Construction of Novel Zinc Vanadate Nanostructure: a Promising Visible-Light Active Photocatalyst for the Degradation of Methylene Blue

M. Thiruppathi, K. Leeladevi, C. Ramalingan, E. R. Nagarajan

Abstract- ***In this study, novel zinc vanadate (ZnV_2O_6) nanoparticles were prepared using simple hydrothermal method. The morphology and structure properties of ZnV_2O_6 were characterized by various spectroscopic techniques such as SEM, EDX, XRD and DRS Spectroscopy. The prepared ZnV_2O_6 was used as photocatalyst for the degradation of methylene blue dye solution under visible light irradiation which degrades within 70 min with excellent reusability and stability of the catalyst up to 4th run.***

Keywords: Methylene blue, Degradation, ZnV_2O_6, Visible light.

I. INTRODUCTION

Water is very vital for all living beings in the earth, nowadays getting pure water for drinking and other domestic purpose becomes a challenge as the pollution caused by human beings is alarmly increasing [1]. Research focusing on environment, water purification, sustainable energy sources and biofuels are growing very fast in recent years, as they decrease the man-made pollution to considerable amount [2]. Major pollutants in water are from industrial effluents from dye industry, pharmaceutical industry, textile industry and so on [3]. Treating this polluted water to reusable one with efficient and economically affordable method is a challenging task. There are different methods for purification of water such as membrane filtration, adsorption, advanced oxidation process, chemical treatment, biodegradation, chlorination, photocatalysis, sonolysis, ozonation, photo-Fenton and coagulation-flocculation [4,5]. Photocatalytic degradation of pollutants using affordable and harmless photocatalyst material is also an efficient method.

Recent years, lot of semiconductor materials widely used for photocatalytic method like as SnO_2, TiO_2, ZnO, WO_3, and V_2O_5 so on [6,7]. This catalysis plays a major role to eliminate the organic contaminant from the environment. Nowadays binary metal oxide photocatalysis like as $CuWO_4$, Nd_2O_3, $AgWO_4$, $BiVO_4$, and Bi_2WO_4 have been reported for photodegradation of organic dyes [8,9]. Vanadate is one of the important transition metal oxide materials used for environmental and energy application in various fields such as catalysis, batteries, antimicrobial activity, sensor, water spelling, solar cells and photocatalyst. The binary metal oxide ZnV_2O_6 prepared for various methods such as wet chemical, solvothermal, sonication, reflection and hydrothermal method [10,11]. The band gap was very low (2.3 eV) the photocatalytic activity enhanced. The ZnV_2O_6 gives a superior photocatalytic activity towards methylene blue which undergoes degradation under visible light irradiation. In this work the ZnV_2O_6 nanoparticles has been prepared by hydrothermal method. The photocatalyst has been used to degrade methylene blue dye solution under visible light within 70 min.

II. EXPERIMENTAL SECTION

A. Materials and methods

Ammonium metavanadate, Zinc acetate, Poly(vinyl alcohol) (PVA), Nitric acid, Ethanol, were purchased from Merck. Methylene blue dye was obtained from Sigma Aldrich, all the experiments were performed using deionized water. The ZnV_2O_6 photocatalyst was crystalline nature, analyzed by PW-1710 X-ray diffractometer (Eindhoven, the Netherlands). The morphology of the ZnV_2O_6 was studied using SEM (ZEISS-EVO 18 Research) with EDX spectrometer (BRUKER-X Flash 6130). The optical studies were using Shimadzu-2450 UV–Vis.

B. Preparation of ZnV_2O_6

The ZnV_2O_6 nanoparticles were prepared by hydrothermal method. 0.5 M ammonium metavanadate [NH_4VO_3] was dissolved in 30 ml of ethanol. 0.5 M zinc acetate [$Zn(O_2CCH_3)_2$] was dissolved in 30 ml of ethanol and it was added drop by drop to the above solution with continuous stirring. After 30 min, 5 ml of nitric acid was added to the solution to maintain the pH of the solution. 1g of PVA was added which will act as a surfactant into the mixture solution.

