PHOTOCATALYTIC ACTIVITY OF UNDOPED WO_3 NANO PARTICLES PREPARED BY HYDROTHERMAL METHOD

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ABSTRACT

Enhanced photocatalytic activity of WO_3 nano particles was prepared by hydrothermal method with different annealing temperatures (350,450 and 550°C).The structural, Morphological and optical studies were carried out using XRD, SEM and UV vis spectroscopy. It was determined that WO_3 nano particles annealed at 550°C possess distinguished and exceptional properties in comparison with the bulk, micro and nanostructured WO_3 synthesized at alternative temperatures. The photocatalytic activities of the WO_3 samples were evaluated by the degradation of methylene blue in a aqueous solution under visible light irradiation.

Index terms: photocatalyst, tungsten trioxide, XRD, SEM

Introduction

Sunlight and water are the most abundant, clean, renewable and natural energy resources on Earth. Their conversion to hydrogen has been described as an ideal solution to counter the depletion of and environmental issues associated with fossil fuels [1]. Photocatalytic water splitting into hydrogen and oxygen using semiconductor Catalysts is an effective method for converting solar energy or sunlight into clean and renewable hydrogen fuel. This process is the most promising and renewable choice for the generation of hydrogen [2-4]. Recently, photocatalytic water splitting has been employed in industrial effluent treatment and has attracted considerable attention. In this technology, the oxidative and reductive reactions take place concurrently, while utilizing solar light [5-7].

Tungsten oxide (WO_3) is an N-type semiconductor material [8] with the energy band gap ~ 2.7-2.8 eV [9]. WO_3 material has been used for virus inactivation [10], energy conversion devices and photo-catalyst for harmful pollutant degradation [11]. As photo-catalyst materials, WO_3 is promising because it proved to show good photo absorption in the visible light. This makes WO_3 can be activated either indoors using a light source of domestic or outdoor conditions using sunlight irradiation.

Photo-catalyst activity under visible light irradiation can be improved by morphology control, the addition of certain elements of doping, engineering co-catalyst and synthesis WO_3 composite with an active material in the visible light [12]. In the degradation of pollutants in liquid phase applications often use the method in which the powder in the powder WO_3 this method directly dispersed into a liquid pollutant. However, this step leads to contamination of the water with the powder WO_3 and requires further separation processes.

Hydrothermal is a single step, cost-effective and easy method used for the synthesis and preparation of nano photocatalysts and is also known as solvothermal technique. Nanoparticles synthesized via this technique show much better crystallinity and grain size. Calcination is very effective technique that is sustainable at high temperature in which reaction is achieved lower the melting points. Explosive fraction is detached, and phase-transition and thermal putrefaction takes place in this method. Calcination may yield at different temperatures dependent of the material to be under calcined.

Experimental Procedure

The Hydrothermal method was used in the preparation of tungstate nano particles. All the chemicals are purchased of analytical grade and used without further purification. Firstly sodium tungstate dehydrate was dissolved 1 lr distilled water and separately calcium chloride was dissolved in distilled water. From this 1.2 m Mole sodium tungstate and 2m Mole calcium chloride was prepared. Then the solution was stirred for 45 minutes at room temperature and the whole solution was kept for 2hours.Finally the obtained white precipitate was separated and washed two times with ethanol and acetone in order to remove the impure ions completely from the precipitate. The resulting precipitate was dried at 60^{o}C. Then the dried substance was soaked in Nitric acid (HNO_3) for 48 hours. Finally the obtained precipitate was washed with ethanol and acetone for 2 times to remove further impurities. The final cleaned substance was annealed at various temperatures 350^{o}C, 450^{o}C and 550^{o}C as nanoparticles.

Results and Discussion

Fig. 1 shows the XRD patterns of WO_3 nanoparticles prepared at different temperatures. All the samples have polycrystalline structure of monoclinic phase with a preferential orientation along the (002); (020) and (200) planes, irrespective of calcination temperature. The reflections are indicating WO_3 as monoclinic phase fit to the JCPDS 83-0950 [13-14]. The sample prepared at 350°C is slightly amorphous in nature. As the deposition temperature is increased, the peaks became sharper suggesting improved crystallinity.

