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VARIOUS TECHNOLOGICAL PROCESSES

Structural and Morphological Properties of Boron Doped V_2O_5 Thin Films: Highly Efficient Photocatalytic Degradation of Methyl Blue

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Abstract—Boron doped vanadium thin films were fabricated on the micro-slide glass substrates by spray pyrolysis technique at substrate temperature of 400°C. Initially, 0.1 M vanadium(III) chloride (VCl_3) solution was prepared in ethanol : water mixture (1 : 4) solvent. To prepare the boron doped vanadium oxide films as the concentrations of 2, 5, 7, 10, 20%, the suitable amount of H_3BO_3 was added in 0.1 M VCl_3 solution for each of the samples. X-Ray diffraction experiment with the produced films showed that tetragonal β-V_2O_5 phases formed. The synthesized boron-doped V_2O_5 thin films having the large surface area demonstrated the efficient catalytic properties in the photocatalytic degradation of methyl blue in water samples under Xenon light. The photocatalytic reaction efficiency was measured by recording the decrease of absorbance at 590 nm in UV-Vis absorption spectra. The methyl blue dye was degradated in approximately 30 min. The photocatalytic experiment results of the produced thin films showed that boron doping amount positively effects the degradation efficiency and reaction time.

Keywords: V_2O_5, spraying pyrolysis, boron, photocatalytic materials, methyl blue

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INTRODUCTION

Dyes bring color to our world and save us from the monotony of black and white, but some of them have polluted fresh water resources and cause waste waters pollutions. Moreover, it has been proven that some of dyes substances also cause cancer. Dyes are needed in medicine, textile, food and many other sectors and at the present time, the amount of use of these substances is increasing rapidly. For these reasons, the pollution caused by dye substances is tried to be eliminated by different methods [1–4]. Although there are various different physical, chemical and biological treatment methods exist, photocatalytic treatment is known as one of the most simple and promising green technology for dealing with wastewater pollutions [5, 6]. Among the available photocatalytic materials, TiO_2 nanoparticles have been examined deeply due to its high efficiency, low cost, non-toxicity and high stability [7–12]. However, its low quantum efficiency and wide band gap limit its application in visible light region [13–15]. So, various different materials, other than TiO_2 nanoparticles, were used as photocatalytic materials. Zinc oxide (ZnO) [16–19], cadmium sulphide (CdS) [20, 21], tungsten oxide/tungsten-trioxide (WO-WO_2/WO_3) [22-24] were some other examples [25].

Vanadium pentoxide (V_2O_5) is an *n* type semiconductor and it is an important transition metal oxide, an application of which is ranging from lithium-ion battery to sensors mainly because of its high-energy density, low cost, and

easy synthesis [26–28]. They have also been used in photocatalyst due to their narrow band gap ranging from 2.2 to 2.8 eV [29]. However photo and electrochemical corrosion of V_2O_5 limits its usability in photocatalyst [30]. Because of this reason V_2O_5 generally doped with different elements or coupled with another material to limit its corrosion and enhance its some important properties. In literature, the degradation of phenol and its derivatives by using V_2O_5 was evaluated [31]. Photocatalytic activity for degrading rhodamine B of hollow V_2O_5 microsphere had studied by Fei et al. [32]. Moreover V_2O_5 [33], TiO_2–V_2O_5 [34], graphene–V_2O_5 [35], SnO–V_2O_5 [29], CsV_3O_8 [36], Co–V_2O_5 [37] and PANI–V_2O_5 [38] systems were investigated. The photocatalytic activity of pure V_2O_5 was increased with addition to different metal oxide M_xO_y–V_2O_5 (M: Ti, Zn, Zr, Bi) has reported [39].

In the present study, V_2O_5 thin films obtained by using simple spray pyrolysis technique. The effect of boron doping concentration on structural and morphological properties of V_2O_5 thin films are studied. Photocatalytic activities of the systematically produced boron doped vanadium pentoxide thin films are also examined deeply.

