Structural and Photocatalytic Analysis of $Niwo_4$ Materials

S. Saravanakumar, D. Sivaganesh, S. Sasikumar, M. Arunpandian, R. Archana

Abstract*: The different pH levels of $NiWO_4$ materials were synthesized by co-precipitation route. The insight unit cell properties were studied by Powder X-ray diffraction (PXRD). The detailed structural analyses were done by Rietveld profile refinement method. The morphology on the surface of the synthesized $NiWO_4$ materials was evaluated by scanning electron microscopic images. The presence of elements in the prepared materials were confirmed by energy dispersive X-ray spectroscopy (EDS) analysis. The photocatalytic activities of prepared materials are performed on methylene blue which is degraded by irradiation of catalyst in 50 minutes under ultra violet light.

Keywords: X-ray diffraction, Rietveld Refinement, scanning charge microscopy, Photocatalytic degradation

I. INTRODUCTION

In modern eras, energy crisis problem and environmental pollution are affects the human health and animals. Semiconducting materials based photocatalyst was well known and most promising materials used for industrial technological applications. These materials also used to solve the environmental pollution problems through photocatalytic degradation by the solar energy [1-3]. Typically, TiO_2 and ZnO has more effective photocatalyst compared to other materials due to the stability, nontoxicity and high activity. The TiO_2 and ZnO based semiconducting materials are possess less active in visible light due the band gap and fast recombination of the electron-hole pair [4, 5]. Therefore, the preparation of stable with less polluted photocatalyst irradiated by the ultra-violet and visible light are more challenging of researchers.

Metal tungstates with general formula AWO_4, where A is a divalent cation (A^{2+} = Mn, Fe, Co or Ni) act as a network modifier. The wolframite type structures with metal tungstates crystalized by monoclinic structure with the space group (P2/c) and two molecular formula units per unit cell (Z=2) [6].

Transition metal based tungstates have most promising catalysts due to the electrical and electrochemical properties and impending application [7]. Normally, metal tungstate based catalyst was great applied for supercapacitor applications [8], Li-ion battery [9], electrochemical

Applications [10], gas sensors [11] and photocatalyst [12]. $NiWO_4$ has low price, narrow band gap and eco-friendly catalyst.

In this context, the photo catalytic properties of pure $NiWO_4$ nanocrystals exhibit interesting industrial applications such as the photodegradation of methylene blue [13], remazol brilliant violet 5R (RBV5R) [14], methyl orange [15], 4-nitrophenol [16] and rhodamine b [17] at room temperature.

The surface area and surface topology are plays an important part in the photocatalytic activity, photoluminescence, conductivity, and so forth properties of the specified materials [18]. The synthesis procedure like pH variation, dopant concentration, molar ratio and calcination temperature are the important candidate for the enhancement of surface area and surface morphology [19]. Recently, $NiWO_4$ were prepared by various preparation methods such as co-precipitation [20], Sol-gel [21], hydrothermal [22], mechanochemical [23] methods. In particular co-precipitation technique is simple way to prepare $NiWO_4$, because of this method is economically effective and easy to prepare the materials. With this mind we prepared the $NiWO_4$ for different pH (7 and 8) to study their structural and photocatalytic degradation of methylene blue. To the best of our research literature knowledge, it is the first time reported to deals the structural nature of NiWO4 using Rietveld refinement [24] through JANA 2006 software [25].

II. EXPERIMENTAL

A. *Sample preparation*

1.8270 gram of nickel nitrate ($Ni(NO_3)_2$) was dissolved in 200 ml deionized water to prepare the 0.05 M of nickel nitrate. 3.2985 gram of Na2WO4.2H_2O was dissolved in 200 ml deionized water to prepared 0.05 M of sodium tungstate. The white precipitates were formed by adding drop wise to the sodium tungstate solution to nickel nitrate solution. Adding NaOH to obtained pH 7. Then gently collects the white precipitate by centrifugation process. Washing with ethanol and deionized water during the centrifugation. Then the washed white precipitate was dried at 80 C for 5 hrs using a hot air oven. The dried sample was calcinated at 600 C for 4 hrs using a muffled furnace.

