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# 1D/2D MIXED NANOCOMPOSITE THIN FILM of SnO2/CARBON NANOTUBE/GRAPHENE

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**ABSTRACT**

Tin oxide ($SnO_2$) has gained much attention in various fields such as optoelectronic industries and gas sensors. $SnO_2$ thin films have been extensively used as electron transport layers (ETL) in planar perovskite solar cells due to their high stability, good processability, and appropriate band alignment. However, it suffers from relatively low charge mobility. Although there were some successful attempts to improve the charge mobility of $SnO_2$ thin films by incorporating carbon nanotubes (CNT) or graphene in its structure, the simultaneous addition of these 1D/2D mixed nanostructures in $SnO_2$, which can lead to far better optoelectronic properties, has never been reported. 1D/2D mixed nanocomposite thin films based on $SnO_2$/CNT/graphene are successfully synthesized in this research, and the structural, morphological, and optoelectrical properties of the films are investigated. For this purpose, $SnO_2$ sols were prepared by dissolving and refluxing $SnCl_2.2H_2O$ in 1-propanol at 87 °C for 2 h. In order to synthesize nanocomposite samples, various amounts of CNT and/or graphene were added to the solution prior to refluxing. The films were deposited by dip coating and subsequently calcined at 180 °C. The thin films were studied using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and UV-Vis spectroscopy. The XRD results confirm the formation of the $SnO_2$ phase. FESEM images thoroughly demonstrate the presence of CNTs and graphene beside $SnO_2$ nanoparticles. The absorbance of the films as well as their band gaps remained almost constant after CNT/graphene addition.

***Keywords:*** *Thin layers; Nanocomposites; Graphene; Carbon nanotubes; Tin oxide; Sol-gel.*

## 1. Introduction

Metal oxide semiconductor nanomaterials present themselves in various areas of science and technology due to their unique physical and chemical properties [1]. Among various metal oxide nanomaterials, $SnO_2$ has become the foremost one because of its wide applications in lithium batteries, supercapacitors, gas sensors, catalysis, and electron transport layers (ETL) in planar perovskite solar cells (PSCs) [2,3]. However, pure tin oxide shows relatively low charge mobility, and planar devices based on pure solution-processed $SnO_2$ ETL still have hysteresis, which significantly limits the application of $SnO_2$ in high-efficiency solar cells [4].

By means of addressing this issue, Tang et al. [5] fabricated a hybrid ETL of $SnO_2$ and carbon nanotube. The addition of CNTs can significantly improve the conductivity of $SnO_2$ films and reduce the trap-state density of $SnO_2$ films, which benefit carrier transfer from the perovskite layer to the cathode [5]. As it is reported, the hysteresis-free PSCs based on $SnO_2$–CNT ETL show higher efficiency than the conventional device [5].

The addition of graphene is another reported approach. Graphene and its nanocomposites with different semiconductor materials have attracted significant research attention in the last decade due to their improved performance in various fields [6]. Adding graphene to $SnO_2$ increases carrier mobility, indicating that rGO-$SnO_2$ has better charge transport due to enhanced electron-hole separation attributed to graphene [7].

It is a surmise that the addition of the CNT/graphene to $SnO_2$ can improve its optoelectronic properties. Thus, a novel 1D/2D mixed nanocomposite thin film of $SnO_2$/CNT/Graphene has been represented in this study.

## 2. Experimental details

$SnO_2$/CNT/Graphene films were prepared by the sol-gel method and coated through the dip-coating process. MWCNT-10 (95%) with a length of 1 μm and diameter of 10 nm was purchased from Shezen NanoTech Co. Graphene oxide (99%) with a layer number of 6-10 and area of 1 $\mu m^2$ was purchased from US Research Nanomaterials Co. (US-Nano). $SnCl_2.2H_2O$, 1-propanol, nitric acid, and sulfuric acid (Sigma-Aldrich Co.) were analytical-grade reagents and were used as purchased without further purification. By synthesizing $SnO_2$/CNT/Graphene nanocomposite, CNTs were first functionalized by adding a 0.05 g CNT to a solution containing nitric acid and sulfuric acid with a 1:3 dilution ratio at 80 °C for one hour. The mixture was collected by centrifugation, washed with distilled water, and dried at 100 °C.

