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Research Article

The Application of Pandan and Soybean Extracts on the Biosynthesis of Tin Oxide Nanoparticles

Irmaizatussyehdany Buniyamin[1,2*], Noor Asnida Asli[1,2], Kelvin Alvin Eswar[1,2,3], Syed Abdul Illah Alyahya Syed Abd Kadir[4], Ameran Saiman[5], Mohd Yusri Idorus[6], Abd Razzif Abd Razak[7], Mohamad Rusop Mahmood[1,8] and Zuraida Khusaimi[1,2*]

[1]NANO-SciTech Laboratory, Centre for Functional Materials and Nanotechnology, Institute of Science, Universiti Teknologi MARA, Shah Alam Selangor, Malaysia
[2]Faculty of Applied Sciences, Universiti Teknologi MARA, Shah Alam, Selangor, Malaysia
[3]Faculty of Applied Sciences, Universiti Teknologi MARA, Sabah Branch Tawau Campus, Tawau Sabah Malaysia
[4]Pusat Asasi Universiti Teknologi MARA Cawangan Selangor, Kampus Dengkil, Dengkil, Selangor, Malaysia
[5]Engineering College, Universiti Teknologi MARA, Shah Alam Selangor, Malaysia
[6]Institute Medical Molecular Biotechnology, Faculty of Medicine, Universiti Teknologi MARA, Jalan Hospital, Sungai Buloh Selangor, Malaysia
[7]Lembaga Pemasaran Pertanian Persekutuan, Kementerian Pertanian dan Industri Makanan, Jalan Persiaran 1, Bandar Baru Selayang, Batu Caves, Selangor, Malaysia
[8]NANO-ElecTronic Centre, Engineering College, Universiti Teknologi MARA, Shah Alam, Selangor, Malaysia
*Corresponding author: syehdany@uitm.edu.my, zurai142@uitm.my

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ABSTRACT

Development of benign and efficient approaches towards the replacement of the conventional methods for producing SnO_2 nanoparticles (SnO_2 NPs) has begun in which a biosynthesis process has been introduced. This study utilizes biomolecules, specifically the flavonoids and carbohydrate groups in pandan and soybean extracts. The biosynthesized nanoparticles underwent characterization through relevant spectroscopies. Fourier transform infrared (FTIR) analysis revealed the absorption bands of SnO_2 and Sn-O-Sn groups, with the complete disappearance of peaks associated with untreated pandan and soybean. X-ray Diffraction (XRD) indicated the formation of tetragonal structure in SnO_2 NPs with primary peaks at 27°, 34°, and 51°. Additionally, UV-Visible diffuse reflectance spectroscopy (DRS) yielded band gap values of 4.86 and 3.45 eV for SnO_2 NPs derived from pandan and soybean, respectively. In summary, the application of biosynthesized SnO_2 NPs as a potential heterogeneous catalyst for purifying dye-polluted water through a photocatalytic process is highlighted.

Keywords: Tin oxide nanoparticles, biosynthesis, pandan, soybean

1. INTRODUCTION

Green nanotechnology is recognised as a pivotal advancement in the realm of sustainable technology, actively pursuing the fabrication of nanomaterials while concurrently minimising environmental degradation stemming from their production (Gebreslassie & Gebretnsae, 2021; Jadhav & Kokate, 2020). Historically, the scientific community has developed a myriad of chemical and physical methodologies for synthesising tin dioxide nanoparticles (SnO_2 NPs), including but not limited to electrochemical and photochemical synthesis, microwave irradiation, hydrothermal processes, and laser ablation. These methods have been extensively applied in the creation of SnO_2 nanomaterials (Haritha et al., 2016). However, these traditional processes often necessitate the employment of noxious chemicals, the application of elevated temperatures, and substantial energy consumption, alongside considerable production expenses (Vidhu & Philip, 2001). In response to growing ecological apprehensions, there has been a pronounced shift towards more sustainable practices within green technology. Notably, this includes the biosynthesis of nanomaterials, utilising biological entities such as plant extracts (Gebre & Senduku, 2019). It is suggested that bioactive compounds found within plant matter, including alkaloids, phenolic acids, polyphenols, proteins, sugars/carbohydrates, and terpenoids, serve as both reducing and capping agents during the biosynthesis process, thereby facilitating the production of nanomaterial-based products (Kavitha et al., 2013; Zulpahmi et al., 2023).