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The above method was followed for the preparation of $NiWO_4$ sample in pH level 8 by the addition of more amount of NaOH.

B. *Evaluation of Catalytic degradation of Pollutants*

Heber multi-lamp (model HML-MP 88) was used as a photoreactor for the degradation of organic pollutant under ultra violet light (λ< 400nm) irradiation. In 250ml beaker about 50mg of the sample was mixed in 100ml Methylene blue dye solution with 10□m conc. This mixture was stirred for 30 mins in dark room to ensure the adsorption-desorption equilibrium of the reaction solution. After completion of stirring, the colloidal mixture was transferred into a reaction vessel. After the reaction in 10 min time intervals, 5ml of the reaction solution was taken and it monitored the absorption peak of MB at 668 nm using UV visible spectrometer. By ultracentrifuge the reacting solution was centrifuged and the catalyst was separated then it is washed with de-ionized water and dried at 60˚C. Finally, it is used for the reusability test.

C. *Sample characterization*

The NiWO4 materials were analyzed by powder X-ray Diffractometer with CuKα (λ=1.54056 Å) radiation in the range of 10° to 75° with the interval of 0.02°. The microstructure and surface morphology of the samples was measured using scanning electron microscopy. Energy Dispersive X-ray Spectrometer (EDAX APEX) was used to analyses purity of $NiWO_4$. The UV – Vis absorption spectroscopy were measured in SHIMADZU UV-1800.

III. RESULTS AND DISCUSSION

A. Structural analysis

The phase pure monoclinic crystal system was identified using PXRD analysis which is compared to the standard JCPDS pattern [26]. There is no additional peaks were presented in the observed X-ray profile which confirms the prepared NiWO4 materials are phase pure system with space group P2/c symmetry. The observed PXRD profiles of different pH level of $NiWO_4$ materials are shown in figure 1. The diffraction peaks shifted towards lower angle side which is leads to the cell constants with increasing the pH level 7 to 8 of $NiWO_4$ materials. The intensity of the diffraction peaks are maximum at pH 8 which may be due to high pH of NiWO4 exhibit high crystallinity compared to the $NiWO_4$ prepared by pH 7. The crystallite size of as prepared NiWO4 materials are calculated by Scherrer equation [27]. The average crystallite size of $NiWO_4$ prepared by pH 7 and pH 8 are 33 nm and 13 nm respectively.

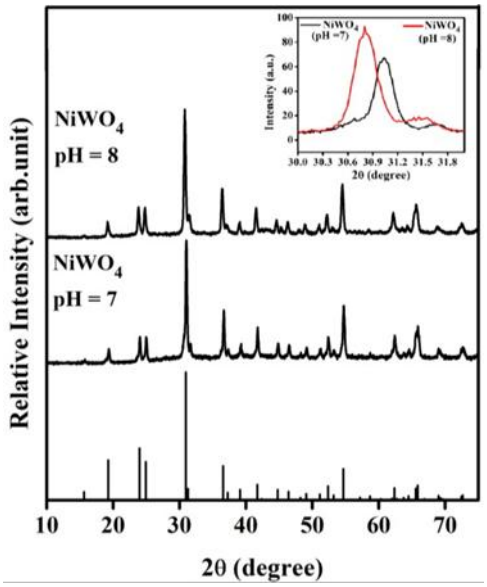

Fig. 1.Observed PXRD profile of NiWO4 materials

The detailed structural analysis of $NiWO_4$ materials are studied by Rietveld refinement technique [24] which was done by JANA 2006 software [25]. This method was used to fit the observed X-ray profile to calculated profile. The refined profiles of $NiWO_4$ materials are shown in figure 2 & 3 and the fitted structural parameters are shown in table 1.

