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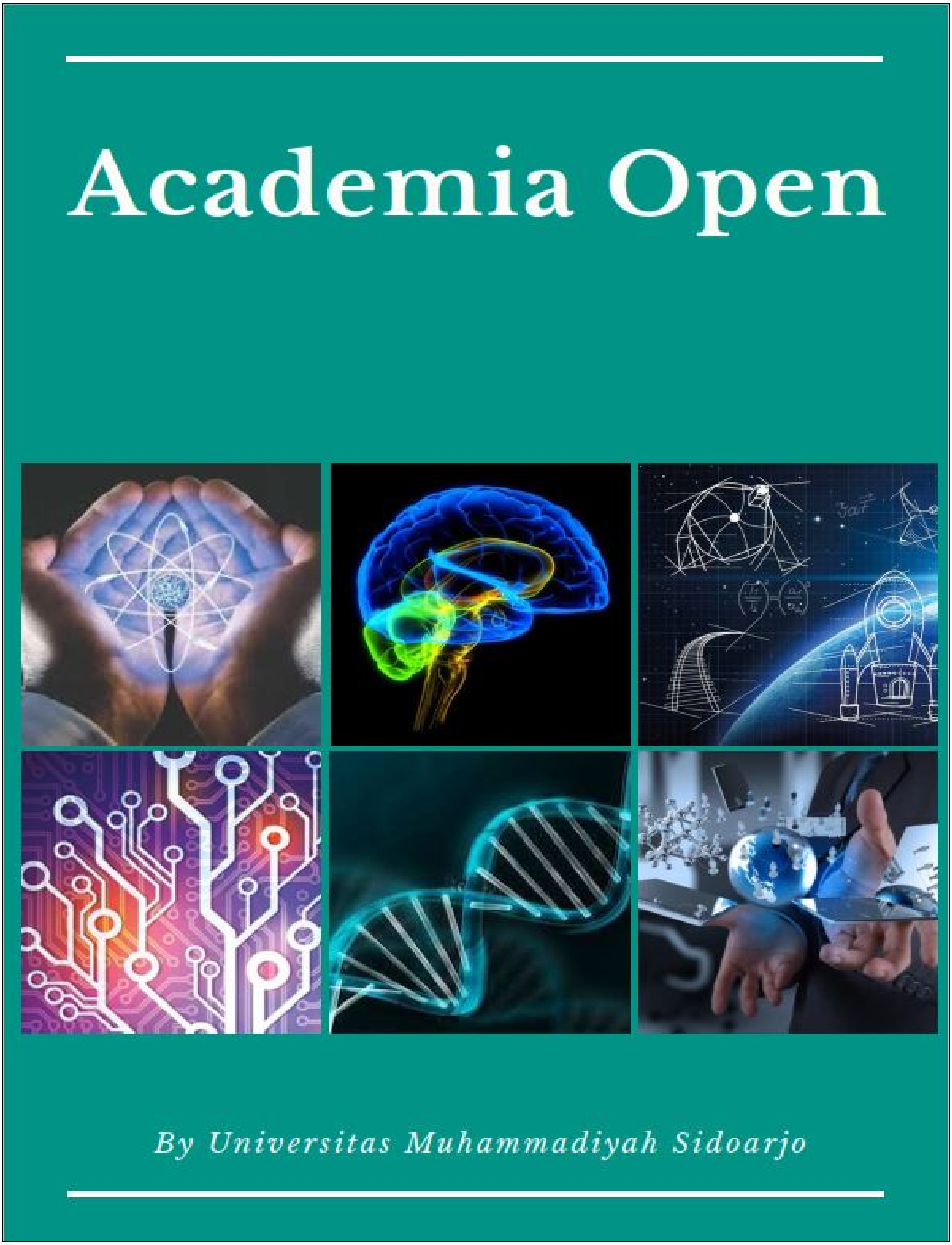
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Sustainable Approaches to Synthesis SnO2/MWCNT Nanocomposite Using Eggplant Extract: Study Structural Optical and Morphological Properties

Pendekatan Berkelanjutan untuk Sintesis Nanokomposit SnO2/MWCNT Menggunakan Ekstrak Terong: Mempelajari Sifat Optik dan Morfologi Struktural

