Optical Materials 76 (2018) 260–270

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Degradation of organic dyes using spray deposited nanocrystalline stratified WO_3/TiO_2 photoelectrodes under sunlight illumination

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ARTICLE INFO

Article history:
Received 6 November 2017
Received in revised form
20 December 2017
Accepted 21 December 2017

Keywords:
Spray pyrolysis
Stratified WO_3/TiO_2 thin films
Rhodamine B
Reactive red 152
Photoelectrocatalysis

ABSTRACT

The need to utilize TiO_2 based metal oxide hetero nanostructures for the degradation of environmental pollutants like Rhodamine B and reactive red 152 from the wastewater using stratified WO_3/TiO_2 catalyst under sunlight illumination. WO_3, TiO_2 and stratified WO_3/TiO_2 catalysts were prepared by a spray pyrolysis method. It was found that the stratified WO_3/TiO_2 heterostructure has high crystallinity, no mixed phase formation occurs, strong optical absorption in the visible region of the solar spectrum, and large surface area. The photocatalytic activity was tested for degradation of Rhodamine B (Rh B) and reactive red 152 in an aqueous medium. TiO_2 layer in stratified WO_3/TiO_2 catalyst helps to extend its absorption spectrum in the solar light region. Rh B and Reactive red 152is eliminated up to 98 and 94% within the 30 and 40 min respectively at optimum experimental condition by stratified WO_3/TiO_2. Moreover, stratified WO_3/TiO_2 photoelectrode has good stability and reusability than individual TiO_2 and WO_3 thin film in the degradation of Rh B and reactive red 152. The photoelectrocatalytic experimental results indicate that stratified WO_3/TiO_2 photoelectrode is a promising material for dye removal.

1. Introduction

Nowadays semiconductor-assisted photocatalytic oxidation of organic pollutants has attracted much attention because it is an economic and eco-friendly solution for the remediation of an environmental pollutant like dyes [1]. As there are several applications of organic dyes in different industries such as textile, paper, pigment, food, cosmetic, and drug manufacturing. Dyes discarded from industries, mostly cause water pollution and pose threat to public hygiene, health, and environment. A large quantity of reactive dyes (30%) is wasted during the dyeing process and dumped into water sources without any active treatment. In general, textile wastewater contains high concentrations of organic compounds, heavy metals, high chemical oxygen demand (COD), high pH and has a strong colour [2,3]. Since some of the dyes and their metabolites are toxic, carcinogenic, and hence the wide use of organic dyes and their hazardous discarding leads to serious environmental problems. Therefore, the elimination of dyes from the wastewater is of vital significance [4]. In this perspective, the advanced oxidation processes (AOP's) are technologies that offer a good route in the treatment of the wastewater containing recalcitrant organic pollutants like dyes, organic acids etc. [5]. Heterogeneous photocatalysis comes under AOP's in which a source of appropriate light and a semiconductor material as catalysts are required to promote a chemical reaction by means of the creation of electron-hole pairs. Due to its ambient condition it is a useful method for the removal of organic pollutants from wastewater [6,7]. Among these Rhodamine B (RhB) have been recognized as, a highly water-soluble azoic dye and it is extensively used for fluorescent labeling and food coloring due to its fastness, low cost. However, it was also found to be toxic and carcinogenic in multiple feeding tests of rats and mice. It is also affecting the human respiratory system, skin, and brain [8]. In the past three decades, lot of studies have shown that TiO_2 is widely

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https://doi.org/10.1016/j.optmat.2017.12.044
0925-3467/

used photocatalyst, material, due to it is stable, inexpensive and non-toxic in nature. However, main drawback of TiO_2 is that it absorbs only 4% photons from the solar spectrum, which limits the effective application of TiO_2 under solar irradiation On the other hand, in order to further improve the photocatalytic efficiency of TiO_2, coupling it with another suitable semiconductor material is one of the most imperative tasks for the application of heterogeneous photocatalysis in the future [9]. Umar et al. conducted review on high-energy (001)-faceted anatase TiO_2 nanostructures and their application in photocatalysis as well as a review of any attempts to modify their electrical, optical and photocatalytic properties via doping [10]. Javaid et al. samarium (Sm) supported on tin oxide–titanium oxide (SnO_2/TiO_2) nanoparticles (Sm/SnO_2–TiO_2) were synthesized by sol–gel, ultrasonic and hydrothermal method and studied the effect of the optical band gap and particle size on the catalytic properties of Sm/SnO_2–TiO_2 nanoparticles [11]. Many different combinations (heterogeneous semiconductor systems) have been investigated, such as CdS/TiO_2, TiO_2/SnO_2, TiO_2/ZnO and TiO_2/WO_3 [12]. Among these WO_3/TiO_2 combinations is better due to the presence of Lewis and Bronsted acidic sites (W^{6+} species) which adsorb a greater amount of OH or H_2O, and hence helps generates more number of OH radicals to degrade organic pollutants. Also the conduction band edge of WO_3 is located at a more positive potential than the one of TiO_2. Therefore, WO_3 can act as a sink for the photogenerated electrons [13]. Therefore, electrons are injected from the conduction band TiO_2 to the conduction band of WO_3, while holes transfer between valence bands occurs in the opposite direction and recombination of photo generated charge carriers is reduced, which further helps to improve the photocatalytic efficiency [14]. Bosko Grbic et al. prepared TiO_2/WO_3 photocatalytic composite coatings prepared by spray pyrolysis and studied the photocatalytic degradation of methyl orange [15]. He et al. prepared WO_3/TiO_2 prepared by plasma electrolytic oxidation and observed that 85% degradation of RhB in 100 min [16]. The WO_3/TiO_2 composite prepared using different methods such as ultrasound-assisted [9], plasma electrolytic oxidation [17], dip coating [18], RF magnetron sputtering [8]. In comparison with the reported methods for forming WO_3/TiO_2 films, our spray pyrolysis process exhibits significant advantages such as easy control of preparation conditions, non-selectivity for substrate and low cost [19]. Even though few studies have been conducted on preparation WO_3/TiO_2 films, to the best of our knowledge, no report on the synergistic effect of light absorption and the photo generated charge carries transport in spray deposited stratified WO_3/TiO_2 photoelectrode for the degradation of RhB and reactive red 152 under natural sunlight illumination.

