YVO₄.The following reaction would have occurred during the synthesis:



The broad absorption band at 3095.19 cm⁻¹ corresponds to the OH groups of H₂O while absorbing to the surface of the crystals. In addition, the FTIR spectra for hydrothermal product show the two bands at 2358.51 cm⁻¹ and 1646.91 cm⁻¹, which are assigned to OH stretching vibration modes for coordinated water. No structural changes could be found in the Infrared spectra of the YVO₄, before and after photodegradation of the Sewage waste water, meaning that FTIR spectra of the YVO₄ were not changed even after the photodegradation. This

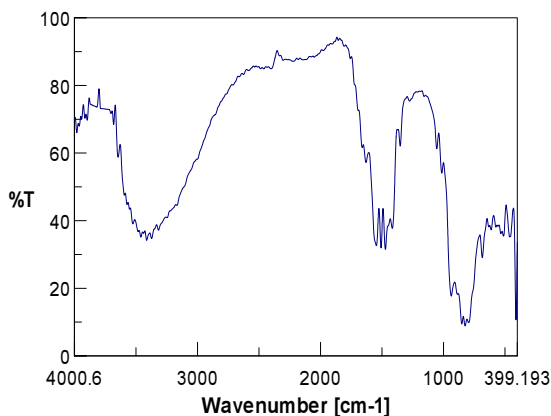


Fig. 2. A. FTIR of the YVO4

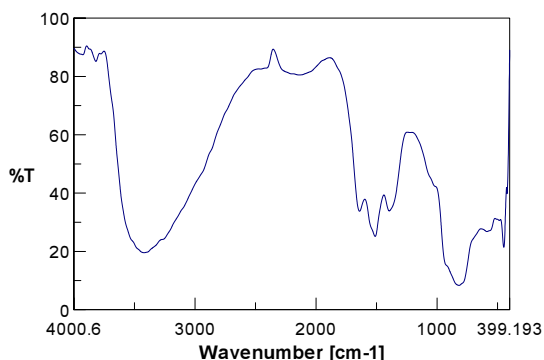


Fig. 2. B. FTIR of the YVO4 crystal after degradation of sewage waste water by sun light.



Fig. 2. C. FTIR of the YVO₄ crystal after degradation of Sewage waste water by UV light.

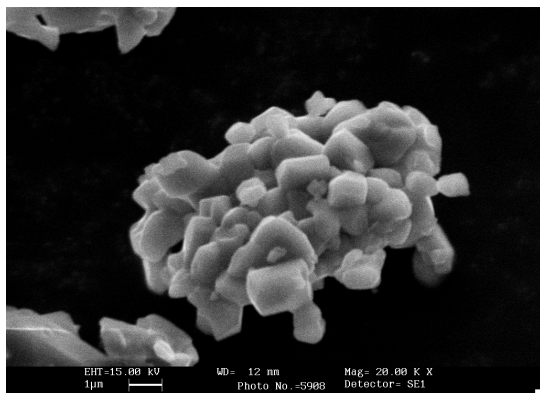


Fig. 3 .A

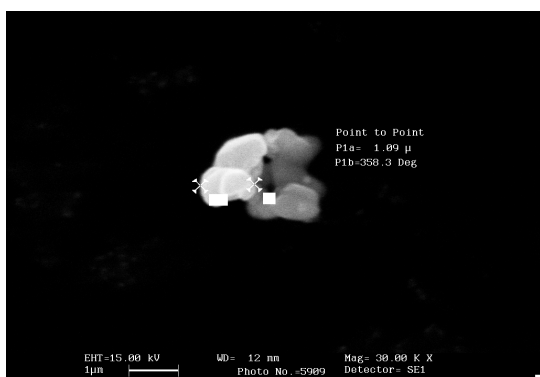


Fig.3.B

Fig. 3. Photo degradation of the Sewage waste water by YVO₄ crystal.

indicated that it performed as a photo catalyst without participation in the chemical reaction. In the present research, it can be conclude that YVO₄ acts as a photo catalyst by accelerating the rate of reaction in presence of sunlight and UV

light without participating in the chemical reaction. In this study, YVO₄ shows more photocatalytic degradation for UV light than natural sunlight.

