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RAPID VISIBLE LIGHT PHOTOCATALYTIC DEGRADATION OF ORGANIC POLLUTANTS USING ZNWO$_4$ NANOPARTICLES

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Abstract- **$ZnWO_4$ nanoparticles have been successfully synthesized via highly effective and environmentally friendly sol-gel method through controlling the reaction time and temperature. The calcined $ZnWO_4$ shows a band gap of 3.2 eV as calculated from UV-DRS. The products were characterized by X-ray powder diffraction (XRD), Scanning electron microscope (SEM), Transmission Electron Microscope (TEM), Fourier infrared spectrum (FT-IR). The photocatalytic visible light irradiation by using 400 W metal halide lamp as light source. The results indicated that the degradation rate of 100 ml aqueous solutions of 20 ppm CI was observed to be 97% after 2.5 hrs and 20 ppm CV was 98% after 2 hrs under visible light irradiation.**

Keywords: **$ZnWO_4$ nano particles, Crystal violet, Carmine indigo, visible light degradation, Sol-Gel synthesis.**

I. INTRODUCTION

Nano zinc tungstate ($ZnWO_4$) has many interesting properties such as luminescence which could be used for flashing materials, LED [1], magnetic and fluorescent materials [2], optical fibre, humidity sensors [3], light emitting materials [4-5], photocatalytic materials [6], scintillator [7], laser host [8] and nanoordered substrate materials [9]. It is also having magnetic [10] and energy related applications [11]. Tungstates have caught the attention of researchers as photocatalysts since tungsten oxide ($WO^{2-}{}_4$) was found to be capable of photocatalytic splitting of H_2O into H_2 and O_2. From the past few years number of synthetic techniques, has been adopted for the hierarchical structures of $ZnWO_4$, such as hydrothermal method [6, 12], Microemulsion method, Sol-gel method [13-16], decomposition of polymeric complex [17], co precipitation and solid-state metathesis [18]. However, there are some drawbacks in the above said methods such as elevated reaction temperatures, long reaction cycles and difficult procedures.

Nano $ZnWO_4$ photocatalyst was successfully synthesized via the sol-gel process at low temperatures. The sol-gel method was said to be a potential route for controlling the bulk and surface properties of the oxides. As this method is carried out in solution phase, tailoring of certain desired structural characteristics such as particle grain size, homogeneity and morphology are possible. So far $ZnWO_4$ has been reported as a photocatalyst for the degradation of Rhodamine B, Methylene blue, Phenol, 4-chlorophenol, Salicylic acid, Acetaldehyde and Methyl orange under UV irradiation around ~ 254 nm.

In view of the above, the present study is undertaken to assess the visible light activity of $ZnWO_4$ for photocatalytic degradation of Caramine Indigo and Crystal violet. The measurements suggested that the photocatalytic property of the sample is related to the crystallinity, surface area, and dimension of particles. Moreover, the catalyst is relatively stable and can be reused.

In the proposed study, nano $ZnWO_4$ was prepared by sol-gel method. The photocatalytic activity of the catalyst was evaluated by the degradation of CI and CV.

II. MATERIALS AND METHODS

A. Materials used -

Zn $(NO_3)_2.4H_2O$ (Zinc Nitrate) [Merck grade], $Na_2WO_4.2H_2O$ (sodium tungstate) [Merck grade], Ethylene glycol (EG) [Merck grade], Caramine Indigo [Merck grade] and Crystal Violet [Merck grade] were purchased from Sigma Aldrich Pure Chemical Industries Co., Ltd. They were used as received without further purification.

B. Catalyst preparation -

Nanoparticles of $ZnWO_4$ were prepared using ethylene glycol (EG) as a capping agent and the reaction was carried out at room temperature. In a typical synthesis procedure 0.946 g of Zn $(NO_3)_2$.4H2O and 1.64 g of $Na_2WO_4.2H_2O$ were stirred separately in EG. After complete dissolution, the two mixtures were added and stirred for 24 h. Excess of sodium was removed by washing with water and finally with ethanol. The formed precipitate was dried at 70°C and which is further calcined at 300^0C for identification of phase.