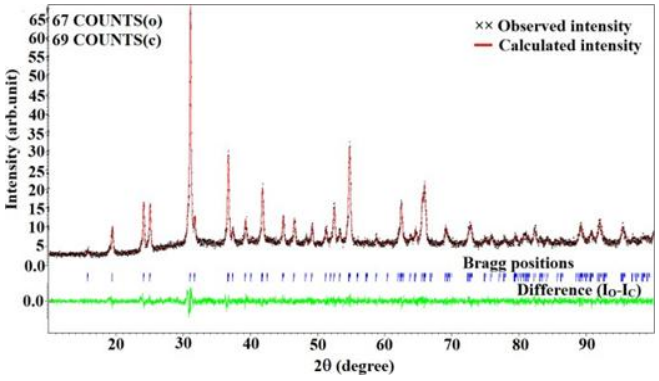

Fig. 2.Refined profile of NiWO4 at pH

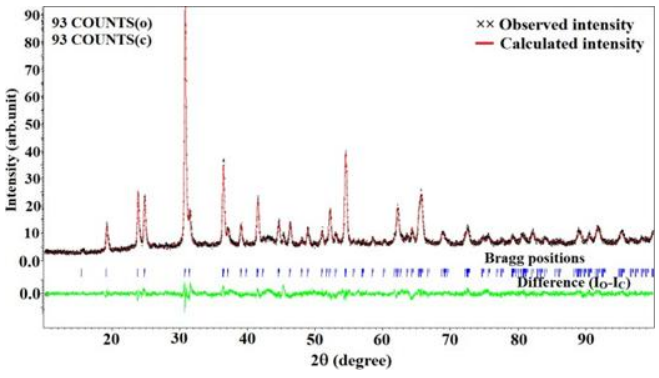

Fig. 3.Refined profile of NiWO4 at pH 8

Table I - Refined Parameters Of $Niwo_4$

Parameters	pH = 7	pH = 8
a (Å)	4.5962(2)	4.6051(5)
b (Å)	5.6636(3)	5.6711(6)
c (Å)	4.9120(6)	4.9162(5)
Volume (Å)	127.86(2)	128.39(4)
Density (g/cm^3)	7.92	7.95
$R_{obs}(\%)^a$	5.81	6.33
$R_p(\%)^b$	1.46	1.98
$F_{(000)}^c$	268	268
GOF[d]	0.19	0.23

R_{obs}- observed profile reliability factor.
R_P - profile reliability factor.
$F_{(000)}$- Number of electrons per unit cell.
GOF – Goodness of Fit.

B. Scanning electron microscopy studies

The microstructure analysis has done by scanning electron mmicroscopic analysis. The surface morphology of the prepared $NiWO_4$ materials are shown figure 4 and 5. Its shows that the highly agglomerated and uncleared morphology were obtained at the $NiWO_4$ prepared by pH 7 materials. At a same time well dispersed morphology were observed for pH 8 sample.

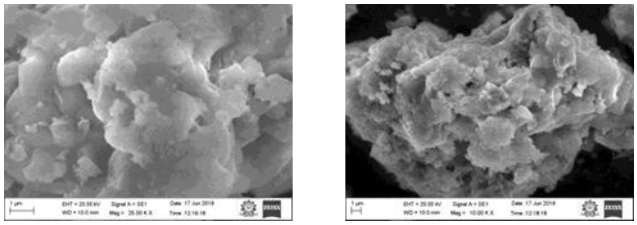

Fig. 4.SEM images of NiWO4 at pH 7 materials

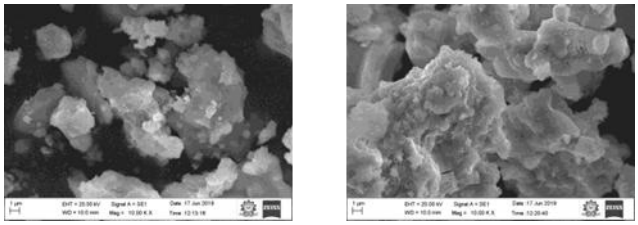

Fig. 5.SEM images of NiWO4 at pH 8 materials

C. *Energy Dispersive X-ray Spectroscopy (EDS) analysis*

The purity of the prepared $NiWO_4$ materials was confirmed by EDS analysis. The sharp peaks of Ni, W and O are indicates that the formation of pure $NiWO_4$ and respective atomic wt% also tabulated in Table.2. The intensity of Ni, W and O peaks are increases in pH 8 which may be due to the high crystallinity of the material as shown in figure 6 (a) and (b).