Oday Jawad Kadhim , Oday.Kadhim@uowasit.edu.iq, (1)
, Iraq

Ahmed A. Thamer , ahmed.kh@uowasit.edu.iq, (0)
, Iraq

(1) Corresponding author

Abstract

To develop eco-friendly methods in nanotechnology, an innovative approach to the fabrication of SnO_2/MWCNT nanocomposites using an easily used yet effective green method was achieved. This study shows a sustainable route to highly reducing chemical synthesis, using the natural reducing properties of the eggplant extract. Working successfully, the research was able to create a hybrid nanomaterial comprised of tin oxide (SnO_2) and multi walled carbon nanotubes (MWCNTs) using a simple co-precipitation technique. Combining SnO_2 and MWCNT resulted in a nanocomposite with an intriguing transformation from nanotubular to flower-like structures and uniform distribution of the particles. Detailed analysis showed a crystallite size of ~ 21.75 nm for pure SnO_2 up to 38.98 nm in the hybrid form and retained good uniformity ~ 45.84 nm. Most importantly, the integration of MWCNTs yielded an optimized bandgap reduction from 3.5 to 3.1 eV, improving the material's light absorption ability. Such improvement opens up exciting applications in photocatalysis, gas sensing and energy storage devices. This eco friendly synthesis method is proven to be viable for creating green advanced nanomaterials, which not only provides proof of concept for green approach in creating advanced nanomaterials but allows for more sustainable practices in nanotechnology development while keeping the high performance standards needed for practical applications.

Highlights:

1. Eco-friendly SnO_2/MWCNT synthesis using eggplant extract
2. Green nanotechnology: improved bandgap, structure, and uniformity
3. Applications in photocatalysis, gas sensing, and energy storage

Keywords: SnO_2 NPs, SnO2/MWCNT, Eggplant Extract, green synthesis

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Introduction

tThe increasing environmental consequences of a range of fabricated devices fueled by echnological advancements in performance, miniaturization and economic efficacy are being recognized. Issues related to these may be addressed by nanotechnology because of the peculiar properties of the same substances at the nanoscale [1]. Nanomaterials with zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) architectures have a myriad of applications in catalysts, sensors, batteries, fuel cells, and drug delivery. The demand for novel nanomaterials, therefore, necessitates innovative approaches for their synthesis. Currently, the bottom-up approach, which involves the self-assembly of atoms and molecules, is being garnering much attention for nanomaterial synthesis [1]. The bottom-up synthesis methods can generally be categorized as chemical synthesis, pyrolisis, hydrothermal/solvothermal processing, electrochemical processing, and biological synthesis [2]. Most of these methods require high-temperature processing and hazardous chemical precursors, which raises concerns regarding the safety and environment of the native surrounding. The green synthesis approach for nanomaterials has therefore emerged as a potential alternative, which uses live or dead biomass of plants, bacteria, fungi, and yeast as the reducing and capping agents to assemble nanomaterials[3].