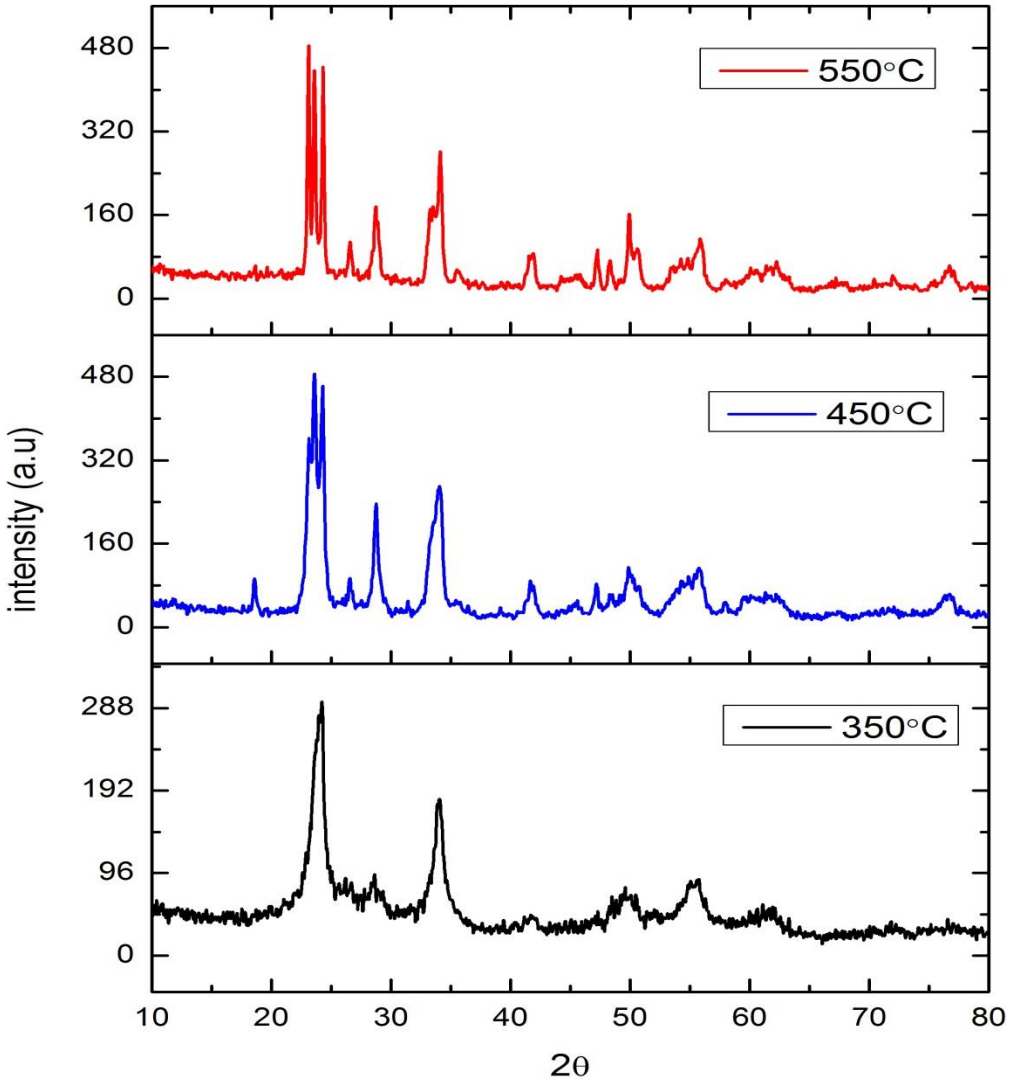


Fig 1. XRD spectra of WO3 nano particles for different annealed temperature

Fig 2. Shows the Scanning Electron Microscope image of the tungsten trioxide nano particles for different annealed temperatures (350,450 and 550°C). In the case of the WO_3 nanoparticles annealed at 350°C, the agglomeration of crystallites appears to be substantial, thereby showing a remarkable increase in the size. As the annealing temperature is increased to 450°C, the surface is partially filled with nanosized grains and with patches of interconnected crystallites which showed that at this temperature, the

morphology undergoes a transition from crystallites to nanosized grains. At 550°C, the morphology undergoes a complete transition to nanoregime with its surface fully covered with nanosized grains which becomes a supporting evidence for its improved crystallinity. From these results the 550°C chosen for the optimized material for further characteristics.

