Synthesis and Characterization of WO_3 Nanoparticles for Photocatalytic Degradation of Methylene Blue Dye

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Abstract: Photocatalysis with semiconductor nanomaterial is a green technology that has been widely applied including especially in environmental remediation field. In this paper, we discuss the synthesis, characterization and photocatalytic activity of pure tungsten oxide (WO_3) nanoparticles prepared by Wet chemical method. Synthesized WO_3 nanoparticles were confirmed via characterization techniques such as UV-visible spectroscopy, X-ray diffraction (XRD), FTIR and Transmission Electron Microscopy (TEM). The photocatalytic activity of the pure WO_3 sample was evaluated by the degradation of methylene blue (MB) in an aqueous solution under UV light irradiation. The result showed that 46.87% MB solution degraded after 30 minutes of UV illumination and reached 90.6% for 120 minutes of UV illumination.

Key words: ***semiconductor, phtocatalytic, Methylene blue, XRD, FTIR, TEM***

I. INTRODUCTION

Water pollution is one of the most leading problems that badly affect the human as well as aquatic life. The main cause of water contamination is the discharge of the industrial effluents that contain mainly toxic chemicals and create major threat to the living systems[1]. Dyes and some organic matters are the major pollutants of water[2]. Most of synthetic dyes are toxic as well as difficult to degrade and produce undesirable color to water. Methylene blue (MB) is a cationic and toxic dye extensively used for photocatalytic studies[3]. Recently, researchers pointed toward the nanosized metal oxides based photocatalyst for its potential utility in the treatment of waste water[4]. Semiconductor photocatalysts offer huge potential for elimination of toxic chemicals .The photocatalytic degradation of organic pollutants in water and air using semiconductors such as WO_3 have been focus of research recently due to their unique ability in the environmental detoxification[5]. In earlier, Mousa Farhadian et al[6] have studied the Morphology dependent photocatalytic activity ofWO_3 nanostructures. Majeed Khan et al reported photocatalytic and electrochemical properties of hydrothermally synthesized WO_3 nanoparticles via Ag loading[7]. X. Wang et al studied Effects of exposed facets on photocatalytic properties of WO_3[8]. A.B.D. Nandiyanto et al studied and reported Synthesis of spherical macroporous WO3 particles and their high photocatalytic performance[9]. Ahmad Nozad Golikanda et al and Ali Fakhric et al studied Preparation and characterization of zinc and copper co-dopedWO_3 nanoparticles: Application in photocatalysis and photobiology[10]. Tungsten oxide (WO_3) is one of the best photocatalysts which has no photo corrosion, good electron transport properties, outstanding stability and high photocatalytic activity. However, as a relatively wide band gap photocatalyst (2.8-3.0eV)[11][12], WO_3 is only excited by the blue and near ultraviolet regions of the solar spectrum.

The main goal of the present work is the synthesis WO_3 nanoparticles by wet chemical technique. In addition, the synthesized WO_3 nanoparticles were categorized by different techniques like X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), UV–Vis absorption and FTIR studies. Likewise, the prepared WO_3 was engaged to the degradation of methylene blue via photocatalytic reaction under UV light irradiation.

II. EXPERIMENTAL PROCEDURE

For the synthesis of WO_3 nanoparticles, simple and environmental friendly Wet chemical technique was adapted. Here Sodium tungstate dihydrate ($Na_2WO_4.2H_2O$) of M.W 329.86g/ml (AR grade) was dissolved in deionized water. This was taken as precursor solution. A curd like precipitate was formed when hydrochloric acid was added drop by drop into the solution. After stirring, Oxalic acid and CTAB were dissolved in deionised water separately and added into the precursor solution. Oxalic acid and CTAB were used to control the structure of the sample. Total solution was stirred continuously for 3 hours at 80^0C in temperature controlled magnetic stirrer. The gel formation occurs with dark yellowish appearance. After gelation the sample was washed with Acetone, ethanol followed by deionized water. Cleaned sample was kept in hot air oven for 1 hour at 60^0C to remove

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moisture. Finally the sample was annealed for 1 hour at 400^0C in muffle furnace. After annealing WO_3 nano powders were collected and stored in air tight, dust free vials for further characterization.