EXPERIMENTAL

General. FTIR spectra were obtained using KBr pellets with Perkin-Elmer Spectrum 400 system in the range 4000–400 cm^{-1}. X-ray diffraction (XRD) patterns were recorded on the PANalytical XPert Pro. X-ray diffraction (XRD) with CuK_α radiation was employed to investigate the structural evolution and the phase identification. The morphology of the powder particles was characterized by SEM with a using Zeiss EVO 10LS scanning electron microscope at an acceleration voltage of 10 kV after the specimen was coated with a vacuum, attached with Bruker Quantax EDS. Photoluminescence spectra were measured using Perkin Elmer equipment. The photocatalytic degradation efficiencies were measured using a Shimadzu UV-1800 ultraviolet-visible spectrophotometer. Luzchem's 300W Xenon photoreactor was used as a light source in the photocatalytic experiments.

Obtaining boron doped V_2O_5 thin films on glass. Appropriate amount of VCl_3 was dissolved in 40 mL distilled water and 10 mL ethanol mixture in order to obtain 0.1 M vanadium(III) chloride solution. The boron concentration in the thin films were adjusted as 2, 5, 7, 10, 20% using appropriate amounts of boric acid (H_3BO_3) for boron source. The spray nozzle-substrate distance was adjusted to 35 cm. The volumetric spray flow rate was set to be about 0.25 mL s^{-1}. Firstly, vanadium (III) chloride solution was sprayed onto the cleaned glass set at 400°C in order to coat with the boron doped–V_2O_5 thin films on the glass surface using airbrush method. After then, these films were annealed at 550°C for 2 h.

Photocatalytic degradation of methyl blue using boron doped V_2O_5 thin films. Melthy Blue ($C_{37}H_{27}N_3Na_2O_9S_3$) was used as a dye in the photocatalytic degradation trials in water samples. 300 W Xenon lamp at a distance 20 cm from sample was used as a light source in the photocatalytic degradation tests. The degradation efficiencies of the boron doped vanadium thin films on the glass were analysed by using UV-Vis spectroscopy during the determined period of time. Firstly, control sample was scanned in the range of 200–800 nm with an 1 nm interval. Maximum absorption for methyl blue (MB) in water was evaluated as 590 nm. The scans of the water samples containing adsorbed dye were recorded between 400–800 nm, absorbance values were collected at 590 nm for each samples. Methyl blue dye solutions [5 ppm (mg L^{-1})] were prepared for each degradation tests. The thin film immersed into 10 mL prepared MB solution. The 2 mL samples were taken and measured in the ranging from 400–800 nm at every 5 min starting from 0 min to 40 min. Degradation efficiency (DE) were calculated using the equation:

$$\mathrm{DE} = \left(1 - \frac{C_t}{C_0}\right) \times 100,$$

where C_0 represents the initial concentration, C_t represents concentration at the sampling time.

RESULTS AND DISCUSSION

Characterization. The surface morphology of the thin film used as a photocatalytic source is very important. The total surface area of a photocatalyst greatly affects the degradation mechanism in the reaction. SEM images of the pure and boron doped vanadium(V) oxide thin films are given in Fig. 1. It has also been observed that the synthesized films have a very dense structure and also adhere homogeneously on to the glass surface.

When the microstructure is examined, it can be seen that the surface of the thin films have the rod structures. This morphological structure of the thin films increases the total effective surface area. SEM images of the the