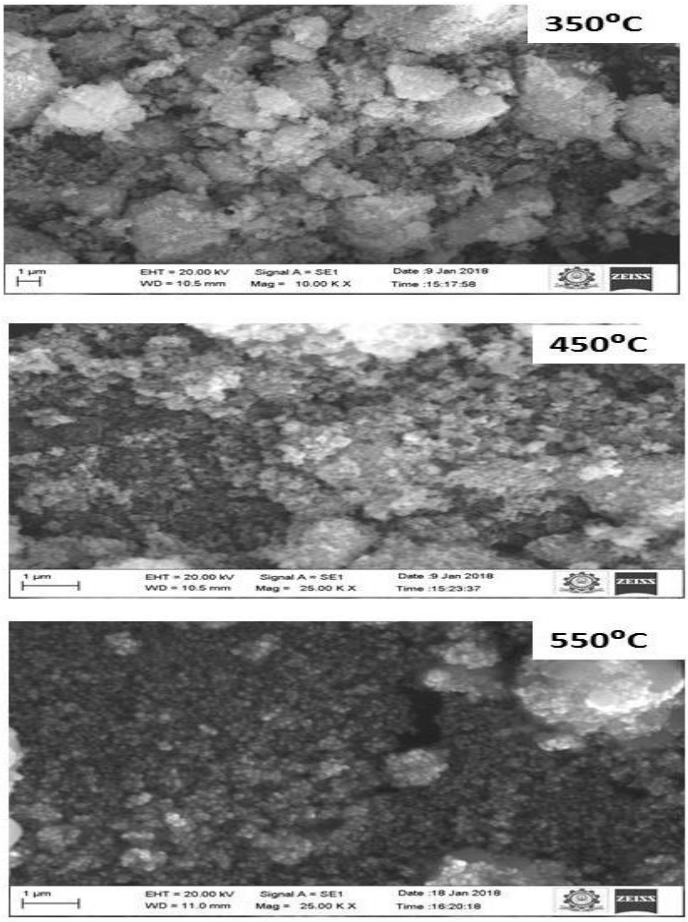


Fig.2 SEM images of WO_3 nano particles

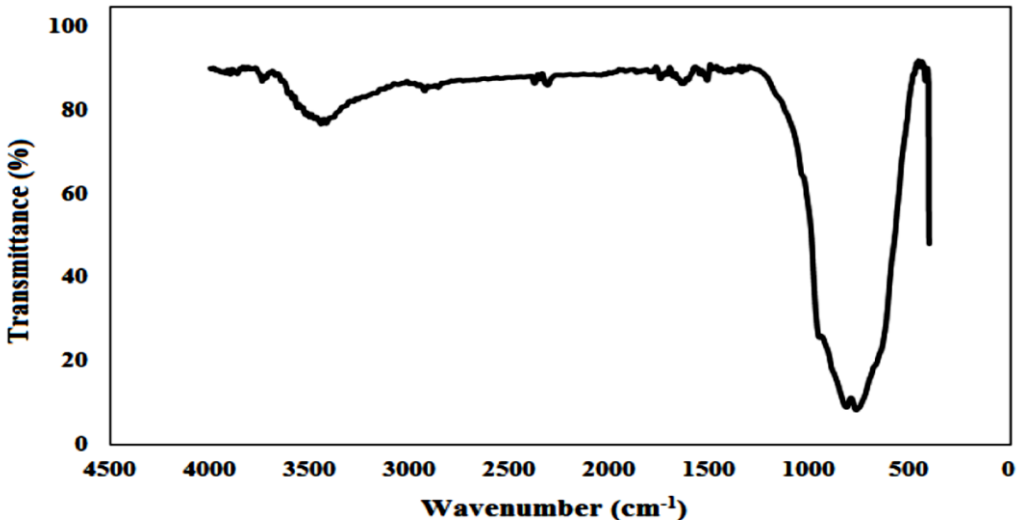


Fig.3 FTIR Spectrum for WO_3 at 550°C

In the spectrum of the WO3 (Fig. 3) a weak band located at 3416 cm^{-1} is assigned to stretching modes of OH groups. A band at 672 cm^{-1} and broad band at 837 cm^{-1} can be assigned to the ν(O-W-O) and ν(W=O) vibrations, respectively.

