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Visible light catalysis of methyl orange using nanostructured WO_3 thin films

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Abstract

WO_3 thin films have been deposited onto glass and FTO coated glass substrates using a simple chemical spray pyrolysis technique. The structural, morphological, optical and photocatalytic properties of WO_3 thin films are studied. The photoelectrochemical (PEC) study shows that, both short circuit current (I_{sc}) and open circuit voltage (V_{oc}) are ($I_{sc}=0.38$ mA and $V_{oc}=0.59$ V) relatively higher at 300 °C substrate temperature. The structure and morphology of WO_3 thin films are studied by X-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM). XRD study reveals that the films are polycrystalline in nature with monoclinic crystal structure. SEM images show that the substrate surface is covered with a uniform and grain like morphology. The AFM images show the rough nature of the film. The structure and local symmetry of the film are studied with the help Raman spectroscopy. The chief vibrational modes of the WO_3 sample, located at 805, 715 and 269 cm^{-1} corresponding to the stretching and the bending of O–W–O bond respectively and are consistent with a monoclinic structure and the low-frequency peaks are observed at 269 and 325 cm^{-1} can be assigned due to the bending δ (O\W\O) vibrations in monoclinic structure. Photoelectrocatalytic degradation of methyl orange (MO) dye in aqueous solutions is studied. The end result shows that the degradation percentage of methyl orange (MO) using WO_3 photoelectrode has reached 98% under visible light illumination after 320 min. The amount of degradation is confirmed by COD and TOC analysis.

Keywords: Tungsten trioxide (WO_3); Methyl orange (MO); Chemical oxygen demand (COD); Total organic carbon (TOC)

1. Introduction

Several industrial processes have been releasing a lot of toxic, degenerative and carcinogenic chemicals every day. Some of them remain in the atmosphere, in the form of pollutants for long time. Textile dye is a type of ecological pollutant that takes very long time to degrade under natural conditions [1]. In addition, many of these dyes are carcinogenic and mutagenic, hence cause substantial injury to human life [2]. It is therefore extremely important to eliminate the organic dyes from the waste water. Nowadays various waste water treatment methods have been explored, but among these the advanced oxidation processes (AOP) have proved to be useful for the degradation of organic pollutants [3]. Photocatalysis comes under advanced oxidation processes (AOP) and represents a possible option for complete degradation the dye molecules, which are harmful to the environment [4]. However, in photoelectrochemical technique, photocatalysts are deposited on transparent electrodes, would make the treatment possible in practical application much easier and have a potential to enhance charge separation by applying external bias to serve higher degradation performance [5]. Photoelectrochemical degradation of dyes in water has the following advantages: (i) the end products can be controlled and are not harmful to the environment, (ii) the degradation process can be turned on or off at any instance and (iii) a real possibility that it could be readily integrated into existing UV water purification systems [6]. Although there are many semiconductor photocatalysts (such as TiO_2, WO_3, Bi_2WO_6, ZnO, Bi_2O_3, CdS etc.) as an environmental friendly photocatalyst for the degradation of organic contaminants in water

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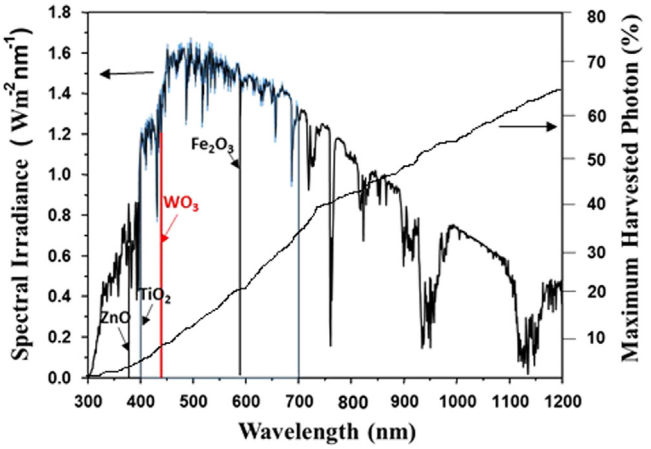

Fig. 1. Solar radiation spectrum.