C. Measurements of photochemical activity –

The photocatalytic activity of nano $ZnWO_4$ catalyst was evaluated by degradation of CI and CV under a 400 W visible light irradiation. Before visible irradiation, an adsorption-desorption equilibrium was established by ultrasonic and mechanical stirring for 30 min in dark. After that, the solution was subjected to magnetic stirring and exposed to visible light irradiation. A little amount of reaction solution for UV-Vis spectroscopy analysis was taken from the photoreactor at appropriate time interval. Progress of decolourisation was followed by determination of residual concentration of the indicator by recording the corresponding absorption spectrum. The same procedure has been adopted for Crystal violet indicator. All the experiments were conducted at ambient conditions.

III. RESULTS AND DISCUSSION

A. X-ray diffraction (XRD) -

The morphology and Phase purity of the calcined and washed powder was investigated with XRD patterns of $ZnWO_4$ photocatalysts were recorded by a PANalytical- X' Pert PRO, Japan 4 X-ray diffractometer operated at room temperature, using Nickel filtered Cu-K_α radiation (λ= 1.54059 Å), over the range of 10-80° with a scan rate of 2° min^{-1}. Fig. 1 shows the XRD pattern of nano $ZnWO_4$ heated for 70^0C followed by calcination at 300^0C for 3 hrs. All peaks in XRD pattern could be indexed to monoclinic wolframite $ZnWO_4$ in terms of JCPDS Card Files: 88-0251 and 14-0676, respectively. It is also seen that an obvious phenomenon of wider diffraction peaks appears, which might be attributed to little dimension of grain. It is noted that the $ZnWO_4$ single phase could be observed in all XRD patterns. The calculated lattice constants a= 4.697 A^o, b= 6.041 A^o, c= 4.925 A^o represents nano $ZnWO_4$ has phase pure monoclinic. The average crystallite size of the catalyst is 10 nm which was calculated from scherrer formula.

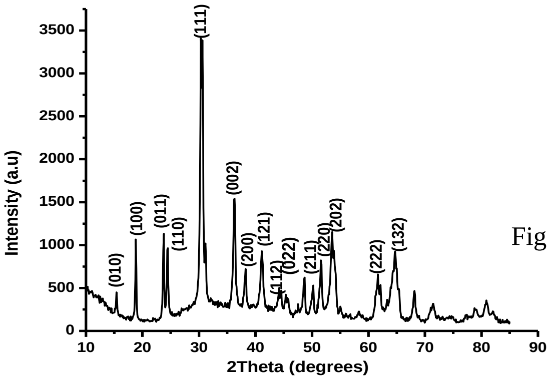


Fig. 2.

Fig. 1. XRD pattern of nano $ZnWO_4$

B. FT-IR -

Fourier transform infrared spectra (FT-IR) were recorded on a Perkin-Elmer 1600 FT-IR spectrometer with a KBr disk. The FT-IR spectrum of nano $ZnWO_4$ is shown in Fig. 2. All the observed peaks are in good agreement with earlier reports [Huang et al, 2007]. The peaks at $463cm^{-1}$ and 585 cm^{-1} are attributed to the bending vibrations of W–O and the peaks at 833 cm^{-1} and 870 cm^{-1} are attributed to streching mode of W-O in WO_6 octahedra. Peaks at 532 and 620 cm^{-1} represents the symmetric vibrations of bridged oxygen atoms of Zn-O-W.

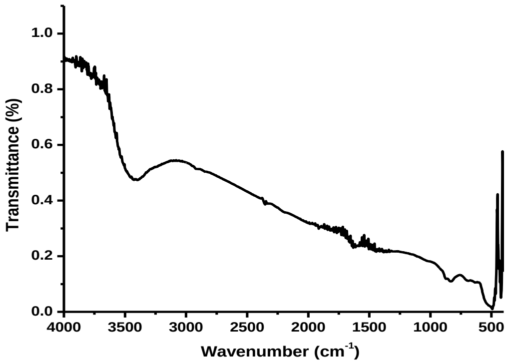


Fig. 2. FT-IR spectra of nano $ZnWO_4$

The absorption bands at 430 and 465 cm^{-1} are due to symmetric and asymmetric deformation modes of W-O bonds and Zn-O bonds in WO_6 and ZnO_6 octahedra respectively. Other peaks at 3600 and 1660 cm^{-1} are due to H-streching vibrations of ethylalcohol and H–O–H bending vibrations.