The morphology and grain size of the YVO₄ particles were characterized with SEM. Fig.3. A and B. shows the SEM images of the YVO₄. The SEM image shows that the products are composed of large quantities of 1D YVO₄ with typical lengths up to several micrometers. An YVO₄ particle, prepared at T-230°C, consists of homogeneous and tetragonal structures. The SEM images shows that YVO₄ particles which are agglomerated may be because of the hydrophobic nature of the mineralizer which is used as a precursor material for the synthesis.

YVO₄ is a semiconductor which turns to a high energy state by receiving light energy and releases electrons from its illuminated surface and jumped to the conduction band leaving a hole in valence band. The hole in the valence band has a strong oxidation power and takes the electron from the OH⁻ (hydroxide ion) in the water at the time OH which takes the electron and, becomes OH radicals of very unstable condition. OH radical takes the electron by the strong oxidation from nearby the organic compound in order to become stable. In this way the organic compound is decomposed by the loss of electron and finally become CO₂ and water and released in to the atmosphere. Fig.4 indicates the photo catalytic process.

COD test is commonly used to measure the amount of organic compound in water; most

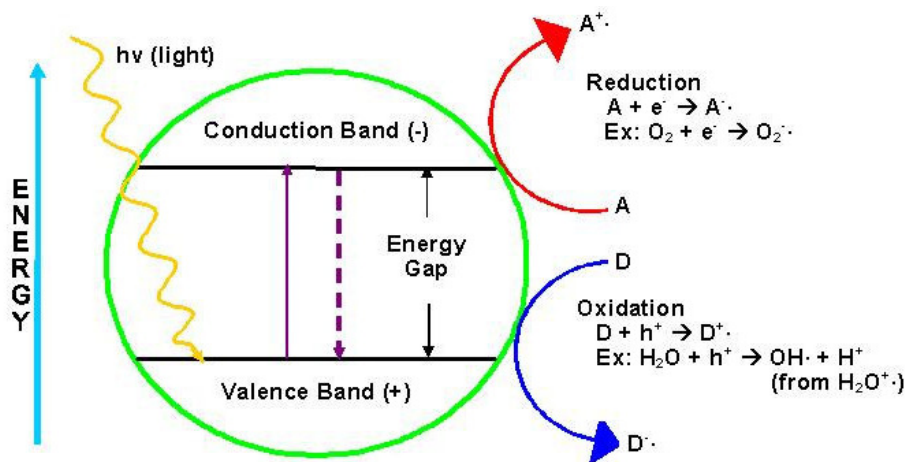


Fig. 4. The above figure shows basic Photo catalytic process (fujishima, 1972)

Table 1. Initial and final COD of the Photo degraded Sewage water by YVO_4 crystal.

COD of the sewage water before photo degradation.	COD of sewage waste water after photo degradation by UV light.	COD of sewage waste water after photo degradation by sun light.
332.28 mg/L.	51.92 mg/L.	259.6 mg/L.

applications of COD determines the amount of organic pollutants found in the waste water making COD a useful measure of water quality.

In this research, 0.1601 gm of Hydrothermally synthesized YVO_4 powder are taken as a catalyst into the five cleaned beakers containing 40 ml of sewage waste water, then the beakers is irradiated to the sunlight and to the UV light for 6 hrs. After 6 hrs of exposure to the UV light and sunlight, the sewage water sample is immediately analyzed for Chemical Oxygen Demand (COD) and UV spectroscopy. Initial COD of the sewage waste water was 256.9 mg/l. However, after being irradiated to the UV light and sunlight reduction was observed in the COD level to 51.92 mg/l and 332.28 mg/l respectively. Spectroscopic measurement showed an increase in the percentage transmission of light. The initial percentage transmission of sewage waste water was 0% and, after the irradiation by sunlight and UV light, the percentage transmission increased

to 90 to 100%. This means that YVO_4 degraded the organic chemicals in the sewage waste water at orbital level. Fig.5 indicates the UV spectroscopic data of the sewage water and Table.1 shows the initial and final Chemical Oxygen Demand (COD) of sewage water before and after photo degradation by YVO_4 .

