INTRODUCTION

Zinc tungstate is technologically important material and much attention due to its structure and reactivity. In recent years scientists show much interest on synthesizing ZnWO₄ because it has wide variety of applications such as in photoluminescence (Vergados, 2012), magnetic properties (Zhang et al., 2002), laser hosts (Yang et al., 2012), flashing materials, humidity sensors (Qu et al., 2000), LED (Tomaszewicz et al., 2009), photocatalytic properties (Fu et al., 2006), phase change optical recording (Kuzmin et al., 1840) and nano ordered substrate materials (Atuchin et al., 2010). Also the ZnWO₄ extensively used in scintillators (Belli et al., 2011), photo anodes, electro optics as well as acoustic and optical fibres (Yoon et al., 2006; Bonanni et al., 1998). From the past few years ZnWO₄ has been prepared by different routes such as Czochralski method (Yang et al., 2008), co precipitation, solid-state metathesis (Huang and Zhu, 2007), hydrothermal method (Fu et al., 2006; Zhou et al., 2003; Fu et al., 2006; Huang and Gao, 2006; Siriwong et al., 2010), decomposition of polymeric complex (Ryu et al., 2004), Microemulsion method (Wu et al., 2007), solid state reaction (Wen et al., 2002), aqueous solution growth (Xiong et al., 2004), template method (Lin et al., 2008) and self propagating combustion method (Dong, et al., 2008). However, there are some drawbacks in the aforementioned methods such as long reaction cycles and elevated reaction temperatures. Sol-gel method was an easy method for preparing ZnWO₄ by controlling morphology and crystal growth orientation. Till now ZnWO₄ has been reported as a photocatalyst for the degradation of 4-chlorophenol, Methylene blue, Rhodamine B, Phenol, Crystal violet, Caramine indigo, Salicylic acid, Methyl orange and Acetaldehyde under UV irradiation around ~ 254 nm. The catalytic activity of ZnWO₄ has been reported by the oxidation of benzyl alcohol to benzaldehyde. In the present study, the synthesis of ZnWO₄ nanoparticles by a facile sol-gel process was reported at low temperatures. The measurements suggested that the photocatalytic property of the sample is related to the surface area, dimension of particles, and crystallinity. Moreover, the catalyst is relatively stable and can be reused. Here we report that different functionalized benzyl alcohols can be selectively oxidised to their corresponding aldehydes using ZnWO₄ nanoparticles.
aldehydes using ZnWO₄ as catalyst in aqueous media. All the products thus obtained are in good yields.

![Chemical structure of benzaldehyde](image)

**MATERIALS AND METHODS**

All the chemicals Zn(NO₃)₂.4H₂O (Zinc Nitrate) (Merck grade), Na₂WO₄.2H₂O (sodium tungstate) (Merck grade), Ethylene glycol (EG) (Merck grade), H₂O₂ (Merck grade), 3, 4-Dimethoxybenzylalcohol (Merck grade), 2-chloro benzyl alcohol (Merck grade), 4-hydroxy benzyl alcohol (Merck grade), 4-hydroxy 3-methoxy benzyl alcohol (Merck grade) and 3-Nitro benzyl alcohol (Merck grade) were purchased from Sigma Aldrich Pure Chemical Industries Co., Ltd and used without further purification. In a typical experiment, Nanoparticles of ZnWO₄ were prepared by dissolving 0.05 mmol of Zn(NO₃)₂.4H₂O and 0.05 mmol of Na₂WO₄.2H₂O was dissolved separately in ethylene glycol under continuous stirring. After complete dissolution, the two mixtures were stirred at constant temperature for 24 h, and cooled to room temperature. Excess of sodium was removed by washing with distilled water and finally with absolute ethanol. The precipitate thus formed was dried at 70°C and calcinated at 300°C for further characterization. ZnWO₄ Nano Particle assemblies were used for benzyl alcohol oxidation as a catalyst. In the reaction mixture, 0.5 mL of substituted benzyl alcohol was added with 25 mL of acetonitrile (as solvent) in a round bottomed flask. Then 100 mg of ZnWO₄ powder and 3 mL of 30% H₂O₂ solution were introduced into the mixture and heated at room temperature for about 12 h. The flask was fitted with aluminium foil to avoid the impinging of atmospheric oxygen. A usual almond smell repents the formation of benzaldehyde, which stipulates the completion of reaction. After completion of the reaction, the products were purified and recrystallized with methanol. The final products were further confirmed by HPLC, ³¹H NMR, FT-IR, and ¹³C NMR studies. The aggregated ZnWO₄ particles were characterized using different spectroscopic tools such as UV-DRS, Scanning Electron microscope (SEM), Transmission Electron microscope (TEM) and FT-IR spectra techniques.