C. UV-DRS -

UV-Vis DRS was performed on a Hitachi (U-3010) between 200 to 800 nm range and $BaSO_4$ was used as a reference. Spectral grade $BaSO_4$ was taken as reference for the reflectance spectra Photoabsorptive ability of the sample is assessed by UV-DRS shown in Fig. 3. UV-DRS shows an absorption edge in the region close to 400 nm from which the estimated band gap of the synthesized $ZnWO_4$ powder is calculated to be 3.2 eV. A band gap of 3.9 - 4.4 eV for $ZnWO_4$ single crystals, while for nano structured powders a direct band gap of 3.31 eV and an indirect band gap of 3.8 eV were reported [6].

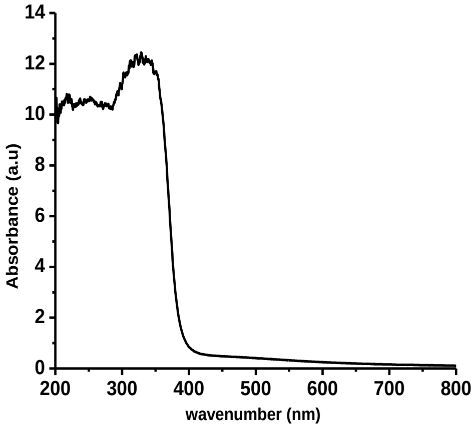


Fig. 3. UV-DRS of nano $ZnWO_4$ powder

D. Scanning Electron Microscope (SEM).

Microstructural investigations of the samples were performed on the powders of the samples using SEM (JEOL-JSM-6610LV, Tokyo, Japan). The morphologies and microstructures of the sample were investigated with SEM shown in Fig. 4. From the SEM image it was found that the nano $ZnWO_4$ particles are in the range of about 1-3 micrometers and agglomerated with uneven particles form.

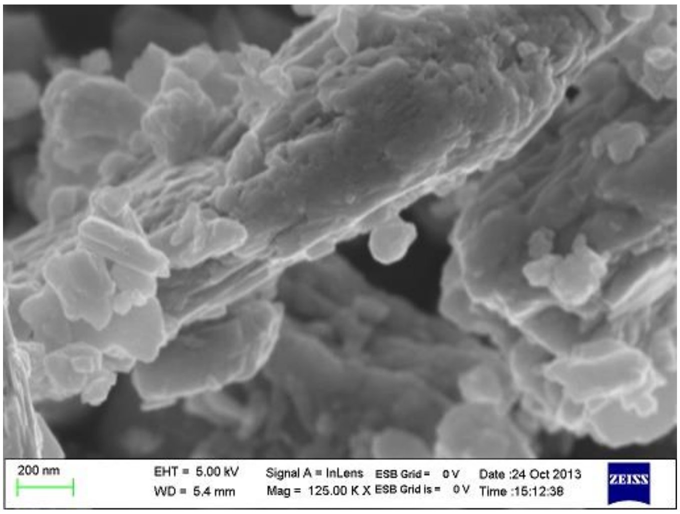


Fig. 4. SEM image of $ZnWO_4$

E. Transmission Electron Microscope (TEM).

The TEM image of the prepared $ZnWO_4$ is shown in Fig. 5. From TEM image it was observed that, all the particles are in spherical shape with uneven size. The average crystallite size of the $ZnWO_4$ particles are in the range of about 7-10 nm. This result is good agreement with the XRD data. Based on the above results it can be concluded that the prepared ZnWO4 particles are in nanometer range with spherical shape.

