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Department of Chemistry, Easwari Engineering College (SRM Group of Institutions), Chennai-600089, India.

Room Temperature Synthesis, Characterization, and Photocatalytic Property of Cobalt Tungstate Nanoparticles

S. Muthamizh[1], K. Giribabu[1], R. Manigandan[1], S. Munusamy[1], S. Praveen Kumar[1], R. Suresh[2], V. Narayanan[1*]

Department of Inorganic Chemistry, University of Madras, Guindy Campus, Chennai, India [1]

Department of Chemistry, SRM University, Ramapuram Campus, Chennai, India [2]

*Corresponding Author

ABSTRACT: Cobalt tungstate ($CoWO_4$) nanoparticles were prepared by simple and cost effective precipitation method. The ($CoWO_4$) nanoparticles were synthesized by reacting 1:1 mole ratio of Cobalt chloride and sodium tungstate. The synthesized nanoparticles were characterized by XRD, Raman, SEM and DRS-UV spectroscopy. The XRD pattern reveals that the synthesized ($CoWO_4$) has monoclinic structure. In addition, by using the XRD data lattice parameter values also calculated. The Raman analysis confirms the presence of Co-O and W-O bonds in ($CoWO_4$) nanoparticles. SEM analysis revels that the synthesized ($CoWO_4$) are in nm rang. The optical property of ($CoWO_4$) nanoparticles was carried out by DRS UV-Visible spectroscopy. The photocatalytic property of synthesis $CoWO_4$ was investigated by degradation of methylene blue as the model pollutant.

KEYWORDS: Nanoparticles, rock like, photocatalyst, methylene blue**.**

I. INTRODUCTION

The organic contaminants in the waste water can be degraded by many methods like photocatalysis [1], advanced oxidation process [2], biodegradation [3]…etc. Among all the techniques photocatalysis is a promising technique for the degradation of organic pollutants. A well-known photocatalytic material TiO_2 was mostly used as an excellent photocatalyst for the degradation of organic pollutants under UV irradiation [4]. Only 5% of the solar energy consists of UV light which reaches the earth surface, which limited the photocatalytic degradation of organic pollutants. So far the past few years researchers have put tremendous efforts to develop visible light driven photocatalyst, which could maximally utilize the clean, safe and abundant solar energy. Various nanomaterials have been prepared like metal oxides [5], oxy halides [6], sulphides [7], tungstates [8], and molybdates [9] and so on. The synthesis of well-crystallized nanostructure $CoWO_4$ crystallites with controllable size and shape has recently drawn increasing attention due to its optical and photocatalytic properties. $CoWO_4$ also attracted our attention because cobalt-based catalysts have recently been center stage in the development of low-cost water oxidation catalysts.

In the present work $CoWO_4$ nanoparticle was synthesised by simple precipitation method and investigated the photocatalytic degradation of methylene blue dye.

II. EXPERIMENTAL DETAILS

2.1. Materials

All the chemicals used in the synthesis such as cobalt chloride, and sodium tungstate were analytical grade reagents purchased from Qualigens and Merck respectively. All the chemicals were used without further purification, double distilled water and ethanol were used as solvents.

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2.2. Synthesis of $CoWO_4$ nanoparticles

$CoWO_4$ nanoparticles were prepared by reacting 1:1 mmol ratio of $CoCl_2$ and $NaWO_4$. 0.5 mol each of $CoCl_2$ and $NaWO_4$ were separately dissolved in 25 mL of distilled water at room temperature. The sodium tungstate solution was added drop by drop to cobalt chloride, a purple precipitate was formed, and the contents were stirred for 2 h. Then the colloidal solution was cooled to room temperature and filtered, the resulting precipitate was washed with deionized water and ethanol for several times.

2.3. Characterization

The XRD pattern of the as synthesized sample was analysed by using Rich Siefert 3000 diffractometer with Cu $K_{\alpha 1}$ radiation (λ=1.5406 Å). Raman spectrum was recorded using laser Raman microscope, Raman-11 Nano Photon Corporation, Japan. DRS UV–Vis absorption spectrum was recorded using Perkin-Elmer lambda 650 spectrophotometer. The morphology of synthesized $CoWO_4$ was analyzed by means of HITACHI SU6600 scanning electron microscopy (TEM).

