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Synthesis, characterization and electrocatalytic activity of SnO_2, Pt–SnO_2 thin films for methanol oxidation

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ABSTRACT

The study demonstrates an approach to synthesize nanocrystalline SnO_2 thin films on TCO (transparent conducting oxide) substrates. Un-doped and Pt-doped SnO_2 thin films have been synthesized from the precursor solution of stannic chloride ($SnCl_4{\cdot}5H_2O$) and chloroplatinic acid ($H_2PtCl_6{\cdot}H_2O$). X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), energy dispersive analysis of X-rays (EDAX) and X ray photoelectron spectroscopy (XPS) techniques were used to characterize the thin films. Optical characterizations were carried out by UV–Vis and photoluminescence (PL) spectroscopy. The present method provides a simple and cost-effective way to deposit highly stable SnO_2 and Pt–SnO_2 thin films. The synthesized films were used as electrode and its catalytic activity towards methanol oxidation was investigated. The study reveals that Pt–SnO_2 electrode is more effective for methanol electrooxidation than SnO_2.

1. Introduction

Recently, syntheses of nanostructure SnO_2 thin films have attracted much attention because of its wide applications and diverse optical, electrical and electrochemical properties [1]. The material is used in several areas, such as electrode material in lithium ion batteries, photoelectrodes, sensors, heterogeneous catalysts [2–5]. Recently SnO_2 materials are extensively used in dye sensitized solar cells [6–8]. Several synthetic methods were applied to prepare SnO_2 thin films including chemical vapor deposition [9], sol–gel [10], spray pyrolysis [11], thermal evaporation [12], sputtering [13], electrodeposition, etc. [14]. But preparation of nanocrystalline SnO_2 thin films on TCO substrate by galvanic method has not been noticed by us, which is being reported here. This technique is simpler than the conventional electrodeposition process of using a potentiostat/galvanostat. SnO_2 is invariably anion deficient and oxygen vacancies are mainly responsible for making available free electrons for the conduction process [15]. Previous reports revealed that incorporating noble elements e.g., Pt, Pd, etc. into SnO_2 material enhance the conduction process and electrocatalytic activity [16]. Pt nanoparticles (NPs) usually possess large surface area which accounts for the number of available active sites towards electrochemical reaction and electron transfer [17]. Thus, the electrochemical reaction could greatly be promoted at the Pt NPs surfaces, leading to a more sensitive and rapid response.

In this article, we have discussed the synthesis and detail characterization of un-doped and Pt-doped SnO_2 thin films. The electrocatalytic activity of the materials was studied. It has been investigated that the doped material i.e., Pt–SnO_2 shows an effective electrocatalytic activity towards methanol oxidation.

2. Experimental

2.1. Synthesis of SnO_2 thin films

A properly cleaned TCO glass substrate and a metallic Zn strip were clamped vertically and dipped into 0.1 M $SnCl_4$ solution in a 100 ml reaction bath. The total volume of the working solution was maintained to 100 ml by adding distilled water. The pH of the solution was adjusted to 2.3 with dilute HCl solution. Zn strip served as an easily oxidisable anode and TCO acted as cathode. The deposition was carried out at 80°C under stirred condition. When the electrochemical cell was externally short-circuited, Zn^{2+} ions were released from the Zn electrode and electrons within the short-circuited path moved to TCO, where they reduced Sn^{4+} ions to Sn^0 (black coloration). Then, H_2O_2 (30%) was added dropwise onto this black surface and it turned white due to rapid oxidation of Sn to SnO_2.

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Anode reaction : $Zn \rightarrow Zn^{2+} + 2e \quad E^0 = 0.7618\ V$ (i)

Cathode reaction : $Sn^{4+} + 4e \rightarrow Sn^0 \quad E^0 = 0.00675\ V$ (ii)

Total reaction : $2Zn + Sn^{4+} \rightarrow 2Zn^{2+} + Sn^0$ (iii)

H_2O_2 readily dissociates as

$H_2O_2 \rightarrow H_2O + [O]$ (iv)

This nascent oxygen [O] readily reacts with elemental tin and finally converts to SnO_2.

$Sn^0 + 2[O] \rightarrow SnO_2$ (v)

A white transparent layer was developed on TCO within 40 min and it was air-annealed at 400°C for one hour.

2.2. Synthesis of Pt doped SnO_2 thin films

Dilute solutions of chloroplatinic acid ($H_2PtCl_6{\cdot}H_2O$) with different Pt percentages (5%, 10%, 15%, 20%) were used as the precursor solution for Pt doping. The synthesized SnO_2 thin films were separately dipped into the precursor solution. Then, after 5 min the films were taken out form the bath, air dried and finally annealed at 300 °C for 30 min. Thus, Pt-doped SnO_2 thin films were synthesized with different Pt percentages.

3. Results and discussion

3.1. Characterization

The structural and morphological analysis were carried out by X-ray diffractometer (XRD) (Seifert P300 Cu Kα radiations) and field emission scanning electron microscope (FESEM), associated with EDAX probe (Gemini Zeiss Supra 35VP, Germany). The optical properties were studied by UV–Vis (JASCO V-530) spectrophotometer and photoluminescence (PL) spectra were recorded with Perkin–Elmer LS-55 Fluorometer. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCLAB KMII using Al as the exciting source. Electrocatalytic activity was measured in standard three electrode system (CH instruments 600 D series).