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The mixture was allowed to stirred for 3 h, the above solution was then transferred into a 100 ml Teflon stainless steel autoclave and it was maintained at 160 ºC for 12 h and then cooled. The obtained precipitate was washed several times with deionized water and ethanol and the product was dried at 80 ºC for 10 h. The product was obtained finally after calcination at 500 ºC for 4 h.

C. Photocatalytic studies

$1X10^{-5}$ M concentrated solution of methylene blue was prepared in deionised water. In the methylene blue solution, 50 mg of ZnV_2O_6 photocatalyst was added and stirrer for 45 min in black condition. Degradation studies were performed under visible light (λ>400 nm) photo chamber by tungsten lamp (150 mW/cm^{-2}). Readings were taken at the interval of 10 min after collected the mixture solution was recorded by UV-Vis spectrometer.

III. RESULTS AND DISCUSIION

A. Characterization of ZnV_2O_6 photocatalyst

The phase pure monoclinic structured ZnV_2O_6 were identified using powder XRD analysis which compared to the typical JCPDS patterns (75-1392). There is no additional peaks are identified in the observed X-ray profiles which conform the as prepared ZnV_2O_6 nanoparticles were single phased with space group C2/m. The XRD pattern obtained of peaks at 20.3°, 25.6°, 27.3°, 28.9°, 32.79°, 37.33°, 38.87°, 40.4°, 41.4°, 44.2°, 48.9°, 51.8°, 56.2°, 60.2° 62.0° and 64.7° were related (-201), (-301), (110), (-202), (111), (-112), (-311), (301), (400), (003), (-403), (020), (113), (004), (-513), and (600) respectively. The well indexed XRD patterns of ZnV_2O_6 were shown in Fig. 1. The average crystallite size of the ZnV_2O_6 nanoparticles were calculated using Scherrer equation and the value is approximately 38.0 nm.

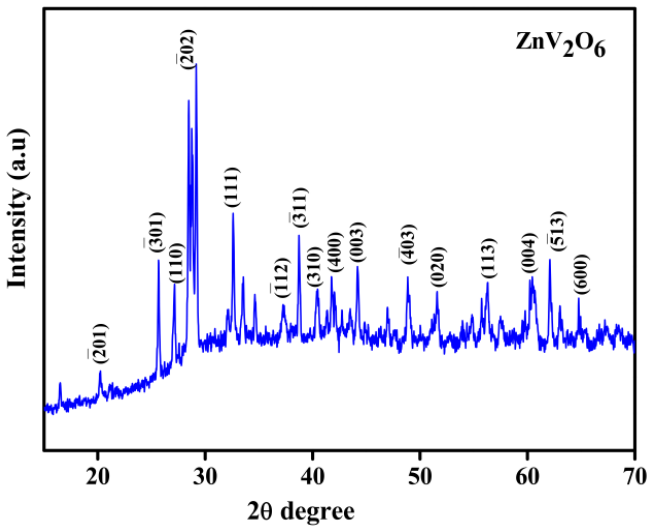


Fig. 1.XRD pattern of ZnV_2O_6 nanoparticle.

The morphology structure of the prepared ZnV_2O_6 nanoparticles were studied using SEM. The SEM image of ZnV_2O_6 photocatalyst with different magnification was shown in Fig. 2. The shape of ZnV_2O_6 was irregular spherical shape and irregular triangle shape particles. Zinc, vanadate and oxygen elements were present in EDX spectra as shown in Fig. 3. No other element or impurities present in ZnV_2O_6 photocatalyst.