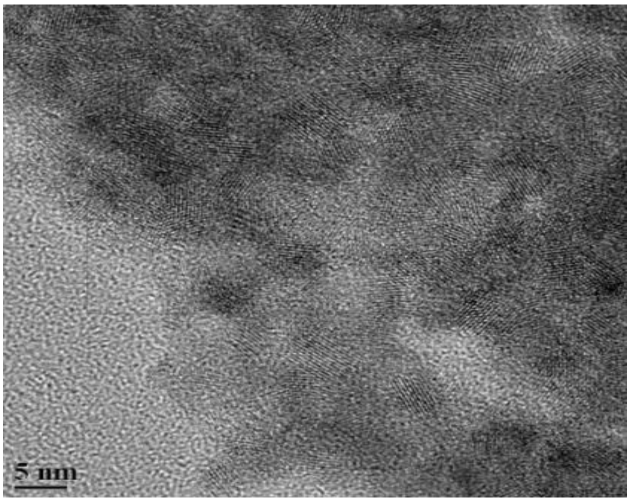


Fig. 5. TEM image of $ZnWO_4$

F. Evaluation of photocatalytic activity of catalyst

Nano $ZnWO_4$, as a semiconductor with a band gap (3.2 eV) around 3.9–4.4 eV, has high photocatalytic activity under Visible light irradiation. The photocatalytic activity was tested via degradation of aqueous CI and CV under Visible light irradiation. The UV-Visible absorption spectral changes taking place during the photo degradation of CI and CV for samples and photocatalytic kinetic curves of samples are shown in Fig. 6.

Fig. 6(a&b) shows the degradation of CI and CV at different time intervals with decreasing intensity of peaks. The degradation was completed in 150 min for CI and 120 Min for CV under visible light irradiation. This result was strongly supported by the UV-DRS spectrum and indicated the band gap energy of nano $ZnWO_4$ was 3.2 eV. There is no change observed in the degradation of CI and CV in the absence of catalyst after continuous irradiation of visible light for 3h. The rate constants of the degrading process also calculated as shown in Fig. 7(c&d), which indicates that entire process follows the pseudo first order reaction.
The linear relationship between ln (C/C_0) and time demonstrates pseudo-first-order kinetics.

$$\eta = \ln (C/C_0) = kt$$

Where C/C_0 is normalized CI and CV concentrations, t is the reaction time, and k is the reaction rate constant (min^{-1}).

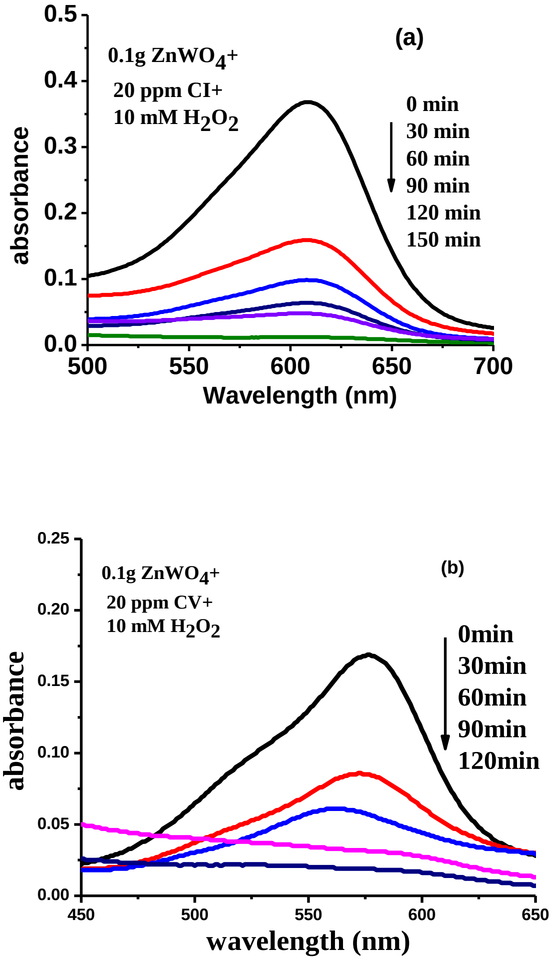


Fig. 6. Photocatalytic degradation of (a) CI (b) CV using nano $ZnWO_4$ under visible light irradiation

On the basis of the above experimental observation, photocatalytic mechanism for $ZnWO_4$ photocatalytic degradation of CI and CV is speculated (Scheme 1&2). $ZnWO_4$ energy band structure was composed by discrete, full-of-low-energy electron valence band (VB) and empty high-energy conduction band (CB); the valence band and conduction band are separated by the forbidden band. When the energy of absorption light is greater than the band gap, the valence electrons are stimulated to the conduction band, making the conduction band with charge, which has a reduction and the valence band resulting hole (h^+) with oxidation. Simultaneously, the poor crystallinity leads to abundant lattice defects acting as holes. These free electrons and holes migrate to the catalyst surface and react with adsorbed water, dissolved oxygen, which generate the high activity of hydroxyl radical ($OH^·$) and superoxide anion (O_2^-), further react with organics in the dyes, and ultimately degraded to CO_2 and H_2O [19-20].