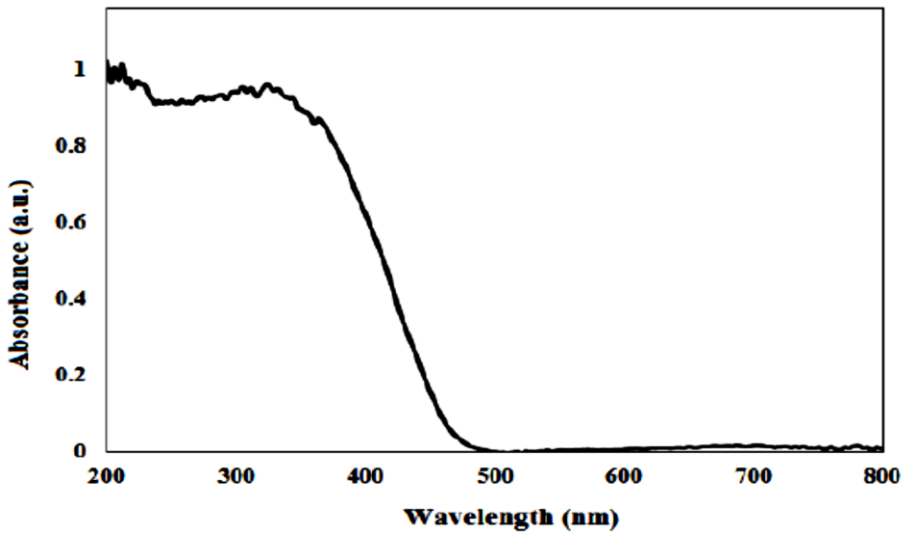


Fig.3 UV absorbance Spectrum for WO_3 at 550^{0}C

UV vis analysis was employed to characterize the light absorption properties of WO_3. UV-vis of the WO_3 catalyst in Fig. 4 showed an absorption maximum at 401 nm. According to literature, the oxygen ligand to metal charge transfer (LMCT) bands for W+6, appeared ~300-400 nm.