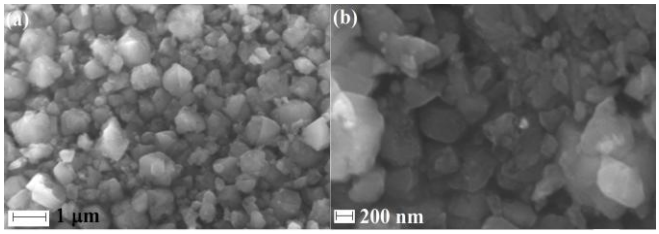
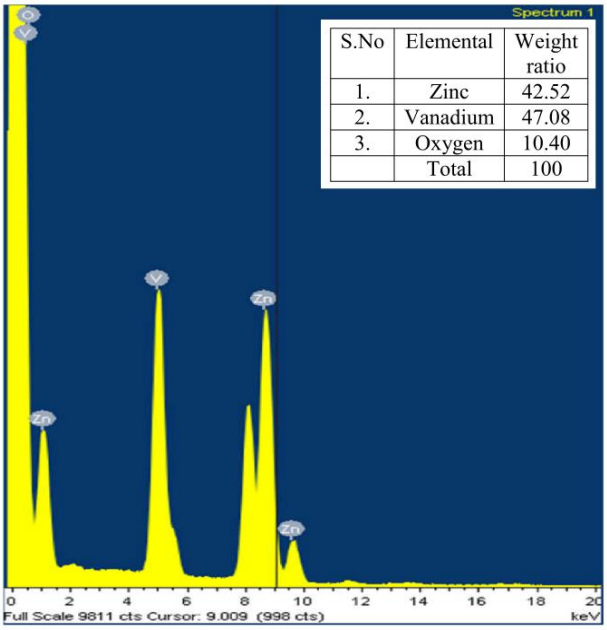


Fig. 2.SEM image of ZnV_2O_6 nanoparticles with different magnification.



S.No	Elemental	Weight ratio
1.	Zinc	42.52
2.	Vanadium	47.08
3.	Oxygen	10.40
	Total	100

Fig. 3.EDX spetrum of ZnV_2O_6 nanoparticle.

The wavelength vs absorbance of ZnV_2O_6 nanoparticles were obtained at around 550 nm as shown in Fig. 4a. The band gap of the ZnV_2O_6 photocatalyst was calculated by Tauc plot, shown in Fig. 4b. The prepared ZnV_2O_6 photocatalyst band gap was observed at 2.3 eV. The low band gap energy, enhanced the photocatalytic activity of prepared ZnV_2O_6 photocatalyst.

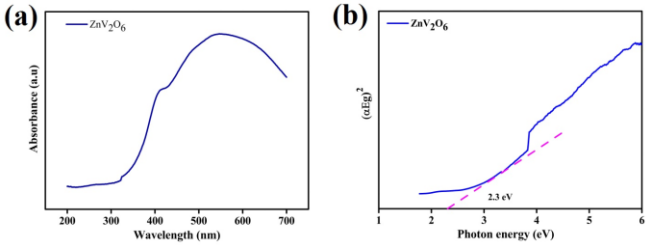


Fig. 4.(a) DRS-UV absorbance spectram (b) Band gap energry of ZnV_2O_6 nanoparticle.

B. Photocatalytic activity of ZnV_2O_6 nanoparticle

The evaluation of degradation of methylene blue with ZnV_2O_6 photocatalyst was studied by varying different parameters like concentration of the dye, amount of the photocatalyst , degradation of dye only presence of light.

Fig. 5a shows the absorbance spectra for methylene blue treated with ZnV_2O_6 photocatalyst, which shows a peak at 653 nm, from initial time at 0 min to 70 min; there is a gradual decrease in the peak intensity in absorbance spectra, in 70 min the peak intensity nearly reaches zero which confirm the complete degradation of methylene blue dye. Fig. 5b shows the effect of light, blank and ZnV_2O_6 photocatalyst on the degradation of methylene blue, when it was irradiated only with light in absence of catalyst the dye degradation is not that much, only negligible amount of degradation is observed; when treated with ZnV_2O_6 photocatalyst, the degradation of methylene blue in appreciable amount was observed.