Experiment for degradation of methyl blue (MB) dye

The photocatalytic activity of tungsten oxide nanoparticles were investigated by the degradation of methylene blue in aqueous medium under UV light source of 570 W xenon lamp was used. In a typical photocatalytic experiment, 75mg tungsten oxide nanoparticles were mixed to the 100 ml aqueous methylene blue solution. The sample was loaded in quartz tube and kept them in UV light irradiation. The concentration of MB dye prior to irradiation was recorded to analyze the initial value by UV spectrum. The irradiation on the solution is recorded for every thirty minutes interval. The radiation is measured continuously until the decolourization of the solution. The percentage of efficiency was calculated at end of decolourization by using the following formula,

$$\textbf{Decolourization efficiency} = \frac{I_0 - I}{I_0} X100$$

Where, $\mathbf{I_0}$ is the absorbance before irradiation of MB dye and **I** is the final concentration of MB dye after irradiation[13].

III. CHARACTERIZATION TECHNIQUES

The structural properties of the synthesized powders were investigated using X-ray diffraction (XRD) technique. The XRD patterns were recorded with a XPERTO-PRO diffractometer system having Cu-Kα radiation (λ=1.5406A^0) as X-ray source at 40KVand 30mA in the scanning angle (2θ) from 10^0 to 80^0. Elemental structures of the synthesized nanoparticles were analyzed with the help high resolution transmission electron microscope HRTEM – JEOL – JEM 2100 at an accelerating Voltage = 200kV. Various functional groups present in the synthesized nanoparticles were analyzed from the data obtained from Thermo Nicolet, Avatar 370 in the spectral range of 4000 – 400 cm^{-1}. Optical properties of the samples were characterized with the help of UV-visible spectrum obtained from JASCO UV-visible spectrometer. Methylene blue concentration in each degraded sample was measured by JASCO Spectrophotometer.

IV. RESULTS AND DISCUSSION

XRD Analysis

XRD technique was used for identification of crystal structure and for finding various lattice parameters. The result shows all the diffraction peaks indexed to tetragonal phase of WO_3 as per the JCPDS data card (ICSD 089092, JCPDS 89-8764; with space group P4/nmm)[12].

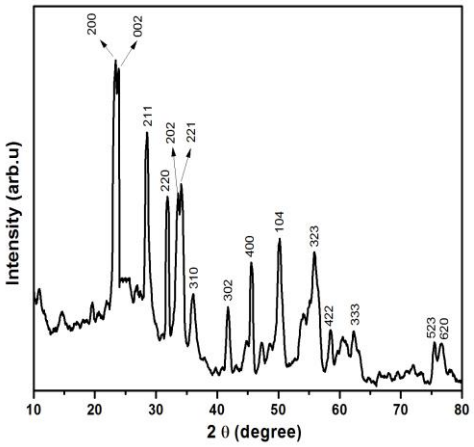

Figure. 1 XRD pattern of WO_3 nanoparticles

All diffraction peaks for the WO_3 sample can be indexed as crystalline tetragonal phase ofWO_3 with no obvious peaks for impurity. The XRD peaks are located at angles (2θ) of 23.21°, 23.21°, 23.73°, 28.43°, 33.43°, 34.27°, 36.09°, 41.72°, 45.60°, 50.07°, 55.89°, 58.49°, 62.33°, 75.39°, 76.7003 corresponding to (200), (002), (211), (220), (221), (302), (400), (104), (323), (422), (333), (523) and (620) planes of WO_3 nanoparticles respectively. The calculated lattice parameters of the tetragonal WO3 phase are a = b = 7.806 Å and c = 7.4373 Å; α = β = γ = 90° which agrees well with reported values. The particle size of the samples is determined by the X-ray line broadening method using the Debye – Scherer equation[14] equals to about 36 nm. Strong and sharp diffraction peaks also indicate a good crystallinity of the sample. No peaks of any other phase or impurities were observed from the XRD pattern.