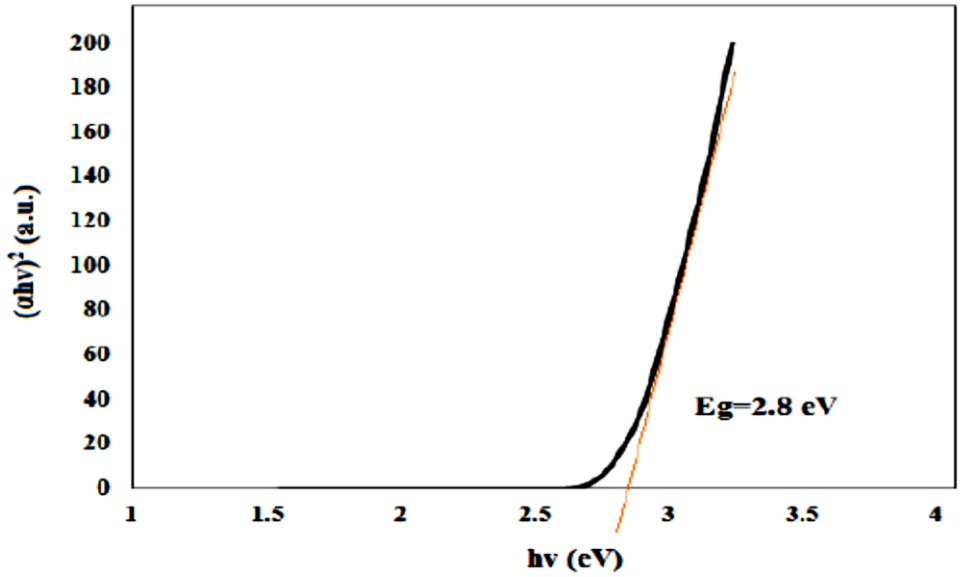
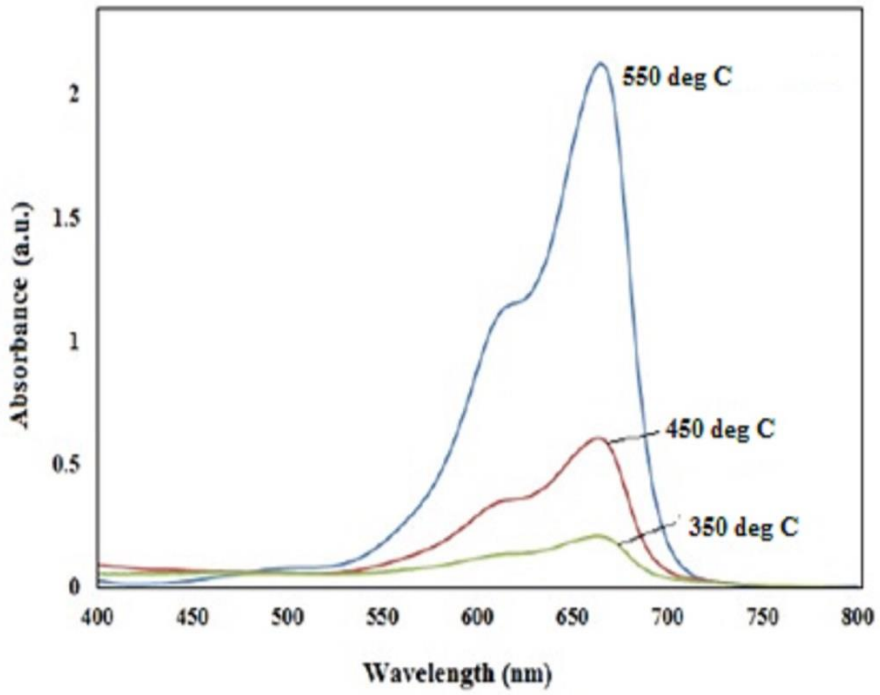


Fig.5 TAUC plot for WO_3 at 550^{0}C

Fig. 5 show that band gap of WO_3 was calculated 2.8 eV. Therefore, this photocatalyst can active in visible range.

Photocatalytic degradation of methylene blue

The photocatalytic activities of WO_3 catalyst were evaluated by the degradation of MB in aqueous solution under sun light irradiation. The photocatalytic activity and adsorption property of WO_3 was compared in Fig. 6. Removal of MB was carried out about 70% by adsorption on WO_3, but MB was degraded in the presence of WO_3 under sun light irradiation about 90%. It is well known that WO_3 has a low band gap of approximately 2.8 eV can effectively absorb visible range of sunlight.



Conclusion

The photocatalytic activities of the samples were evaluated by measuring the photodegradation of methylene blue. For this 1 ppm of methylene blue was prepared from this solution 10^{-4} g of MB was prepared and the solution was stirred well for 5 minutes before the photocatalytic activity.0.01 g of tungsten tri oxide nano particles was measured for photocatalytic degradation of methylene blue at 350°C, 450 °C and 550°C .The concentration change of MB was monitored by measuring UV-VIS absorption of the suspension at regular intervals.WO_3 as visible-light-driven photocatalysts was prepared by hydrothermal method. Visible light photocatalytic activity of the prepared catalyst was investigated by degradation of MB. After visible light irradiation for 1 h, about 90% of MB molecules were degraded on WO_3.

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