III. RESULT AND DISCUSSION

3.1. X-ray diffraction study

The XRD pattern of synthesized $CoWO_{4\ is}$ shown in Fig. 1. The observed diffraction peaks were well matched with standard file card (JCPDS.01-072-0479). The synthesized $CoWO_4$ has monoclinic geometry with space group of p_2/c and the lattice parameter of a = 4.66 Å, b=5.68 Å and c = 4.95 Å. There are different peaks for $CoWO_4$ are narrow which shows the crystalline nature of the synthesized nanoparticle. The obtained diffraction peaks corresponds to planes (010), (100), (011), (110), (111), (020), (120), (121), (130), (221), (113), (023).

3.2. Raman Analysis

Raman spectrum of synthesized $CoWO_4$ is shown in Fig. 2. The bands observed for $CoWO_4$ were 881, 769, 681, 546, 408, 335, 275, 129, and 93 cm^{-1}. Which are obtained from different modes of absorption of different translational levels. A very strong band appeared at the region of 878 cm^{-1} corresponds to the strong symmetric stretching of WO_2 group in the $CoWO_4$. The bands at 769 cm^{-1} indicates the presence of weak asymmetric stretching vibration mode of W–O–W bond. The peak at 546, 681, 408 cm^{-1} is attributed due to stretching vibration of Co–O. The band at 335 cm^{-1} confirms the medium scissoring of both WO_2 and W–O–W [30]. A weak band appeared at 275 cm^{-1} indicates the bending mode of $[WO_6]^{6-}$. [10]

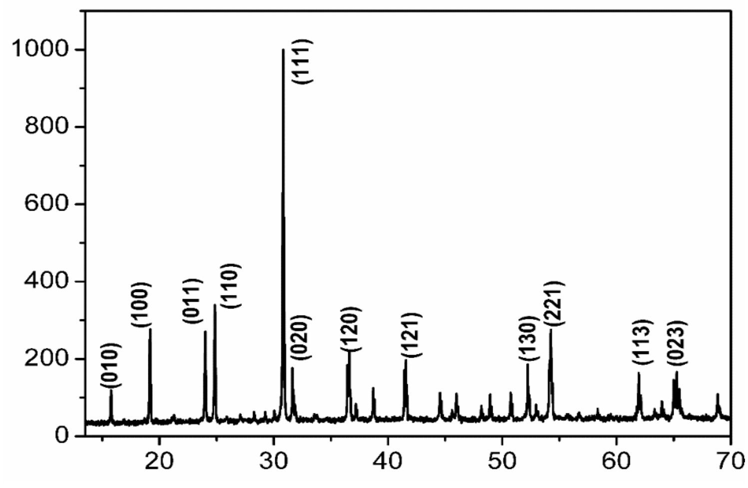

Fig. 1 XRD pattern of $CoWO_4$ nanoparticles.

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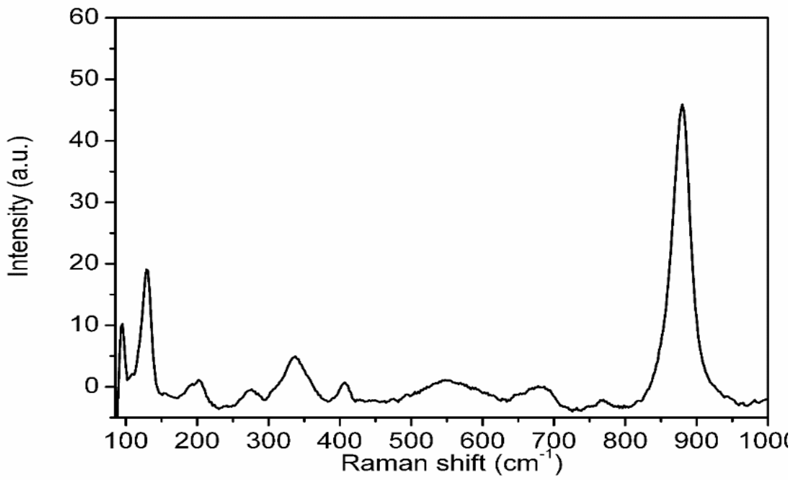

Fig. 2 Raman spectrum of $CoWO_4$ nanoparticles

3.3. Optical property of $CoWO_4$

Diffuse Reflectance Spectroscopy (DRS) is a useful tool for characterizing the optical absorption property for semiconductor materials, The UV-Vis diffuse reflectance spectra of synthesized $CoWO_4$ nanoparticle is shown in Fig. 3. As a crystalline semiconductor, the optical absorption near the band edge follows the formula,

$(h\upsilon\alpha)^{1/n}=A(h\upsilon-E_g)$

where h-Planck's constant, ν-frequency of vibration, α-absorption coefficient, E_g-band gap, A-proportional constant. By using the above formula band gap of the synthesised $CoWO_4$ was calculated to be 2.9 eV which is shown in Fig 4. Which is a well match with previous reported value? From this we can conclude that the synthesised nanomaterial is a promising photocatalyst towards organic pollutant.[11]