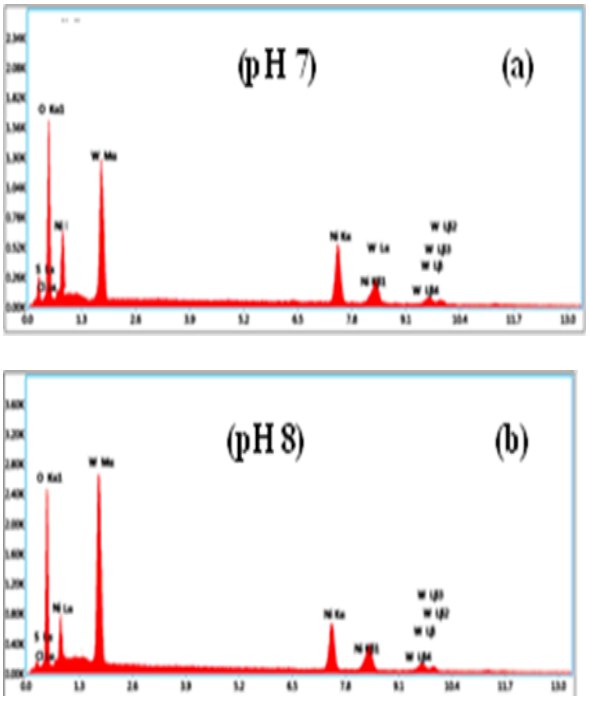

Fig. 6.EDS spectrum of NiWO4 materials

D. *UV-Vis analysis*

The absorption spectra were observed for the prepared $NiWO_4$ materials in the range from 200 – 900 nm with 1 nm interval as presented in figure 7. The observed absorption peaks obtained at the wavelength of 230-300 nm with broader shoulder. The energy band gap of prepared NiWO4 materials determined by liner fit of the extrapolated graph and the graph drawn between energy (Eg) and $(\alpha hv)^2$ as shown in figure 8. The energy band gap is calculated by Tacu plot [28] and the values of $NiWO_4$ in pH 7 and 8 are 3.15 and 3.2 eV.