Catalyst load is really important to optimise as we should use minimum amount of catalyst as possible for photocatalytic degradation of dye which is shown in Fig. 5c. We start with 10 mg and increased our catalyst load upto 75 mg, among this we get nice results when we use 50 mg, in 75 mg there was decrease in degradation of methylene blue, this may be due to more particles may does not allow the light to involve in photocatalytic reaction. The concentration of methylene blue dye is varied and we found as the concentration increases the degradation ability decreases, Fig. 5d shows complete degradation with ZnV_2O_6 photocatalyst at $1X10^{-5}$ concentration.

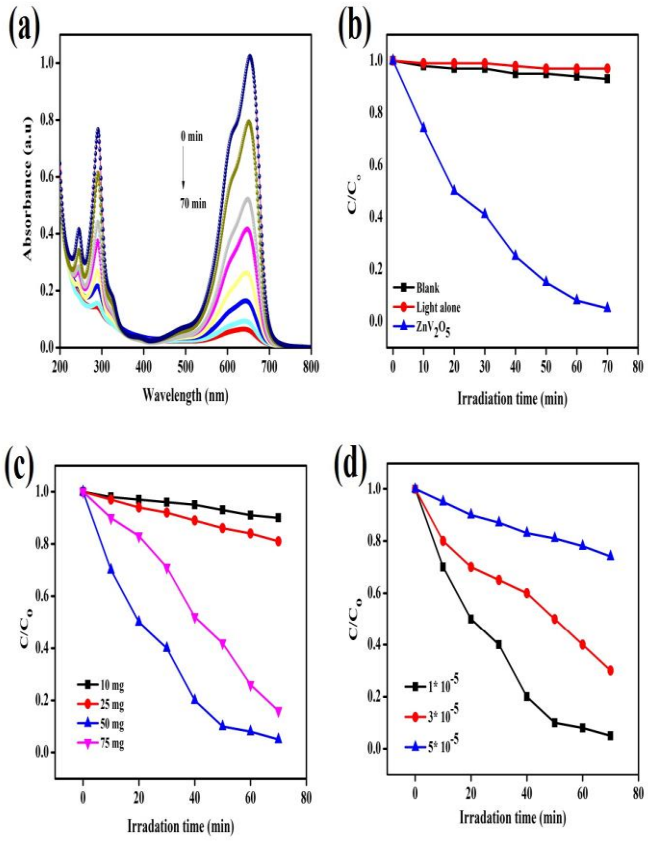


Fig. 5. (a) Absorbance spectra of methylene blue dye solution under visible light irradiation in the presence of 50 mg ZnV_2O_6 nanoparticle, (b) Catalyst optimization, (c) Different amout of photocatalyst, (d) Various conc. of methylene blue dye solution.

Reusability is an essential property for catalyst, ZnV_2O_6 catalyst was tested for its reusable efficiency. Fig. 6 shows that even after 4 cycles the efficiency of photocatalyst is good enough to degrade the methylene blue dye.

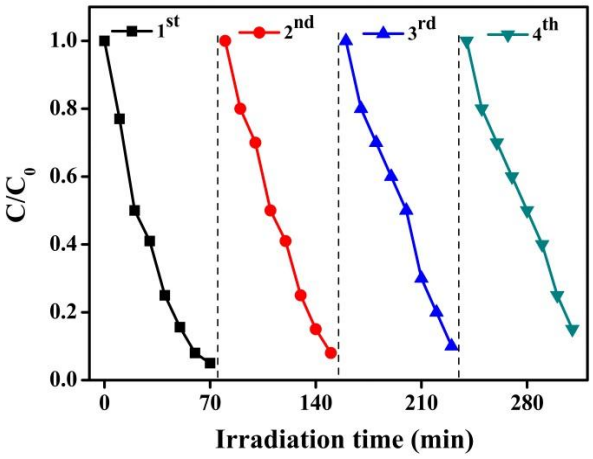


Fig. 6.Recycle efficiency of ZnV_2O_6 photocatalyst.