Among the various green synthesis approaches, the use of plant extract is considered superior due to its simple processing technique, rapid formation of nanomaterials, and co-existence of multiple phytochemicals, which assist in controlling the size and morphology of nanomaterials. The metal oxide semiconductors (MOSM) nanomaterials are of great interest due to their wide applications in energy, sensor, optical, pharmacological, and catalytic devices [4]. Tin oxide (SnO2) is a commercially available n-type oxide semiconductor with a band gap of ~3.6 eV and a wide range of applications in gas sensors, lithium-ion batteries, transparent conductors, dye-sensitized solar cells, photocatalysis, and supercapacitors. Carbon-based materials have gained significant attention in developing advanced nano-bio sensors, drug delivery systems, and electrochemical devices due to their high surface area, biocompatibility, and good conductivity[5]. These materials are tube-like 1D nanomaterial with inner diameter of 2-100 nm and high aspect ratio of 500-10000. On account of its good electrochemical activity and high intrinsic conductivity, MWCNT has attracted interest in nano bio devices and energy applications. Enhancing the electrochemical activity of the devices is a feasible route combining MOSM with carbon nanomaterials [5]. A dual nano-composite of SnO2/MWCNT has been successfully synthesized via a one-pot hydrothermal approach using eggplant extract. Eggplant extract is rich in polyphenolic compounds, which synthesize the SnO2/MWCNT dual nano-composite and enhance its electrochemical performance. The structural and morphological properties of the synthesized SnO2/MWCNT dual nano-composite are characterized using various techniques[6]. The use of nanomaterials has been considered a game changer for various sectors in past decades. Nanomaterials (NMs), by definition, are materials having at least one dimension in the nanometer scale (1-100 nm). Nanomaterials have the potential to revolutionize electronics, catalysis, coatings, energy storage and conversion, cosmetics, healthcare, food safety, and environmental remediation owing to their unique chemical, physical, and biological properties compared to their bulk equivalent [7]. Tin oxide (SnO2) nanomaterial is a wide bandgap (3.6 eV) n-type semiconductor oxide with a number of applications like gas, humidity, and UV sensors, electrochromic devices, anode material in lithium-ion batteries, photocatalytic pollutant degradation, dye-sensitized solar cells, and supercapacitors [4]. In addition, there has been growing interest in carbon based nanomaterials. The carbon derived material, multiwalled carbon nanotube (MWCNT), is a well known carbon based nanomaterial which posses a large aspect ratio, high electrical conductivity, high surface area, good mechanical strength and chemical stability. Such applications include drug delivery, energy storage devices, FET device, sensor and polymer composite reinforcement [8]. The combination of SnO2 and MWCNT can result in new hybrid nanomaterial with superior properties and performance integrating the individual advantages. Hybrid SnO2/MWCNT nanomaterial has been used in supercapacitors, lithium-ion batteries, and photocatalytic pollutant degradation[9].

Conventional synthesis methods of nanomaterials mostly involve harsh operating conditions and toxic chemical reagents. Therefore, the synthetic methods greatly affect the economic viability and environmental sustainability of nanomaterials[10]. As an alternative, the use of biological equivalents for the synthesis of nanomaterials (biogenic nanomaterials) has been an area of focused research. The biogenic nanomaterials are either using biological templates or biomolecules for the synthesis of nanomaterials. Most of the biogenic fabrication processes are eco-friendly, inexpensive, nontoxic, sustainable, and easy to handle. The outbreak of COVID-19 emphasized the importance of food-derived natural extracts with potential antioxidative, antimicrobial, and antiviral properties. Therefore, recent studies have focused on the use of natural extracts for the green synthesis of nanomaterials. Natural extracts are rich in various phytochemicals that can facilitate the synthesis and stabilization of nanomaterials. In addition, the use of natural extracts for the synthesis of nanomaterials adds value to the food industry by minimizing the waste. Using food-derived extracts, the SnO2 nanomaterial has been synthesized. Hybrid NMs are a combination of two or more different NMs or one NM integrated with other materials. However, up until now, there has been no study on the use of food-derived natural extracts for the hybrid nanomaterials synthesis. The motivation of this research is to fill this gap by investigating the possible use of eggplant extract for the green hybrid SnO2/MWCNT NMs synthesis[11].

Methods

SnO2/MWCNT nanomaterials were successfully synthesized using a one-pot method with Chemical Co-Precipitation technique employing Eggplant Extract as a greener precursor. Eggplant has enormous bioactive compounds that help in the reduction process and acts as a capping agent in the formation of nanocomposites.

The detail procedures for preparing the Eggplant Extract and its application in synthesizing SnO2/MWCNT nanomaterials are given below. All the chemicals and reagents used in this study were of analytical grade and were used without further purification. The Eggplant was taken from the local market. The Eggplant was washed with distilled water to remove dust and cut into small pieces. Then, it was boiled in 200 mL distilled water for 10 minutes and filtered using Whatman filter paper to obtain the Eggplant Extract.

Pure SnO2 nanoparticles and SnO2/MWCNT nanocomposites were synthesized using a phytochemical co-precipitation method with eggplant extract. For pure SnO2, mix 100 mL of eggplant extract with 50 mL of 0.5 M SnCl2·5H2O solution under magnetic stirring for 15 minutes. The pH was adjusted to 10 using 1M NaOH, followed by 120 minutes of continuous stirring.