In the second step, $SnCl_2.2H_2O$ was dissolved in 1-propanol to reach a 0.1 M solution. Meanwhile, 0.0006 g of pre-treated MWCNTs and 0.0006 g of Graphene oxide were dispersed in another portion of 1-propanol (10 ml) separately by an ultrasonic bath. In the third step, $SnCl_2.2H_2O$ solution (9 ml), graphene oxide, and MWCNT suspensions (0.5 ml of each) were mixed and refluxed at 87 °C for 2 h. The final product was coated on standard glass slides through the dip-coating process, then, calcined at 180 °C. For comparison, films of bare $SnO_2$, $SnO_2$/CNT, and $SnO_2$/graphene were prepared according to the above procedure.

The morphologies, crystal phases, and absorbance of the as-prepared films are investigated by field emission scanning electron microscope (FESEM; MIRA3; TESCAN co.), X-ray diffraction (XRD; Xpertpro Philips; 40 kV, 30 mA, Cu-kα radiation), and UV-Vis spectrophotometer (Photonix Ar 2015; 230 V ± 5%, 50 Hz, 85 W).

## 3. Results and discussion

Fig. 1 presents FESEM images of (a-1, a-2) bare $SnO_2$, (b-1, b-2) $SnO_2$/CNT, (c-1, c-2, c-3) $SnO_2$/graphene, and (d-1, d-2) $SnO_2$/CNT/graphene films synthesized through the sol-gel method and calcined at 180 °C at different magnifications. It can be illustrated that the addition of functionalized CNT and/or graphene to the primary sol controls the cubic $SnO_2$ particles' nucleation and the final size of $SnO_2$ particles reduces. Although the proportion of CNT and graphene is low (1%wt), figures 1(b-d) show a good distribution and dispersion of CNT and graphene in the prepared nanocomposites.

Fig. 1b shows that CNTs present within the

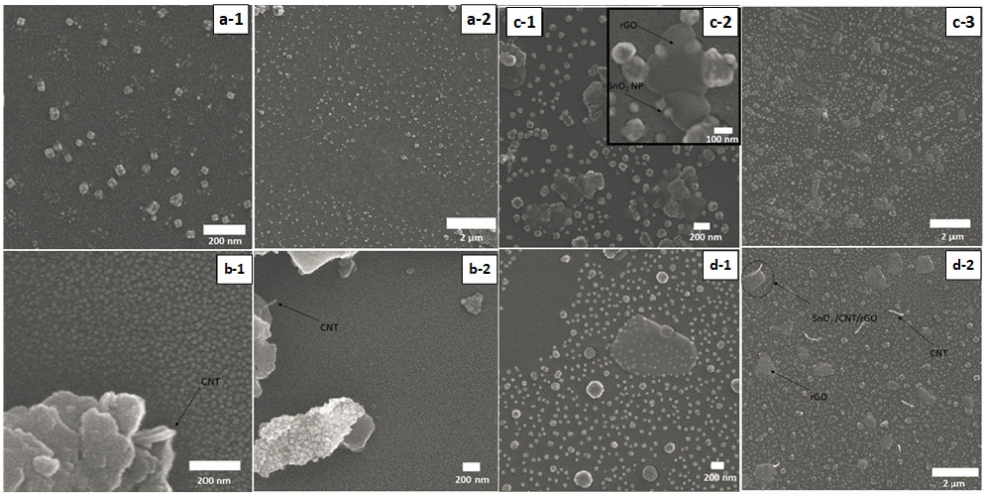


Fig. 1- FESEM images of (a) bare $SnO_2$, (b) $SnO_2$/CNT nanocomposite, (c) $SnO_2$/graphene nanocomposite, (d) $SnO_2$/CNT/graphene nanocomposite.

agglomerated $SnO_2$ and in Fig. 1c, the presence of tiny $SnO_2$ nanoparticles uniformly distributed on the graphene sheets is clearly observed. In Fig. 1d light lines, wide transparent sheets, and spherical particles attribute to CNT, graphene, and $SnO_2$ nanoparticles, respectively, which proves the formation of $SnO_2$/CNT/graphene nanocomposite.

Fig. 2 shows the XRD patterns of $SnO_2$ after being calcined at 500 °C (a) and $SnO_2$/CNT/graphene nanocomposite after being calcined at 180 °C (b) for 1h. In both Fig. 2a and 2b, $SnO_2$ diffraction peaks are identified according to JCPDS card no. 7534-900-96. In Fig. 2b, broad XRD peaks with low intensity are visible indicating that the crystallization of $SnO_2$ nanoparticles was initiated. In addition, it is noticeable that the broad XRD peaks indicate a much smaller crystal size for $SnO_2$ nanoparticles. The poor signal-to-noise ratio may be due to the poor crystallinity of the $SnO_2$ nanoparticles. Due to the low proportion of CNT and graphene (1%wt) and the overlap of their XRD pattern with $SnO_2$, no separate CNT and graphene characteristic diffraction peaks are observed.