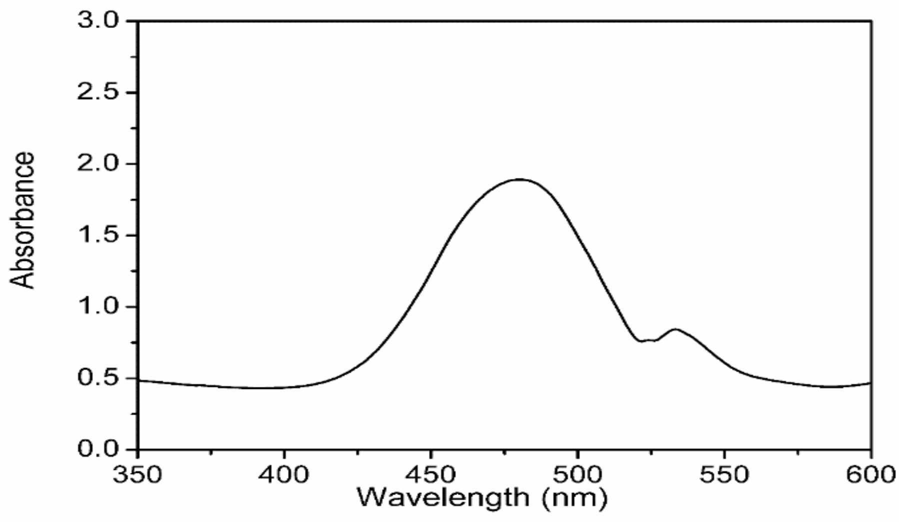

Fig. 3 DRS- UV Vis spectrum of $CoWO_4$ nanoparticle

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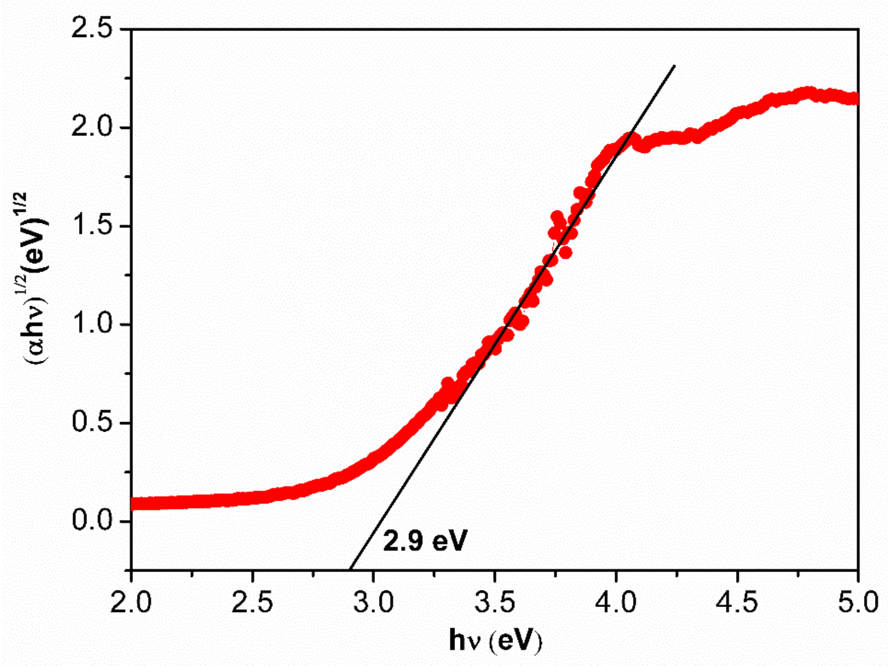

Fig. 4 Band gap plot of $CoWO_4$ nanoparticle.

3.4. Morphological Analysis

Morphology of the synthesized $CoWO_4$ was investigated by TEM analysis. Fig. 5 shows the obtained TEM image. Morphology of synthesised $CoWO_4$ was found to be rock like image in nano meter range.