4.2 HRTEM Studies

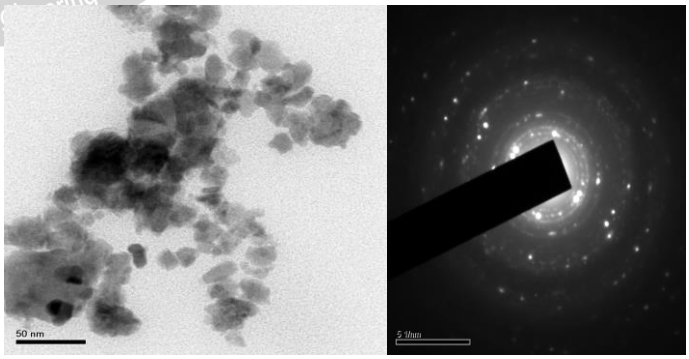

Figure. 2 HRTEM images of WO_3 nanoparticles

Figure.2 shows the high resolution transmission electron microscope (HRTEM) images of the synthesized WO_3 nanoparticles. The HRTEM image clearly shows that the inter-planar spaces along the [200] and [002] directions were 0.385 and 0.370 nm, respectively, which agreed with the XRD results.

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FTIR Studies

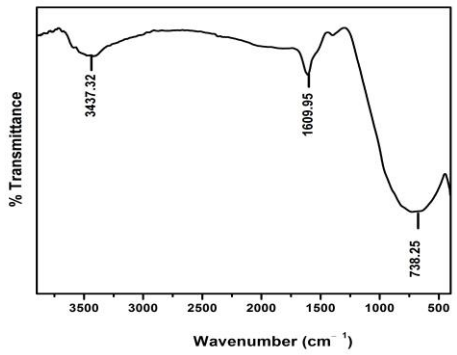


Figure. 3 FTIR of WO_3 nanoparticles

The surface composition and presence of functional groups were investigated by Fourier transmission infra-red (FT-IR) spectroscopy. Figure. 3 represents the FTIR spectrum of WO_3 nanoparticles over the frequency range of 400-4000 cm^{-1}. The distinctive band located at 738.25 cm^{-1} was related to vibrating modes of O-W-O bond[15][16]. The distinguished bands at 3437.32 cm^{-1} and 1609 cm^{-1} were attributed to -OH stretching vibrations of internally bonded or surface adsorbed water molecules and OH bending vibrations of water molecules, respectively [17].

UV - Visible Studies

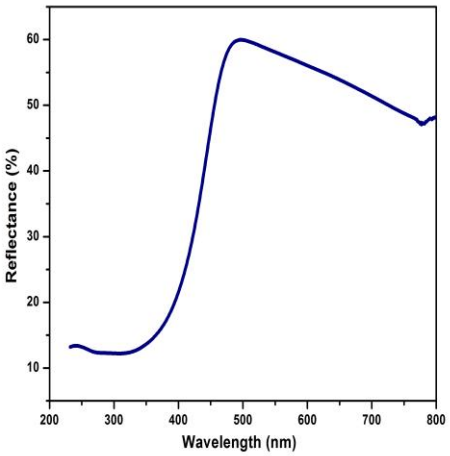
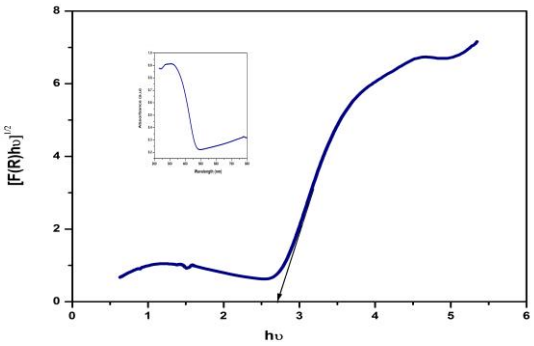