Fig. 3 presents a comparison between UV-Visible spectra of bare $SnO_2$, $SnO_2$/CNT, $SnO_2$/graphene, and $SnO_2$/CNT/graphene nanocomposite films. As it is shown in the UV-vis spectra and tauc's plots of samples, the band gap (3.598 eV) and absorbance of

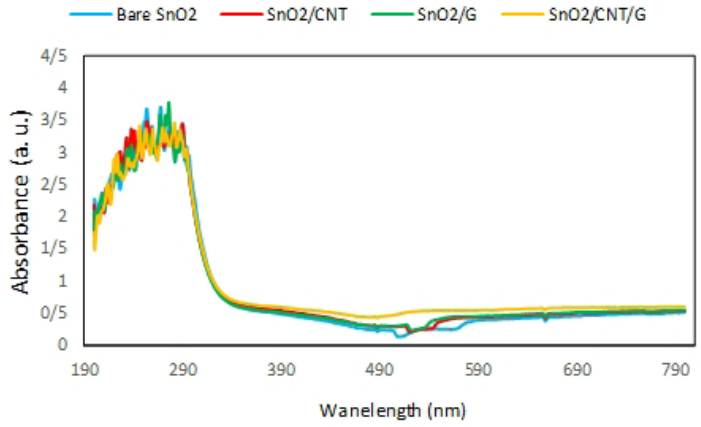


Fig. 2- XRD patterns of bare $SnO_2$ after being calcined at 500 °C (a) and $SnO_2$/CNT/graphene nanocomposite after being calcined at 180 °C (b).

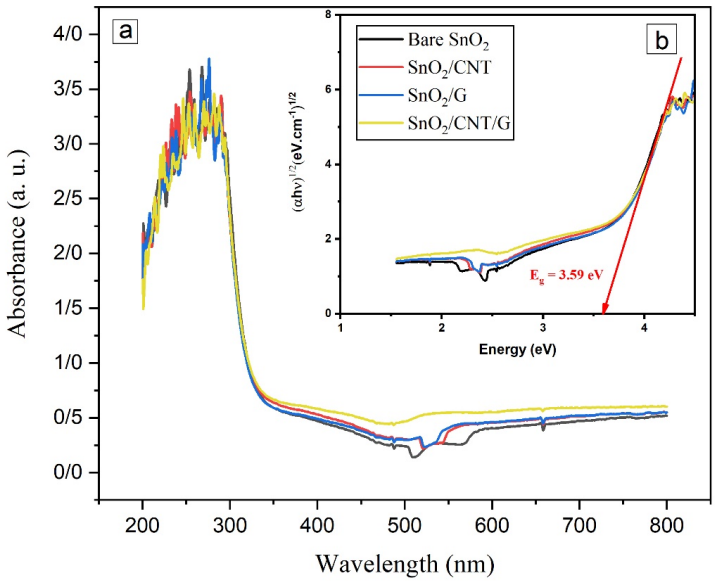


Fig. 3- (a) UV-Visible spectra and (b) The Tauc's plot of bare $SnO_2$, $SnO_2$/CNT, $SnO_2$/graphene, and $SnO_2$/CNT/graphene nanocomposite films.

the films after the addition of CNT and graphene has been remained constant due to the low proportion of CNT and graphene. Moreover, the transmittance of the films does not change dramatically by CNT/graphene addition.

## 4. Conclusions

In summary, in the present work, $SnO_2$/CNT/graphene films have been successfully synthesized through the sol-gel method and coated by the dip-coating process. XRD analysis showed the $SnO_2$ crystal structure initiation for the sample calcined at 500 °C, and a low degree of crystallinity for the sample calcined at 180 °C. Also, it has been observed from FESEM figures that the $SnO_2$/CNT/graphene nanocomposite was well-formed. To be added, UV-visible spectroscopy results showed that the transparency and bandgap of the films remained constant with CNT/graphene addition. Thus, in this novel study, a hybrid of $SnO_2$/CNT/graphene nanocomposite film was well synthesized by the sol-gel method.

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