3.2. XRD analyses

Fig. 1a shows the XRD pattern of TCO and SnO_2/TCO thin films. XRD patterns for TCO and SnO2 thin films are similar but their intensities are different. The similar 2θ value for each case is due to presence of same elements (SnO2) in all the films. The Conducting layer of commercially purchased TCO is FTO (fluorine doped tin oxide, SnO_2:F) i.e., F doped SnO_2. For the as deposited SnO_2 thin films, the thin layer of SnO_2 was deposited on this conducting layer. Hence, all the two layers are basically tin oxide, so, their diffraction peaks were same. An excess of SnO_2 due to the as deposited SnO_2 thin films is responsible for the comparative high intensity than the TCO substrate. In Fig. 1a, major diffractions were observed from (112), (006), (200), (130) planes whose 2θ value matches well with JCPDS # 78-1063 (orthorhombic). XRD pattern of Pt–SnO_2 (10% Pt) shows intense extra peaks at 39.2°, 43° and 64.43° along with SnO_2 peaks (Fig. 1b). These extra peaks are due to platinum (Pt) incorporation into SnO_2. No other diffraction peaks were observed in the XRD pattern, meaning that the deposited material is pure.

3.3. FESEM analyses

Fig. 2 represents the FESEM images of (a) TCO, (b) SnO_2/TCO and (c) Pt–SnO_2 (10% Pt) thin films respectively. SEM image of SnO_2 (Fig. 2b) shows a porous flake like nanostructure uniformly grown on TCO substrate. The grain growth is likely due to the assimilation of the smaller grains in a controlled manner to give a definite shape, with the consequent formation of pores in between the larger grains. For Pt–SnO_2 thin films a drastic change in morphology is clearly observable from Fig. 2c. The growth of Pt nanoparticles on SnO_2 surface is discrete and results a porous morphology. The composition analysis was carried out by energy dispersive X-ray (EDX) spectroscopy (associated with SEM instrument) which confirms presence of Pt, Sn and O. EDAX of Pt–SnO_2 (10%) shows 1.82% Pt incorporation in the SnO_2 material (Fig. 2d). The detail of compositional analysis was shown in Table 1.

3.4. Optical studies

Fig. 3a shows the UV–Vis absorption spectra of SnO_2, a sharp increase in absorption was observed from ~400 nm. It is well-known that for a crystalline semi conductor the optical absorption near the band edge follows the equation $(\alpha h\nu)^{1/n} = A(h\nu - E_g)$, where, $h\nu$ is the incident photon energy, 'A' is a constant and 'n' is the exponent, the value of which is determined by the type of electronic transition causing the absorption and can take the values 1/2 or 2 depending upon whether the transition is direct or indirect, respectively. Since, SnO_2 is well established as a direct band gap semiconductor, we can evaluate the value of E_g from the plot of $(\alpha h\nu)^2$ vs. $h\nu$. The E_g value was calculated by plotting $(\alpha h\nu)^2$ vs. $h\nu$ and extrapolating the linear portion of the curve to the x-axis; α being the absorption coefficient and $h\nu$ the photon energy [18]. From the plot E_g value was calculated to 3.48 eV (Fig. 3a inset) comparable to bulk SnO_2 (E_g = 3.6 eV) [19].

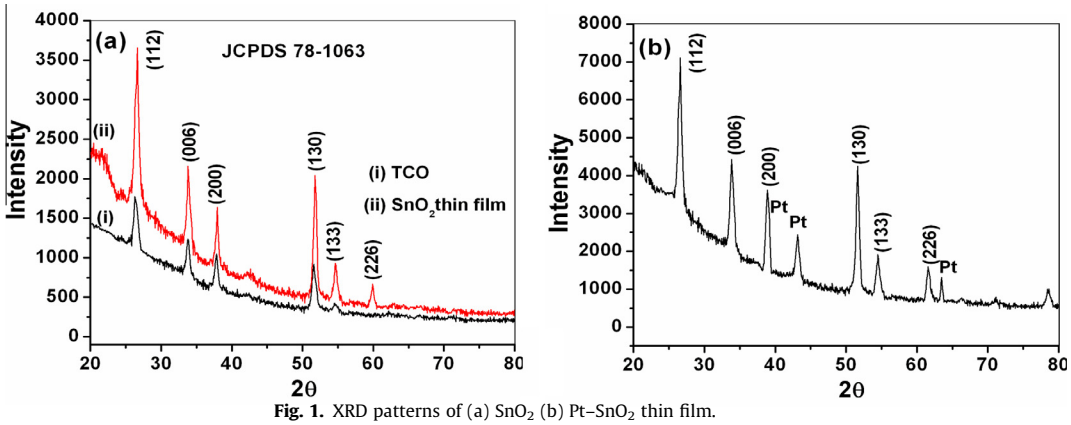

Fig. 1. XRD patterns of (a) SnO_2 (b) Pt–SnO_2 thin film.