under ultraviolet light irradiation. Amongst these semiconductor materials, tungsten trioxide (WO_3), as an important n-type semiconductor material with a band gap energy of 2.8 eV having a strong absorption within the solar spectrum (440 nm), it attracts considerable attention. It has ability to recover from photocorrosion as well as its stable physicochemical properties [7]. WO_3 is regarded as an attractive contestant for a photoelectrode, as it covers about 5% of the solar spectrum as shown in Fig. 1 [8]. Absorption at moderate hole diffusion length of WO_3 (~150 nm) compared with α-Fe_2O_3 (2–4 nm) is inherently good and electron transport properties (~12 $cm^2 V^{-1} s^{-1}$) as mobility also good compared with TiO_2 mobility (0.3 $cm^2 V^{-1} s^{-1}$) [9]. Tungsten oxide (WO_3) materials exhibit remarkable optical, electrical, chemical and catalytic properties could be used in a wide range of practical applications [10]. Due to its extended photosensitivity into the visible range, it becomes an interesting candidate as a photocatalyst for photochemical water (and air) purification [11]. The WO_3 films are typically made by different deposition techniques such as sputtering [12], evaporation [13], spray pyrolysis [14], anodization [15] and chemical vapor deposition [16]. Among these techniques, spray pyrolysis can offer a cost-effective way to obtain uniform and large area coatings [14]. Effective photoelectrocatalytic degradation of naphthol blue black [17,1], remazol black b [6], nitrite ions [18], 2, 4-dichlorophenol [19], methyl blue [20] and basic red 51 [21] have been achieved. Qing Zheng and Changha Lee studied the methyl orange (MO) degradation under the visible light irradiation and observed 95.7% degradation of MO in 3 h by using the anodized nanoporous WO_3 and during the experiment NaH_2PO_4 used as a supporting electrolyte [10]. Gómez-Solís et al. showed that photoelectrocatalytic degradation of Rhodamine B using Tungsten (VI) oxide (WO_3) powder synthesized by a simple precipitation method and observed a 38% mineralization of Rhodamine B after 96 h under irradiation with a Xe lamp [22]. Zhang et al. investigated photocatalytic degradation of RhB and MO under visible light irradiation by using Ag_3PO_4/WO_3 composites were prepared by a deposition–precipitation method and observed 97% degradation [23]. Rodríguez-Pérez et al. prepared WO_3 thin films on FTO by using a electrophoretic deposition (EPD) method and studied different morphologies and crystal structure of WO_3 thin films. Among these monoclinic crystal structure is a promising for photoelectrochemical water oxidation and getting photocurrent 10.3 μA under illumination in AgCl electrolyte [24]. Neumann-Spallart and Sadale [25] synthesized polycrystalline WO_3 films by a drop casting method and reported the photosensitivity which extends toward the visible region up to 470 nm. They reported the photocatalytic activity of WO_3 photocatalyst for decolorization of azo dye acidorange7 (AO7) under UVA broad-band illumination. Wang et al. studied the photodegradation of methyl orange using PANI-modified BiOCl synthesized via a facile chemisorptions method under visible light irradiation and observed 67% degradation of MO [26]. The use of WO_3 photoelectrode prepared by spray pyrolysis technique and its use in degradation of MO is not yet reported.

In the present work, WO_3 thin films have been deposited onto the amorphous and FTO coated glass substrates, because indium is costly as compared to fluorine therefore, preferred to use fluorine. The deposited thin films are characterized by the photoelectrochemical (PEC), XRD, SEM, Raman Spectroscopy and UV–vis spectroscopy techniques. This paper presents detailed studies on degradation of methyl orange (MO) using WO_3 photoelectrodes. Methyl orange has been successfully degraded using WO_3 thin films, without the use of external catalyst like $HClO_4$, NaH_2PO_4 etc. and get maximum photocurrent and degradation efficiency as compared to the literature survey.

2. Experimental

2.1. Materials synthesis

The precursor solution was prepared by dissolving tungsten metal powder (99.9+%, pure supplied by Sigma-Aldrich) in an ice-cooled beaker containing about 30% H_2O_2 and with vigorous agitation leads to the formation of a yellow–greenish solution. Spray rate was kept constant as 5 ml/min. Quantity of spraying solution was optimized to be 50 ml by the PEC technique. The precursor solution of 0.05 M concentration was then sprayed onto the preheated cleaned corning glass substrate, at various substrate temperatures, where pyrolytic decomposition was occurring. The substrate temperature varied from 225, at the interval of 25–325 °C. The substrate temperature was optimized by using the PEC technique. The nozzle-to-substrate distance (32 cm) was kept constant during all experiments and all depositions were carried out in locally fabricated automated spray pyrolysis deposition system. The compressed air was used as a carrier gas. To study, the photoelectrocatalytic degradation experiment, WO_3 photoelectrode was deposited onto large area (10 cm × 10 cm × 0.125 cm) FTO coated glass substrate with sheet resistance of 10–20 Ω cm^{-2} by the spray pyrolysis technique at an optimized substrate temperature of 300 °C. After deposition all the films are annealed at 400 °C in the air for 4 h.