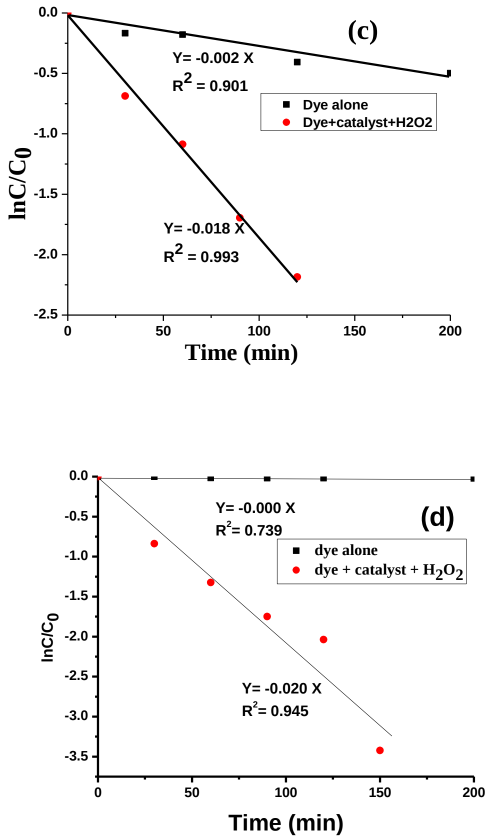
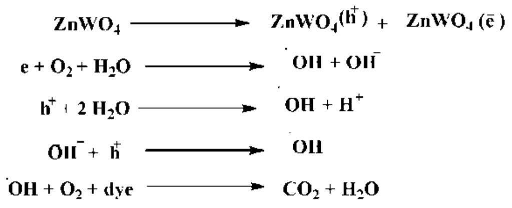
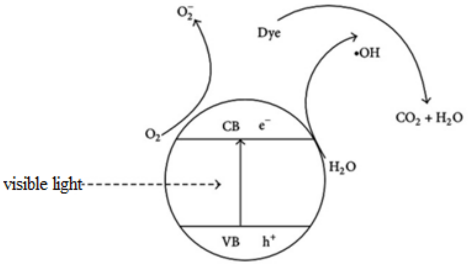
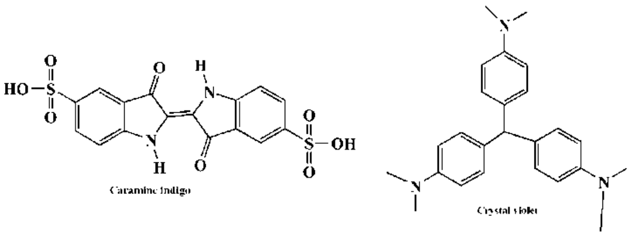


Fig. 7. Rate constants of (c) CI (d) CV using nano $ZnWO_4$ under visible light irradiation.



Scheme 1





Scheme 2

Fig. 8. Structures of CI and CV

IV. CONCLUSIONS

$ZnWO_4$ nanoparticles have been successfully synthesized by sol-gel method at room temperature. The products were characterized by X-ray powder diffraction (XRD), Scanning Electron Microscope (SEM), Fourier infrared spectrum (FT-IR) and Transmission Electron Microscope (TEM). The photocatalytic activities of $ZnWO_4$ nano crystals were evaluated by testing the photo degradation of Caramine Indigo (CI) and Crystal violet (CV) dyes under visible light by using 400 W metal halide lamp as light source. The results indicated that the degradation rate of 100 ml aqueous solutions of 20 ppm CI reached 97% after 2.5 hrs and 20 ppm CV was 98% after 2 hrs under visible light irradiation.

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