**RESULTS AND DISCUSSION**

The morphology and Phase purity of the calcined and washed powder was investigated with XRD patterns of ZnWO₄ photocatalysts were recorded by a PANalytical- X’ Pert PRO, Japan 4 X-ray diffractometer operated at room temperature, using Nickel filtered Cu-Kα radiation (λ= 1.54059 Å), over the range of 10-80° with a scan rate of 2° min⁻¹. UV-Vis DRS was performed on a Hitachi (U-3010) between 200 to 800 nm range and BaSO₄ was used as a reference. Spectral grade BaSO₄ was taken as reference for the reflectance spectra. Micro structural investigations of the samples were performed on the powders of the samples using SEM (JEOL-JSM-6610LV, Tokyo, Japan). Fourier transform infrared spectra (FT-IR) were recorded on a Perkin-Elmer 1600 FT-IR spectrometer with a KBr disk.

**Figure 1. XRD pattern of nano ZnWO₄ calcined at 300°C for 3hrs**  
Fig. 1(a) shows the XRD pattern of ZnWO₄ nanoparticles at 70°C followed by calcination at 300°C for 3 hrs. All the peaks in XRD pattern indicates the structure ZnWO₄ nanoparticles could be to monoclinic wolframite in terms of JCPDS Card Files: 88-0251 and 14-0676, respectively. A little dimension of grain was observed due to appearance of some wider diffraction peaks. The calculated lattice constants of the catalyst were a= 4.697 Å, b= 6.041 Å, c= 4.925 Å represents nano ZnWO₄ has phase pure monoclinic.

**Figure 2 (a) FT-IR image of ZnWO₄ (b) UV-vis diffuse reflectance spectrum of ZnWO₄ powder**
The FT-IR spectrum of ZnWO$_4$ particles is shown in Fig. 2(a). All the observed peaks are in good agreement with earlier reports (Huang et al., 2007). The bands at 833 cm$^{-1}$ and 870 cm$^{-1}$ are attributed to stretching mode of W-O in WO$_6$ octahedra and the bands at 463 cm$^{-1}$ and 585 cm$^{-1}$ are attributed to the bending vibrations of W–O. The bands at 532 and 620 cm$^{-1}$ represents the symmetric vibrations of bridged oxygen atoms of Zn-O-W. 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 bands at 3600 and 1660 cm$^{-1}$ are due to H-stretching vibrations of ethylalcohol and H–O–H bending vibrations. Photoabsorptive ability studies of the catalyst were evaluated by UV-DRS shown in Fig. 2(b). From the figure it is noted that an absorption edge in the region close to 420 nm was observed and from which the estimated band gap of the synthesized ZnWO$_4$ powder is calculated to be 2.9 eV. For nano structured powders a direct band gap of 3.31 eV and an indirect band gap of 3.8 eV and for ZnWO$_4$ single crystals 3.9 - 4.4 eV were reported.

![Figure 4. TEM image of ZnWO$_4$.](image)

Fig. 4 shows the TEM image of the prepared ZnWO$_4$. 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 5-7 nm. Based on the above results it can be concluded that the prepared ZnWO$_4$ particles are in nanometer range with spherical shape.