IV. CONCULSION

For using hydrothermal method, the above nanomaterial's ZnV_2O_6 were prepared successfully and their characterizations are detailed. The ZnV_2O_6 nanoparticles were good crystalline nature and average crystalline size 38.0 nm and irregular spherical shape morphology structure of ZnV_2O_6 nanoparticle. The pollutant, methylene blue was degraded under visible light irradiation within 70 min and the efficiency was observed that above 95%. The enhanced photocatalytic activity of the ZnV_2O_6 nanoparticle finds more in environmental applications.

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REFERENCES

1. S. Dong, J. Feng, M. Fan, Y. Pi, L. Hu, X. Han, M. Liu, J. Sun, J. Sun, "Recent developments in heterogeneous photocatalytic water treatment using visible light-responsive photocatalysts: A review," *RSC Advances*, Vol. 5, pp. 14610-14630, 2015.
2. D.J. Garcia, F. You, "The water-energy-food nexus and process systems engineering: A new focus", *Computers and Chemical Engineering*, Vol. 91, pp. 49-67, 2016.
3. H.M. Pinheiro, E. Touraud, O. Thomas, "Aromatic amines from azo dye reduction: Status review with emphasis on direct UV spectrophotometric detection in textile industry wastewaters", *Dyes and Pigments*, Vol. 61, pp. 121-139, 2004.
4. O. Amuda, I. Amoo, O. Ajayi, "Performance optimization of coagulant/flocculant in the treatment of wastewater from a beverage industry", *Journal of Hazard Materials*, Vol. 129, pp.69-72, 2006.
5. S. Ghafari, H.A. Aziz, M.H. Isa, A.A. Zinatizadeh, "Variability of parameters involved in leachate pollution index and determination of LPI from four landfills in malaysia", *Journal of Hazardous Materials*, Vol. 163, pp. 650-656, 2009.
6. H. Wang, L. Zhang, Z. Chen, J. Hu, S. Li, Z. Wang, J. Liu, X. Wang, "Semiconductor heterojunction photocatalysts: Design, construction, and photocatalytic performances", *Chemical Soicety Reviews*, Vol. 43, pp. 5234-5244, 2014.

7. A. Fujishima, T.N. Rao, D.A. Tryk, "Investigation of photocatalytic degradation of methyl orange by using nano-sized ZnO catalysts", *Journal of Photochemistry and Photobiology C; Photochemistry Reviews*, Vol. 1, pp. 1-21, 2000.
8. M. Thiruppathi, J.V. Kumar, M. Vahini, C. Ramalingan, E.R. Nagarajan, "A study on divergent functional properties of sphere-like $CuWO_4$ anchored on 2D graphene oxide sheets towards the photocatalysis of ciprofloxacin and electrocatalysis of methanol", *Journal of Materials Science: Materials in Electronics*, Vol 30, pp. 10172-10182, 2019.
9. M. Arunpandian, K. Selvakumar, A. Raja, P. Rajasekaran, M. Thiruppathi, E.R. Nagarajan, S. Arunachalam, "Fabrication of novel Nd_2O_3/ZnO-GO nanocomposite: An efficient photocatalyst for the degradation of organic pollutants", *Colloids and Surface A; Physicochemical and Engineering Aspect*, Vol. 567, pp. 213-227, 2019.
10. A. Bafaqeer, M. Tahir, N.A.S. Amin, "Synthesis of hierarchical ZnV_2O_6 nanosheets with enhanced activity and stability for visible light driven CO_2 reduction to solar fuels", Applied *Surface Science*, Vol. 435, pp. 953-962, 2018.
11. C. Mondal, M. Ganguly, A.K. Sinha, J. Pal, R. Sahoo, T. Pal, " Robust cubooctahedron Zn3V2O8 in gram quantity: A material for photocatalytic dye degradation in water", *Cryst. Eng. Comm*., Vol. 15, pp. 6745-6751, 2013.

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