For the SnO2/MWCNTs nanocomposite, the procedure was similar, but 0.02 g of MWCNTs was added to the mixture after the initial complexation step, without the need for NaOH addition. In both cases, the resulting white precipitates were filtered, washed with deionized water and ethanol, dried at 80°C for 2 hours, and finally annealed at 300°C for 2 hours. This green synthesis approach utilizes eggplant extract's phytochemicals as both reducing and stabilizing agents, offering an environmentally friendly alternative to conventional chemical methods.

Characterization Techniques

To understand the structural and morphological characteristics of the synthesized SnO2/MWCNT nanomaterials, different characterization techniques were employed. X-ray diffraction (XRD) was used to determine the possible phases and crystallinity of the synthesized nanocomposites. The diffractometer employed copper Kα radiation as the source operated at 30kV and 15 mA. XRD patterns recorded in a range of 20–80° were used to analyze the samples. Scanning electron microscopy was used to investigate the morphological characteristics of the SnO2/MWCNT nanocomposites, and uv-spectroscopy was used to study the electronic transition and energy band gap.

Results and Discussion

X-ray diffraction (XRD) analysis.

The SnO_2 nanoparticles have significant peaks at 2-theta values of 27.09, 34.37, and 52.23, corresponding to the (110), (101), and (211) Miller indices, respectively. The peaks show the existence of a cubic structure, as evidenced by the COD card number (96-10-0063). The mean crystallite size is determined to be 21.75 nm.

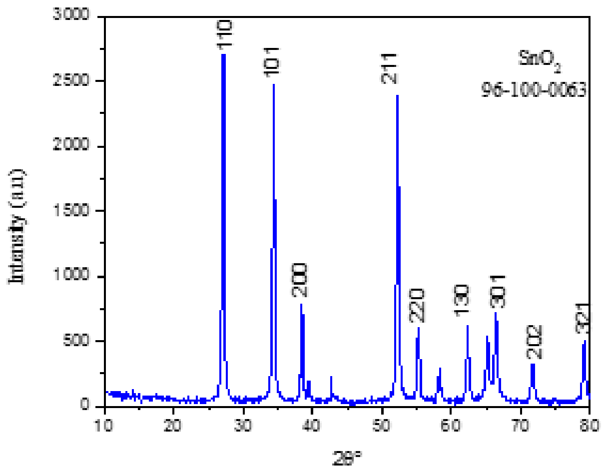


Figure 1. *XRD pattern of SnO_2 NPs*

Sample	SnO 2 NPs		
Two θ(Deg.)	Strongest three peaks		
	27.09	34.37	52.23
hkl	110	101	211

FWHM (Deg.)	0.36	0.39	0.42
Crystallite size (nm)	22.78	21.31	21.16
Average Crystallite size (nm)	21.75		

Table 1. ***Structural properties of SnO $_2$ NPs***

Figure 2 show the XRD pattern of SnO2/MWCNTs the peak intensity of SnO_2 decreases in the nanocomposite, indicating the wrapping of MWCNT on the SnO_2 surface. The average crystallite size of the SnO_2 nanostructure was calculated using the Scherrer formula. The average crystallite size of the SnO2 is about 38.98 nm, indicating that the synthesized SnO2 is increased when adding MWCNTs.

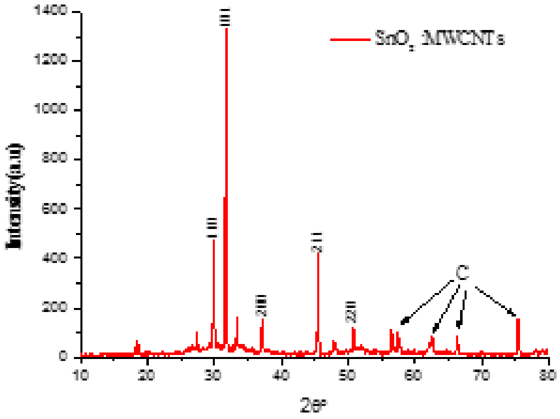


Figure 2. *XRD pattern of SnO_2: MWCNTs*

Sample	SnO 2 : MWCNTs				
Two θ(Deg.)					
	29.88	31.73	37.15	45.49	50.77
hkl	110	101	200	211	220
FWHM (Deg.)	0.23	0.16	0.24	0.20	0.31
Crystallite size (nm)	36.46	36.46	36.46	36.46	36.46
Average Crystallite size (nm)	38.98				