Table 1 represents the oxidation of Substituted alcohols to aldehydes. It was noticed that the electron withdrawing substituent’s on the aromatic ring give moderate to good yields. The presence of nitro substitution on the aromatic ring gave high yields rather compared to electron releasing groups according to mesomeric effect. In IR spectra these compounds showed characteristic absorption at a range 700-2940 cm$^{-1}$. In 1H NMR spectral studies a chemical shift for CHO group ain the range of 9.5 - 9.836 ppm for all the compounds were observed.

### Spectral data of the compounds

#### 1. 4-hydroxy 3- Methoxybenzaldehyde

IR (KBr pellet) : 3300 cm$^{-1}$, 3100 cm$^{-1}$, 1660 cm$^{-1}$, 1600 cm$^{-1}$, 1100 cm$^{-1}$; ¹H NMR (400 MHz/CDCl$_3$) δ ppm : 7.17(1H,d), 7.32(1H,s), 6.72 (1H, d), 9.87 (1H, s), 3.62 (1H, s); ¹³C NMR (22.5 MHz/CDCl$_3$) δ ppm : 189.2, 149.2, 148.3, 130.1, 117.2, 116.7, 55.5; Mass-ESI: 151 (M)

#### 2. 3, 4-Dimethoxybenzaldehyde

IR (KBr pellet) : 3250 cm$^{-1}$, 3100 cm$^{-1}$, 1660 cm$^{-1}$, 1600 cm$^{-1}$, 1250 cm$^{-1}$; ¹H NMR (400 MHz/CDCl$_3$) δ ppm: 9.78 (1H, s), 6.70(1H, d), 6.56(1H, s), 6.80(1H, d), 6.38 (2H, s), 3.79(6H, s); ¹³C NMR (22.5 MHz/CDCl$_3$) δ ppm : 189.0, 167.40, 152.00, 150.20, 126.50, 120.00, 116.10, 107.50, 55.25; Mass-ESI: 166 (M)

#### 3. 3-Nitro benzaldehyde

IR (KBr pellet) : 3350 cm$^{-1}$, 3050 cm$^{-1}$, 1650 cm$^{-1}$, 1600 cm$^{-1}$, 1350 cm$^{-1}$; ¹H NMR (400 MHz/CDCl$_3$) δ ppm: 9.78 (1H, s), 8. 29 (1H, d), 8. 29(1H, t), 8.10(1H, d), 8.45(1H, s); ¹³C NMR (22.5 MHz/CDCl$_3$) δ ppm : 189.0, 167.50, 150.20, 139.50, 127.00, 120.30; Mass-ESI: 152 (M)
4. 4-Hydroxy benzaldehyde

IR (KBr pellet) : 3100 cm⁻¹ 3200 cm⁻¹, 3300 cm⁻¹ 1630 cm⁻¹, 1600 cm⁻¹, 1200 cm⁻¹; ¹H NMR (400 MHz/ CDCl₃) δ ppm : 9.85(1H, s), 7.85(1H, d), 7.85(1H, d), 6.82(1H, d), 6.10 (1H, s), 5.15(1H, s); ¹³C NMR (22.5 MHz/CDCl₃) δ ppm : 189.0, 167.12, 160.00, 127.16, 125.96, 116.00; Mass-ESI: 137 (M).

5. 2-Chlorobenzaldehyde

IR (KBr pellet) : 3350 cm⁻¹, 3050 cm⁻¹, 1540 cm⁻¹, 1610 cm⁻¹, 610 cm⁻¹; ¹H NMR (400 MHz/ CDCl₃) δ ppm : 10.35 (1H, s), 7.79 (1H,d), 7.24(1H,d), 7.48(1H, s), 7.49 (1H, s); ¹³C NMR (22.5 MHz/CDCl₃) δ ppm : 190.0, 137.1, 136.22, 132.10, 130.00, 128.5, 127.1, 129.4; Mass-ESI: 139 (M).

Conclusions

ZnWO₄ nanoparticles have been successfully synthesized by sol-gel method at low 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). Moreover nano ZnWO₄ has been applied as catalyst for the conversion of Substituted benzyl alcohols to their corresponding aldehydes with good yields.

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REFERENCES


Table 1. Oxidation of substituted Benzyl alcohols

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