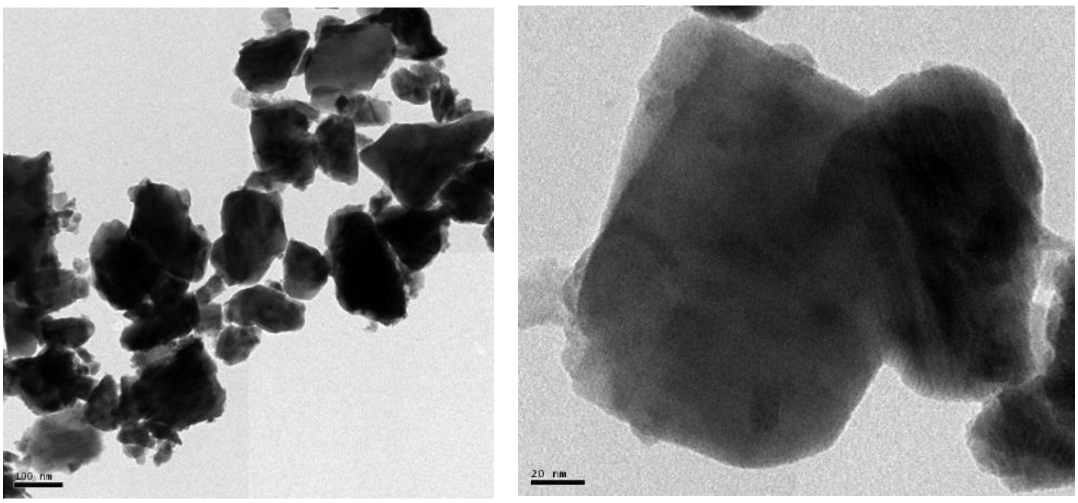

Fig. 5. TEM image of $CoWO_4$ nanoparticle

3.5. Photocatalytic properties

The photocatalytic activity of the fabricated pure $CoWO_4$ was investigated towards the degradation of organic dye Methylene blue (MB) under visible light irradiation was shown in Fig. 6. 25 mg of photocatalyst was taken and transferred into a beaker which contains 100 ml of 1×10^{-5} M MB dye solution. Prior to light exposure, the mixture of

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dye and photocatalyst was kept under dark in order to attain adsorption – desorption equilibrium between the photocatalyst and dye. After 30 min the reaction mixture is exposed to visible light under constant magnetic stirring. The reaction mixture was collected every 10 min and subjected to UV-Vis analysis. It can be seen that the intensity of the absorption peaks decreased as the reaction progressed with $CoWO_4$ as the catalyst. After 40 min of irradiation, the intensity of the absorption peaks decreased to 70 % of that of the initial MB solution. [12]

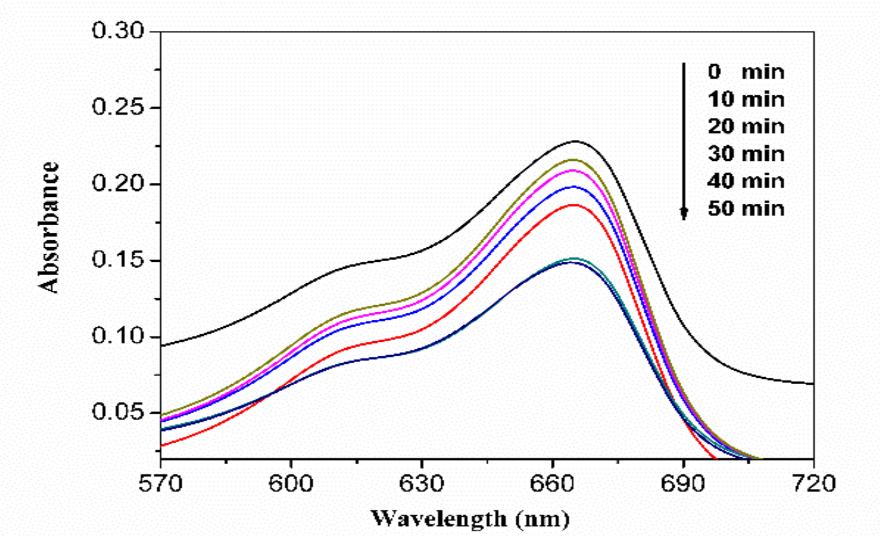

Fig.6. UV–Vis spectrum of the MB solution (100 ml, 10^{-5} M) after solar irradiation for different times with the $CoWO_4$ nanoparticles as the catalyst: 0 min; 10 min; 20 min; 30 min; 40 min; 50 min; and 60 min.

IV .CONCLUSION

Cobalt tungstate nanoparticles were synthesized by simple precipitation method. The structure of the $CoWO_4$ nanoparticles was characterized by XRD, and Raman spectroscopy. The morphology of the $CoWO_4$ was confirmed by TEM. The synthesized nanoparticles were employed for the degradation of methylene blue dye.

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