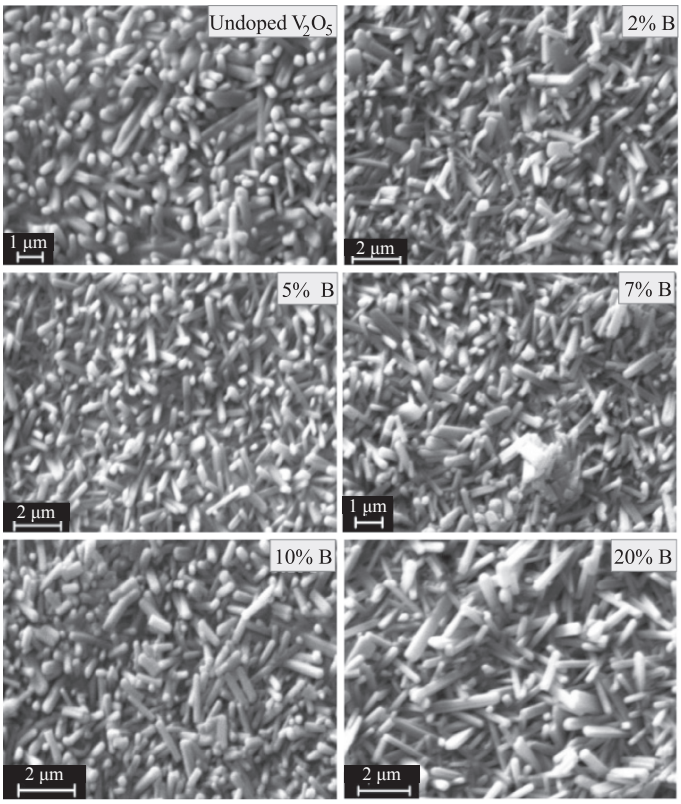

Fig. 1. SEM images of pure and boron-doped vanadium(V) oxide thin films.

boron doped V_2O_5 thin films fabricated by the sprayed pyrolsis of vanadium(III) chloride (VCl_3) solution are shown in Fig. 2. The thickness of the films was measured as approximately 1 μm.

Figure 3 shows the X-ray diffraction patterns of boron doped vanadium(V) oxide thin films deposited at 400°C on glass substrates in a 0.1 M solution without additives and with 2, 5, 7, 10, 20%. For undoped and boron doped vanadium oxide thin films, a dominant peak (200)* was observed. XRD pattern indicate that the structures of the obtained films have tetragonal structures with the β-V_2O_5 phase (JPDS-45 1074). This result is consistent with the literature [40, 41]. As seen from the figure, other peaks were negligibly small. With the effect of boron doping, it is seen that the intensity of the (200)* peak is also slightly reduced. It is thought to cause deterioration in the structure of the vanadium oxide by boron doping. Furthermore, no peaks of boron or its compounds were observed.

Photocatalytic degradation of methyl blue. The time and amount-dependent photocatalytic degradation of methyl blue were investigated under the xenon light at room temperature. The glass samples having the different percentages of boron doped-V_2O_5 thin films were added in methyl blue samples in water (5 mg L^{-1}) and stirred for 40 min. The samples were collected at 5, 10, 15, 20, 30, and 40 min for each trial and scanned in UV-Vis spectrophotometer in the range of 400–800 nm. The degradations of methyl blue in the water samples were determined by recording the decrease in absorbance at 590 nm in UV–Vis absorption spectra.

UV-Vis absorbance spectra shows the degradation of methyl blue in the range of 400–800 nm (Fig. 4). The time-dependent degradation percentages are given in Fig. 5. The possible photocatalytic reaction mechanism is schematized in Fig. 6. According to the probable mechanism of the heterogeneous photocatalytic degradation of methyl blue under the xenon light irradiation in solar simulator we can suppose that, firstly,

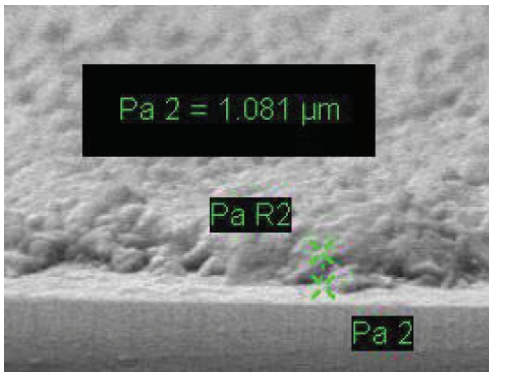

Fig. 2. (Color online) Cross-sectional thicknesses of thin films.