Table 2. *Structural properties of SnO_2: MWCNTs.*

Field Emission Scanning Electron Microscopy (FE-SEM)

The distribution and morphology of the nanocomposites were examined by field emission scanning electron microscopy (FE-SEM). The FE-SEM image of SnO_2 is shown in Figure 3(A, B). The SnO_2 is uniformly distributed, and the average particle size is about 45.84 nm. The FE-SEM image (C, D) of SnO_2/MWCNT nanocomposite shows good uniformity, and it is clear that the SnO_2 is coated and wrapped on the surface of MWCNT. The addition of SnO_2 changes morphology from nanotubular to nanoflower-like structure. The low magnification FE-SEM image of SnO_2/MWCNT nanocomposite shows clearly that the SnO2 is well wrapped on the surface of MWCNT.

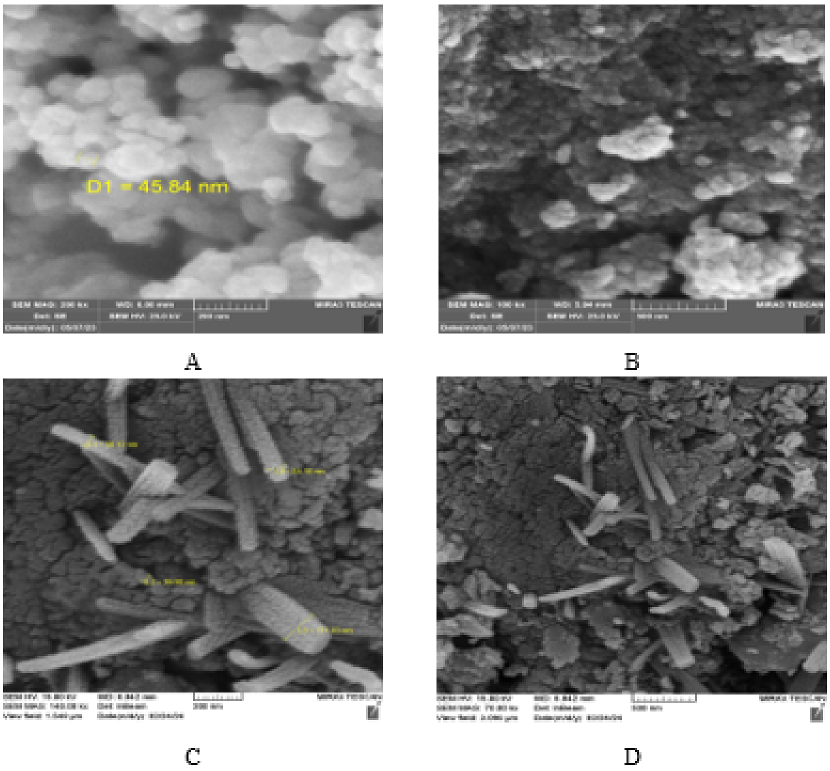


Figure 3. *The FE-SEM image of (A, B) SnO_2, (C, D) SnO_2: MWCNTs*

Optical properties

The UV spectroscopy was used to compute the absorbance data for colloidal nanoparticles. SnO_2 absorption spectra, which spans from 200 nm to 350 nm and is within the low-wavelength band with high UV energy, is shown in Figure 4. This indicates that SnO2 may absorb high-energy blue hues.