Figure. 4 UV – DRS spectrum of WO_3 nanoparticles

Figure. 4, 5 shows the absorption spectra of pure tungsten oxide sample transformed from the UV–Visible diffuse reflectance spectrum (DRS) according to the Kubelka-Munk (K-M) theory. Band gap energy (Eg) has been calculated using Kubelka–Munk (K–M) model as described below. The K–M model at any wavelength is given by

$$\frac{(1-R)^2}{2R} = \frac{K}{S} = F(R)$$



.Figure. 5 Kubelka – Munk fuction graph of WO_3 nanoparticles

F(R) is the so called remission or Kubelka–Munk function[18].

A graph is plotted between $[F(R)h\nu]^{1/2}$ and hν[19]. Here, 1/2 meant for direct band gap semiconducting materials. The intercept value gives the band gap energy Eg of the sample. The optical band gap value of the sample is calculated for pure tungsten oxide nanoparticle as 2.61 eV[20] which is matched well with the reported band gap energy value.

Photocatalytic Studies

The photocatalytic activity of WO_3 nanoparticles were

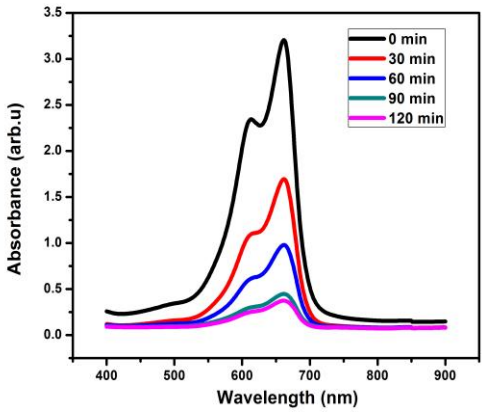


Figure. 6 Photocatalytic Absorbance Spectrum of WO_3 nanoparticles

Shown in Figure. 6 NPs were examined by the changes in the absorption spectra of the MB dye solution during their photo degradation process. This result shows that the illumination time of UV light source of 570 W xenon lamp increases, the concentration of MB dye decreases, which was shown by the decrease in UV-absorbance spectra. It can be seen that the intensity of the absorption peak gradually decreases with increasing UV illumination time.

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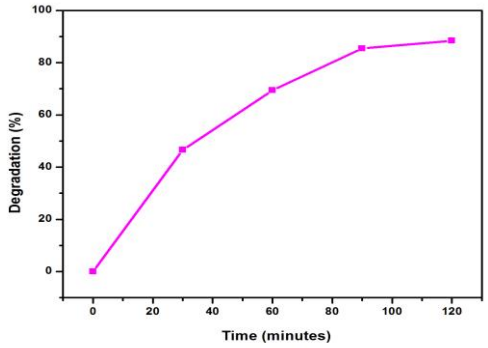

Figure. 7 Photocatalytic Degradation of WO_3 nanoparticles

Figure.7 displays the variation of the photocatalytic activity of the WO_3 sample. This result showed that 46.87% MB solution degraded after 30 minutes of UV illumination and reached 90.6% for 120 minutes of UV illumination. From above results, WO_3 acted as a promising material for photocatalytic applications.

V. CONCLUSION

In summary, WO_3 nanoparticles have been successfully prepared via simple wet chemical method. In powder X-ray diffraction pattern, all diffraction peaks for the sample can be indexed as crystalline tetragonal phase of WO_3 with no obvious peaks for impurity. The HRTEM image clearly showed that inter planar spaces along the [200] and [002] directions were 0.385 and 0.370 nm, respectively which agreed well with the XRD results. Distinctive bands located at 738.25 cm^{-1} were related to vibrating modes of O-W-O bond confirmed from FTIR study. Optical band gap value of the sample is calculated for pure tungsten oxide nanoparticle as 2.61 eV. Photocatlytic degradation of methylene blue results confirmed that WO_3 acted as a promising material for photocatalytic applications.

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