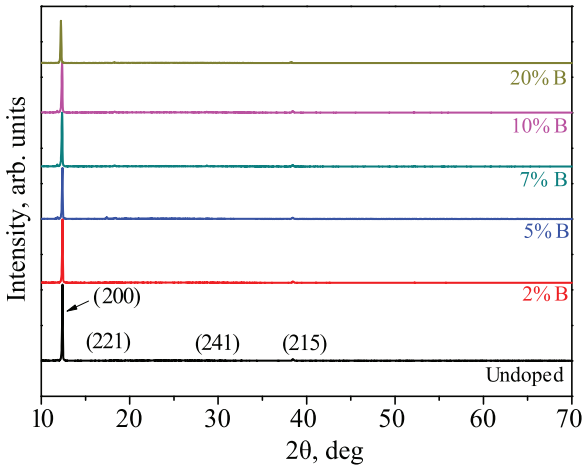

Fig. 3. (Color online) XRD images of undoped and boron doped vanadium oxide thin films.

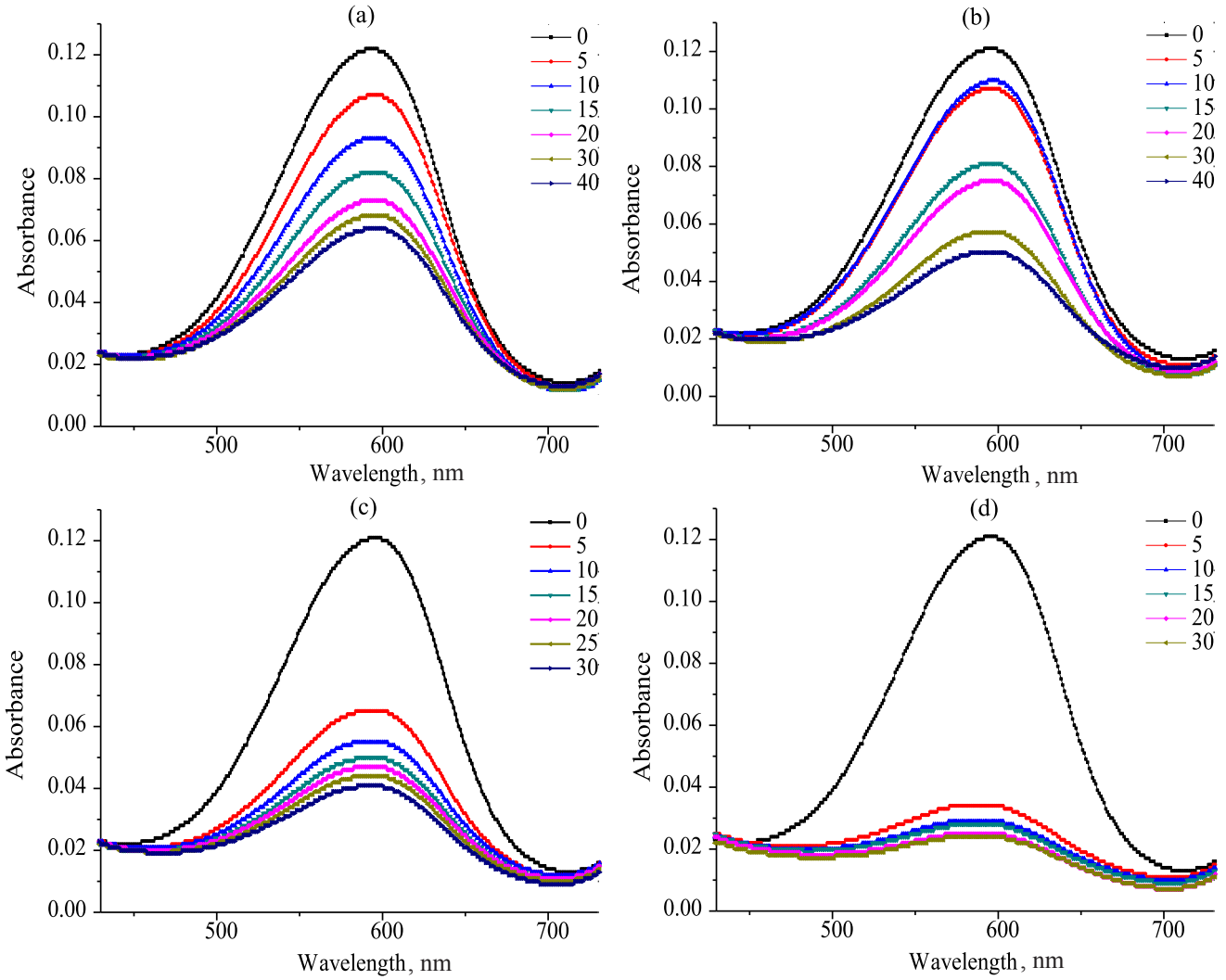

Fig. 4. (Color online) Visible spectra of photocatalytic degradation of methyl blue. (a) Undoped, (b) 2% , (c) 10% , (d) 20% boron-doped V_2O_5 thin films.

the electrons in the valence band in the thin film can be excited to the conduction band and the positive holes left in the valance band on the surface of the material. Photo-generated electrons in conduction band react with acceptors and a radical anion $O^{\bullet 2-}$ formed. In addition, the boron doped V_2O_5 structure gets an electron for positive holes from water and produced $OH^{\bullet}$ radicals. During this step, methyl blue having negative sulfonate groups electrostatically attracts to the positively charged the surface of the thin film. Finally, the dye is oxidated by the radical moieties to carbon dioxide and water [42, 43]. It can be said that 20% of boron doped V_2O_5 thin film is the best catalyst in the photocatalytic degradation of methyl blue amount compared with the all others. In other words, as the sample boron content increases, photocatalytic activity also increases.

