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Investigations into the physical properties of SnO_2/MoO_3 and SnO_2/WO_3 bi-layered structures along with photocatalytic and antibacterial applications

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ABSTRACT

This work covers the surface defects effect of SnO_2/MoO_3 and SnO_2/WO_3 structures on photocatalysis. One micrometer thick SnO_2 bottom layers with porous microstructure and 0.1 thick micrometers of MoO_3 or WO_3 top layers were consecutively deposited onto glass substrates using the thermal evaporation technique. First, these bi-layered structures were characterized by X-ray diffraction, Raman spectroscopy and atomic force microscopy in order to identify both their structures and their morphological properties. Second, both UV–vis-NIR spectrophotometer measurements and ellipsometry spectroscopic proved that the band gap decreased from SnO_2 to coupled SnO_2/MoO_3 and SnO_2/WO_3. In addition, a comparison of the photocatalytic degradation of methylene blue (MB) was done under UV–visible light irradiation. The results showed that these structures exhibit promising candidates to degrade methylene blue (MB). Based on the characterization, it was found that SnO_2/MoO_3 and SnO_2/WO_3 structure showed higher photocatalytic activity than that of SnO_2. This relatively high photocatalytic activity may be attributed to the charge transfer between those bi-layered oxides. Finally, the antibacterial activity test towards Pseudomonas Aeroginosa showed that only SnO_2/WO_3 thin film has exhibited antibacterial effect.

1. Introduction

Transition Metallic Oxides (TMOs) belong to oxides class, they are one of the greatest range of properties such as; superconducting, ferromagnetic, ferroelectric, dielectric and conducting [1,2]. Transition Metallic Oxides are strongly used for photovoltaic cells, electrochromic devices, sensors and photocatalytic activity [3,4].

The organic pollutants photocatalytic degradation in the presence of semiconductors was considerable as it's a promising, environmental and cost-effective technology for the contaminated groundwater and wastewater treatment [5–7]. The study of SnO_2 transparent conducting thin films oxides are interesting due to their unique interesting properties like uniformity, no toxicity, high optical transmittance, low resistivity and their relatively low cost.

The crystal faces control is also significant as they contribute to the separation of holes and electrons. As for WO_3 and MoO_3, there are several reports on reactive faces and mechanism of photocatalytic degradation [8,9], and the degradation or decomposition by photocatalysis is a method for the treatment of air and water pollutant, the photocatalytic activities of carbon-doped MoO_3 have also been reported [10].

Various semiconducting metal oxides including TiO_2, SnO_2, WO_3, MoO_3, ZnO, etc. have been widely studied as a photocatalyst. Its characteristics such as crystal structure, morphology and particle size have been investigated to improve their photo- activity [11].

Coupling two semiconductors with different band gap widths is one of the most effective ways to slow the electron-hole pairs recombination [12,13,14], and the photocatalysis process depends mainly on the electron-hole pairs energy and separation extent [15]. Indeed, many coupled semiconductor systems, such as ZnO-SnO_2, SnO_2-Fe_2O_3, WO_3-SnO_2, etc. have shown high photocatalytic efficiency for increasing the charge separation and extending the energy range of photoexcitation, where these mixed oxides in thin films have been prepared by various processes such as: hydrothermal method, sol-gel, spray pyrolysis and thermal evaporation method [16,17]. Also, these thin films have been applied in: photovoltaic solar cells, photodetector, as gas sensors or as nanofibers [18,19].

Reports in the literatures on metal oxide bilayers such as SnO_2-ZnO, WO_3-SnO_2 or $TiO_2/SnO_2/WO_3$ indicate that these films could be suitable candidates for sensing applications, significantly enhance the gas

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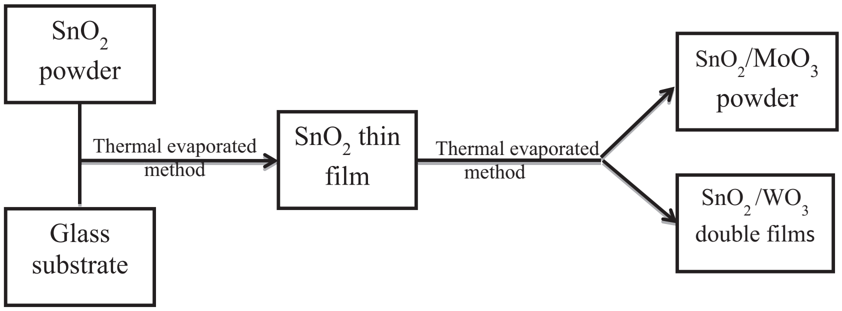

Fig. 1. A schematic illustration for the preparation process of the evaporated SnO_2, SnO_2/MoO_3 and SnO_2/WO_3 thin films.

sensing properties [20], the photocatalytic degradation of 1,2- dichlorobenzene under UV and visible light [21] and have applications in biomedical and environmental technologies [22].

This work aims to compare the photocatalytic activity between SnO_2/MoO_3 and SnO_2/WO_3 thin films prepared by the thermal evaporated technique. The preparation and analysis of structural, optical and photocatalytic properties of highly transparent SnO_2/MoO_3 and SnO_2/WO_3 thin films are reported. These films have been investigated by means of XRD, Raman technique and atomic force microscopy. The antibacterial properties as well as the photocatalytic activity of SnO_2/MoO_3 and SnO_2/WO_3 thin films in the degradation of Methylene Blue (MB) solutions under UV–visible irradiation were evaluated.