In this paper, we reported on the preparation of stratified WO_3/TiO_2 photoelectrodes by two step spray pyrolysis method. In the first step, a homogenous WO_3 thin film was deposited on FTO substrate. Afterwards, TiO_2 nanosheets were deposited onto the WO_3, as a result, stratified WO_3/TiO_2 photoanodes exhibited strong light absorbance in the whole visible region of solar spectrum. The synergism in light absorption and charge transport in the stratified WO_3/TiO_2 films was used for the photoelectrochemical degradation of Rhodamine B and reactive red 152 under natural sunlight illumination. RhB and reactive red 152 has been successfully degraded using stratified WO_3/TiO_2 photoelectrodes, without the use of external catalyst like $HClO_4$, NaH_2PO_4 etc. and got maximum degradation efficiency. The results demonstrated that the spray deposited stratified WO_3/TiO_2 photoelectrode exhibited a higher photocatalytic activity than the single WO_3 and TiO_2 sample under visible light irradiation. A mechanism of photodegradation and improvement in photocatalytic activity of stratified WO_3/TiO_2 was also discussed.

2. Material and methods

2.1. Materials

The tungsten metal powder (Sigma Aldrich), absolute ethanol and hydrogen peroxide (H_2O_2) (30% W/V, Thomas Baker) were analytical grade and used as received. Titanylacetylacetonate (TiAcAc) ($C_{10}H_{14}O_5Ti$) (AR grade, 99.9% pure, Merk made, Germany) and used without any further purification.

2.2. Preparation of stratified WO_3/TiO_2 photoelectrodes

The spray pyrolysis method has been adopted for the synthesis of WO_3, TiO_2, and stratified WO_3/TiO_2 thin film photoelectrodes on glass and Fluorine doped tin oxide (FTO) glass substrates of size $10 \times 10 \times 0.125$ cm^3 with sheet resistance of 15–20 Ω cm^2. WO_3 thin film electrodes were fabricated by spray pyrolysis process [20]. Briefly, in first step WO_3 thin film was prepared by dissolving tungsten metal powder in hydrogen peroxide (H_2O_2) (30% W/V) solution and greenish yellow colored precursor solution is formed, which is sprayed onto glass and FTO coated glass substrate. Substrate temperature was maintained for the deposition of WO_3 is 300 °C. In the second step, the TiO_2 layer was deposited on WO_3 by sequentially varying the quantity of sprayed ethanolic solution of titanylacetylacetonate (TiAcAc) ($C_{10}H_{14}O_5Ti$) at 470 °C on predeposited WO_3 thin films. During the spray pyrolytic deposition of WO_3 and TiO_2 films, the distance between the nozzle and glass substrate was 32 cm and compressed air was used as a carrier gas at a constant spray rate of 4 cc/min.

2.3. Catalyst characterization

To investigate the crystallographic properties of deposited thin films the X-ray diffraction patterns obtained using Bruker powder diffractometer (AXS) Analytical Instruments Pvt. Ltd., Germany, Model:D2 Phaser (k = 1.5406 Å for Cu K_α). To investigate the chemical composition and the oxidation states of an element present in WO_3, TiO_2 and stratified WO_3/TiO_2 thin films photoelectrodes, X-ray photoelectron spectroscopy (XPS) was recorded with Thermo Scientific, K-Alpha set up using monochromatic Al Kα X-ray source and a standard peak of C1s (284.6 eV). Raman scattering spectrum was recorded in air at room temperature with micro Raman system from Jobin Yvon Horibra LABRAM-HR Jobin Yvon Horiba LABRAM-HR visible within 100–800 cm^{-1}. The Raman spectra were excited using the He–Ne 632 nm laser source with 600 and 1800 lines/mm gratings and CCD detector. The measurement of the BET specific surface area of the photocatalysts was carried out using a nitrogen adsorption instrument at 77 K (Micrometrics, ASAP 2020). The surface morphology of the films and distribution of grains were studied by JEOL, Japan made scanning electron microscope (SEM) model JSM-6360. The three-dimensional (3D) morphology was obtained using AFM model INNOVA 1B3BE. AFM images were collected in contact mode on a molecular imaging system using a silicon nitride cantilever. Elemental composition (energy dispersive X-ray spectroscopy) of stratified WO_3/TiO_2 photoelectrode was carried out by using OXFORD (X- act) and MIRA 3 LMH TESCAN. The optical absorption study was carried out using Shimadzu UV-1800 spectrometer, Germany. The thickness was calculated using Steller Net Inc. USA spectroscopic reflectometer.

2.4. Photoelectrocatalytic degradation

In order to study photocatalytic experiments, large area (64 cm^2) WO_3, TiO_2 and stratified TiO_2/WO_3 thin films were