For the first time, an attempt was made to find the photo catalytic activity of the Yttrium Orthovanadate (YVO_4) in degrading sewage waste water. Therefore, the good crystallization and band gap can be considered as key factors, which enhance the photocatalytic performance of the YVO_4 powder.

4. CONCLUSIONS

Homogeneous particles can be easily prepared by a simple and convenient hydrothermal method. Their synthetic temperature can be lowered to T- 230°C and their pressure to P-100 bars, their tetragonal YVO_4 micro particles with 1 μm in diameter can be obtained. Obtained results revealed that YVO_4 acts as a photo catalyst and plays a key role in degrading the organic pollutants in the sewage waste water. The major advantage of this research is that the photo degraded sewage waste water can be reused for the external purposes like cleaning and washing and the photo catalyst can be reused for the further research in photocatalytic activities. The influence of hydrothermal treatment temperature on micro particles YVO_4 was revealed by XRD and FTIR measurements. FTIR spectrometry data are in good agreement with XRD results which clearly indicates the VO_4 vibration. As a necessary condition for developing a photocatalyst with a high performance, it would



Fig. 5. Photo degradation of the Sewage waste water by YVO_4 crystal.

be important, that the system be designed in a way to produce short water catalyst. Considering the above mentioned results can be concluded that YVO_4 micro particles are promising alternative materials for phtocatalyst and may find potential applications in the related fields.

REFERENCES

1. Gupta, K. R., water crisis in India, Atlanta publications, (2008), 4181, ISBN: 81-269-0958-2.
2. Lixz, Liuh., photo catalytic oxidation using a new catalyst- TiO_2 micro sphere-for water and waste water treatment(2003),.1:37(17):3989-94.
3. Liu, Y., Li, J., Novel TiO_2 nano crystals for waste water purification-trapping energy from sun. Water Practice and technology vol No 4 @ IWA publishing 2006, doi:10.2166/wm.2006072.
4. Shinichi k., keilchimaki., degradation of organic compounds on TiO_2 prepared by hydrothermal method in the presence of NH_4F . 2009, boi: 10.1007, 64-009-0029-5.
5. Byrappa, K., Ramaningaiah., Growth and morphology of Nd: YVO_4 under hydrothermal conditions. Journal of material science, 2006, 41:1415-1421.
6. OConnor, J., Unusual Crystal-Field energy levels and efficient laser properties of YVO_4Nd , Appl.Phys.Lett. 1966, 9,407-9.
7. Haiyan xu, Hao W. Preparation and photo catalytic properties of YVO_4 nano powders. Journal of hazardous materials, 2007, 144:82-85.
8. Guicunli, k., Hydrothermal synthesis and characterization of YVO_4 and $YVO_4:Er^{3+}$ nanobelts and polyhedral microcrystals. JPhys. Chem, 2008, 112(16): 6228-6231.
9. Byrappa, K., Chandrasekhar, C. K, Growth morphology and mechanism of rare earth vanadate crystals under mild hydrothermal conditions, 2007, 306:94-101.
10. Byrappa, K., Nirmala, B., crystal growth of rare earth vanadate laser hosts and in-situ fabrication of their crystal morphology under mild hydrothermal conditions, 2002, PINSA, 68, A, No.3, pp.193-200.
11. Yiminghe, Y., visible light photo degradation of organics over YVO composite catalyst. Journal of hazardous material, 2009 doi: 10.1016.
12. Haiyan xu, Hao W., Preparation and photo catalytic properties of YVO_4 nano powders. Journal of hazardous materials, (2007), 144:82-85.
13. Baglio, J.A and Gashurov, G, Yttrium orthovanadate and its structure, Acta Cryst, (1968).B24, 292.