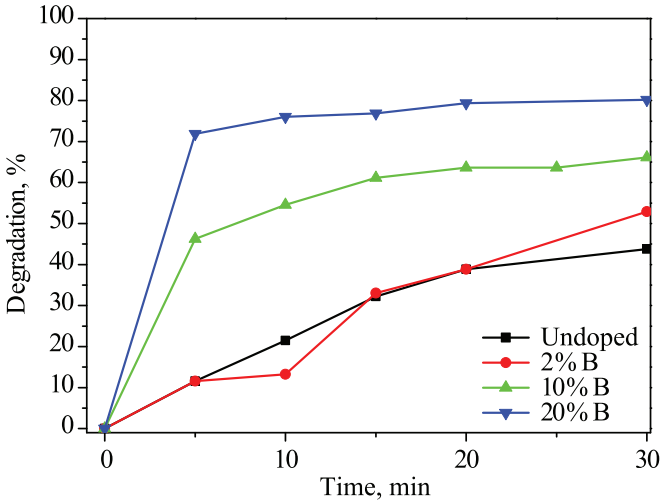

Fig. 5. (Color online) The photocatalytic degradation of MB in the presence of boron-doped V_2O_5 thin films.

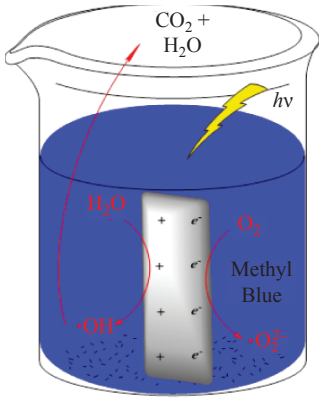

Fig. 6. (Color online) Possible photocatalytic degradation mechanism of methyl blue using boron-doped.

CONCLUSIONS

In the study, boron doped V_2O_5 thin films having different percentages of boron were synthesized by spray pyrolysis and photocatalytic properties of these boron doped V_2O_5 thin films were investigated in the degradation of methyl blue. The surfaces of the almost all films in SEM images are quite intense and the films are hold on the glass substrates very well. XRD results were found to be in accordance with the references. XRD results show that all films have the tetragonal β-V_2O_5 phase structure and (200) preferentially grown. Also, the importance of large surface area in photocatalysts was noted and dye was degradated approximately in 30 min using 20% boron doped V_2O_5 thin film on the glass.

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