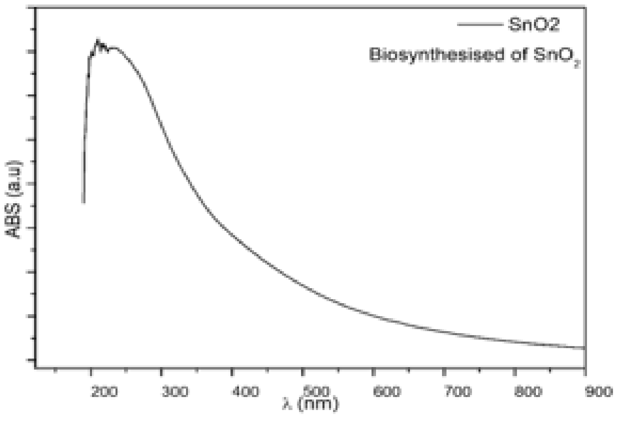


Figure 4 UV-Visible absorbance of SnO_2 NPs

Figure 4. *UV-Visible absorbance of SnO_2 NPs*

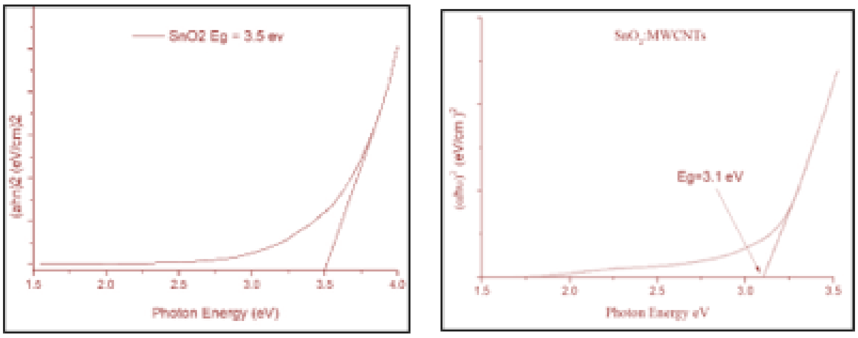
The energy gap was calculated using the Tuce equation

$$\alpha(E) = A(E - E_g)^n$$

Figure 5.

A: stands for a proportionality factor that is equal to the absorption coefficient E denotes the energy of the photon, hv E_g refers to optical bandgap energies, while n is an exponent depending on the features of the electronic transitions during the absorption, where r is equal to 1/5 Thus, by plotting $(\alpha h\nu)^2$ against $(h\nu)$, one gets to define the slope of the tangent to the straight line that intersects the energy axis of incident photons at the point of $(\alpha h\nu)^2$ that represents the energy band gap value for the optical transitions. A was suggested due to an increase in the granular size of the precipitant material that creates donor levels within the energy gap and near the conduction band, thereby increasing the absorption of the low-energy photonic band, in concordance with the finding.

The energy band gap of synthesized SnO2 by the Green method was estimated and is given in Figure 5, and an average value of 3.5 eV was observed.



A

B

Figure 6. *Optical energy gap of (A) SnO_2 NPs , (B) SnO_2:MWCNTs .*

The reduction of the band gap from 3.5 eV (pristine SnO_2) to 3.1 eV after incorporating MWCNTs is due to several factors. The conception of contact between the SnO2 and the carbon nanotubes provides that the two materials have a high density of electronic states that interact. This interaction results in orbital hybridization that alters the character of the valence as well as the conduction bands. The characteristics of MWCNTs cause insertion of crystalline defects and oxygen vacancies into the SnO2 lattice. It is these defects to the formation of the intermediate energy levels that lower the energy needed to excite electrons. Also, using carbon nanotubes as the reinforcing phase results in good electrical conductivity and charge transfer, and improved electron carrier mobility in the composite material. These combined effects therefore improve light absorption ability of SnO2/MWCNT thus making the composite suitable for photocatalytic degradation, gas sensing devices and additional energy storage applications.

Conclusion

The aim of the study was successfully achieved thereby establishing a green approach for the synthesis of SnO_2/MWCNT nanocomposites using eggplant extract as a reducing as well as a capping agent. The structural characterization also supported the synthesis and deposition of crystalline SnO_2 nanoparticles with proper dispersion and interconnection with the MWCNTs. MWCNT incorporation positively affected the properties namely the bandgap energy decrease from 3.5eV to 3.1eV, light absorption and morphological transforms from nanotube to nanoflower. The synthesis with eggplant extract attempt shows that green chemistry methods can indeed be applied to create new forms of nanomaterials. Further, the synthesized nanocomposite can be effectively used in photocatalytic degradation, gas sensing, and energy storage, which can be environmentally benign as compared to the conventional synthesis methods without compromising with the functionality of nanocomposite material.

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