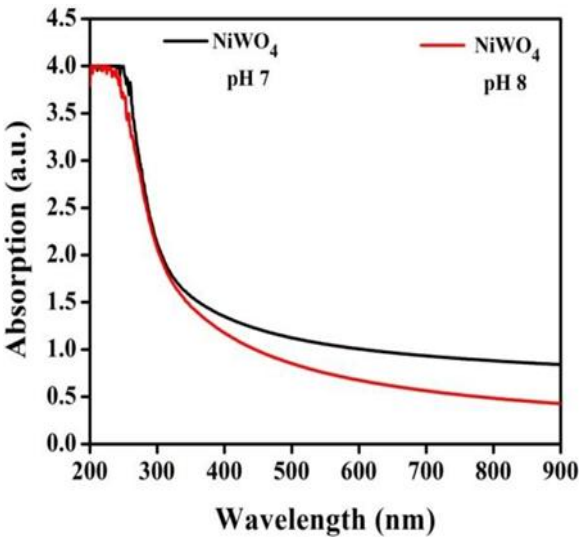

Fig. 7.UV-Vis absorption spectra of NiWO4 materials

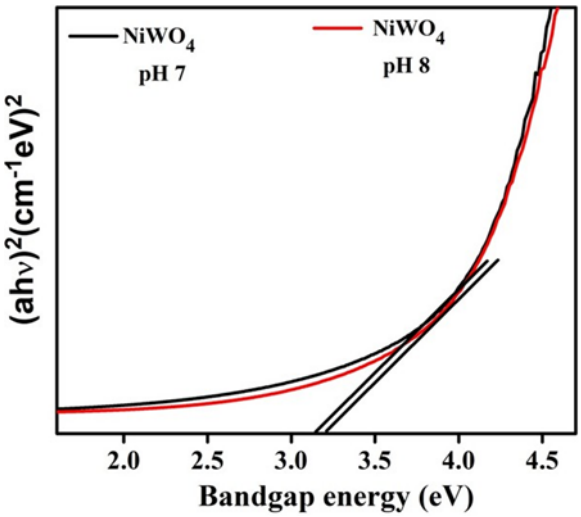

Fig. 8.Tauc plot of NiWO4 materials

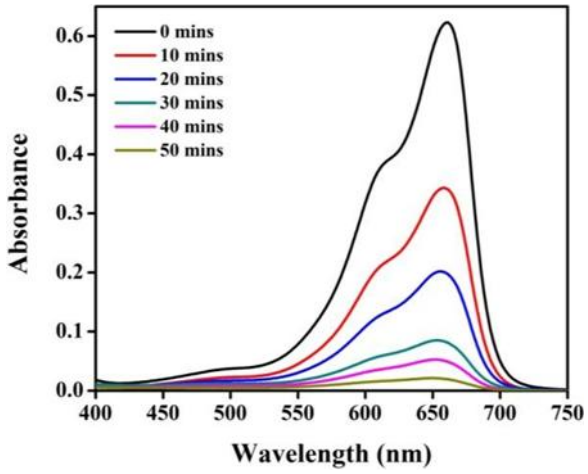

Fig. 10. Photo degradation of MB solution under NiWO4 catalyst

E. *Photocatalytic decomposition of organic pollutants*

The catalyst NiWO4 is degrading MB dye under ultra violet irradiation. About 50 mg of $NiWO_4$ catalyst are takes 50 mins for the completion of the MB degradation under ultra violet radiation with pH 7 and pH 8. That time the C/C0 range becomes almost zero. Moreover, the efficiency of the catalyst at pH 8 is very high compared to pH 7.

The efficacy of the catalyst loading was analyzed and differed from 30-60 mg. But in 50mg catalyst are very effective for the degradation than those others. If highly amount of catalyst is used for the degradation process then decrease the efficiency and the surface area of the degradation material are increased which leads to an increase in the reactive sites.

In $NiWO_4$ nanomaterial [50 mg] the degradation of MB (1 X 10-5 M) is analyzed the absorption spectra values by different time intervals and predict absorption peaks corresponds to pollutant degradation. Thus, the absorption value 668 nm correspond MB respectively. From figure 9 shows the photo degradation efficiency of catalyst at pH 7 & 8 and figure 10 shows the absorption spectrum for the degradation of MB by $NiWO_4$ material

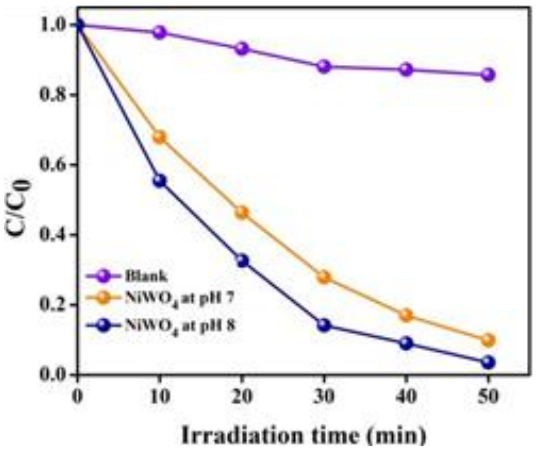

Fig. 9.Band gap estimation from UV – Vis spectra of NiWO4 materials

IV. CONCLUSION

The pure phase monoclinic structured $NiWO_4$ materials were prepared by simple co-precipitation technique. The structural analyses were confirmed by PXRD analysis. The morphological and purity of the materials have done by SEM and EDS analysis. The photocatalytic degradation of methylene blue has done by irradiation of ultra violet light at 50 mins.

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