2. Materials

2.1. Films preparation

SnO_2/WO_3 and SnO_2/MoO_3 structures were obtained through the thermal evaporated technique following two steps and the typical procedure was outlined in Fig. 1. The high purity of SnO_2, MoO_3 and WO_3 powder (Aldritch, 99.9%) was deposited by evaporation technique in a high vacuum chamber under pressure of about 10^{-9} Pa using a tantalum boat filament. First, the powder of SnO_2 was deposited at the first step as thin films. After that, these films were used as substrates from the second powder of WO_3 and MoO_3 to grow respectively films of tungsten and molybdenum oxides.

2.2. Technical characterization

First, the X-Ray Diffraction spectra of tin oxide, molybdenum trioxide as well as tungsten trioxide were analyzed by a copper-source diffractometer (Analytical X Pert PROMP D), using Cu $K\alpha_1$ radiation (λ = 1.5418 A) with 2θ ranging from 10° to 70°. Raman scattering experiments were recorded at room temperature with micro Raman system from Jobin Yvon Horibra LABRAM-HR visible within 200–1200 cm^{-1}. A 632.8 nm line of a He-Ne laser was used for off-resonance excitation. Topography of the obtained thin films was performed by atomic force microscopy (AFM) using VEECO digital instrument 3D microscope. The sample was probed in tapping mode with a nanometer scale. Second, the optical reflection and transmission spectra of SnO_2, SnO_2/WO_3 and SnO_2/MoO_3 thin films were carried out in the wavelength range of 250–2500 nm using a SHUMADZU UV 3100 UV-vis-NIR spectrophotometer. Moreover, spectroscopic ellipsometry (SE) measurements were recorded with a GES5 SOPRA made rotating polarizer spectroscopic ellipsometer, in the energy range of 250–900 nm, at an incidence angle of 75°. All the calculations were performed using the Winelli_II software.

The structures photocatalytic activity based on both MoO_3 and WO_3 thin films was estimated from measuring the decomposition rate of methylene blue (MB) aqueous solution under UV irradiation by using a OSRAM germicidal lamp (256 nm, 16 W). The experiments were carried out using cylindrical batch reactor opened at the air. Methylene Blue MB (Aldrich) was chosen as a model molecule for the photocatalytic tests. The initial concentration of MB was 14 mg/L. The aqueous suspension containing MoO_3 and WO_3 thin films as photocatalysts and MB was irradiated with UV light under constant stirring. To reach the effect of UV irradiation on MB solution, the analytical samples were collected from the solution after every 30, 60, 90 and 120 min from the suspension. The MB concentration in each sample was analyzed via UV–vis spectrophotometer.

Finally, the evaluation of the antibacterial properties of SnO_2, SnO_2/MoO_3 and SnO_2/WO_3 thin films was carried out by counting forming unity (CFU). The gram negative bacterium Pseudomonas Aeroginosa was used as the experimental strain. The bacterial cells were grown at 37 °C in Tryptic Soya Broth (TSB) medium, until reaching an optical density (OD) of 1 at a 660 nm. The culture, then in its exponential growth phase, was an inoculums of 10^6 CFU in a fresh TSB medium and dropped (10 µL) on the SnO_2, SnO_2/MoO_3 and SnO_2/WO_3 thin films and finally incubated at 37 °C for 48 h in the dark. Inert glasses without thin films were treated by the same procedure and used as control. After incubation, bacterial suspensions were then serially diluted and plated on Tryptic Soya Agar (TSA) plates of 9 cm diameter for CFU counting. The decrease in CFU/mL was considered as the effect of thin films against the bacterial growth. The residual bacterial viability was calculated as:

$$\% \text{ viability} = (\text{CFU with thin films/CFU of control}) \times 100.$$

3. Results and discussion

3.1. Microstructural study

Fig. 2 shows X-Ray diffraction (XRD) patterns of SnO_2, SnO_2/MoO_3 and SnO_2/WO_3 thin film structures. For SnO_2 thin film, a well-defined diffraction peaks were observed at 2θ = 26.58, 33.82, 37.91, 51.73 and 54.75° corresponding to (110), (101), (200), (211) and (220) respectively planes of tetragonal structure identified using standard (JCPDS no: 41-1445) with lattice constants: a = b = 4.738 and c = 3.187 [23].

The crystal grain size was estimated by applying the Debye Scherrer equation [24]:

$$D = k\lambda/\beta\cos\theta \qquad (1)$$

where D is the crystallite size (nm), λ is the x-ray wavelength (0.5418 nm), β is the full width at half maximum (radians) and θ is the Bragg angle (degrees).

The crystallite size of the SnO_2 thin film was calculated as approximately 48 nm.

For SnO2/MoO_3 structure, the diffraction pattern reveals the coexistence of SnO_2 and MoO_3·That diffraction pattern was proved by the appearance of two other low intensities peaks (260) and (190) related to orthorhombic MoO_3 which were consistent with reference data of (JCPDS no: 05-0508) card and the grain size is around 30 nm. Ivanovskaya et al. [25] have observed that no differences between diffraction patterns from the pure SnO_2 and Mo-doped SnO_2 (99:1) according to XRD data. So, the addition of molybdenum into the SnO_2 does not lead to appearance of phases other than tetragonal SnO_2 one.