This research delves into the potential of two biomaterials endemic to Malaysia; pandan leaves and soybeans for the biosynthesis of SnO_2 NPs. Pandan, scientifically termed *Pandanus amaryllifolius*, is indigenous to Malaysia and has been traditionally harnessed for its flavour-enhancing properties in food and beverages. This plant is particularly rich in flavonoids, compounds that have shown efficacy as reducing and capping agents for tin cations (Thatsanasuwan et al., 2015; Zakaria at al., 2020; Buniyamin et al., 2021). Conversely, soybeans are a staple in human nutrition, serving as a base for infant formulas, flours, protein isolates and concentrates, and textured fibres, with tempeh and tofu being among the most prevalent soy-based foods (Friedman & Brandon, 2001). Carbohydrates, constituting nearly 35% of the soybean, whether structural or non-structural, share a molecular resemblance with flavonoids, notably the presence of adjacent hydroxyl groups. These groups are proficient in electron donation, thus facilitating the conversion of metal cations into nanoparticles. Their presence is instrumental in binding to nanoparticle surfaces, which assists in their stabilisation and prevents agglomeration (Kavitha et al., 2013; Lokuruka, 2010; Yasar et al., 2020). This investigation presents findings on the use of pandan and soybean extracts in the synthesis of SnO_2 NPs, including characterization and an examination of their energy band gap values, particularly in relation to their prospective applications in photocatalysis. This analysis is meticulously aligned with established scientific principles, ensuring a robust and systematic exploration of the subject matter (Vasiljevic et al., 2020; Abbasi & Hasanpour, 2017; Wang, 2018; Yuan & Xu, 2010).

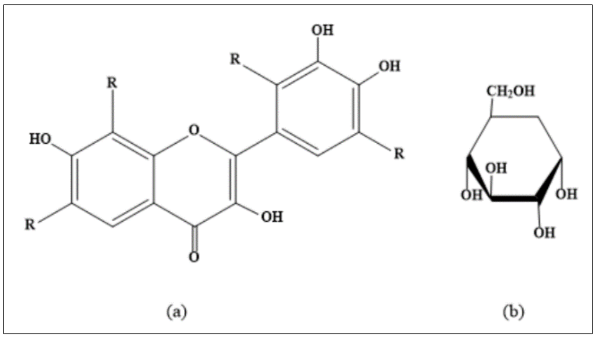

Figure 1. General molecular structure of flavonoid (a) and carbohydrate (b) group.

2. MATERIALS AND METHODS

In the preparation of each extract, pandan and soybean materials were individually combined with 100 ml of water and heated to a temperature range of 60-70°C. The filtration procedure utilised Whatman filter paper no. 1, following which the resultant stock solution was preserved at a temperature of 4°C. Subsequently, approximately 200 ml of the crude extract was incrementally introduced to a vigorously stirred solution of 0.05 M tin chloride pentahydrate, with the solution being left to stand for a duration of 3 hours at ambient temperature. Over time, this mixture underwent a transformation into a gelatinous consistency, which was then subjected to dehydration in a conventional oven, resulting in the formation of a black precipitate. The calcination process was meticulously executed for 3 hours at temperatures of 700°C and 600°C for soybean and pandan-based experiments, respectively, with the objective of converting the precipitate into pure SnO_2 NPs (Buniyamin et al., 2021). The analytical phase encompassed a diverse array of characterization methodologies. Initially, Fourier-transform infrared (FTIR) spectroscopy was applied to delineate the chemical bonds present, while X-ray diffraction (XRD) analysis was undertaken to elucidate the structural attributes of the nanoparticles. Moreover, the optical properties were scrutinised through UV-diffuse reflectance spectroscopy (UV-DRS) analysis, utilising the Kubelka-Munk function for the calculation of the energy band gap, providing a comprehensive insight into the intrinsic properties of the synthesized SnO_2 NPs.

3. RESULTS AND DISCUSSION

3.1. *Probable reaction mechanism of SnO_2 NPs*

By considering the reaction mechanism based on the flavonoid group is described in references (Gawade et al., 2017; Bhosale et al., 2018; Ahmed et al., 2017), herein the functionality of the carbohydrate group is suggested as shown in Figure 2. For better clarity, the mechanism for carbohydrate group is presented in chair conformation. The mechanism is initiated with the addition of soybean extract into the stirring solution of the salt precursor solution of $SnCl_4$. $5H_2O$ that would lead to a chemical association. The carbohydrate molecules, possesses a hydroxyl group, would later form a bridging network with Sn^{4+} of the salt precursor. The tetravalent of Sn^{4+} cation is attached to four hydroxyl groups of two carbohydrate molecules and this networking keeps the molecules steadily as one unit by capping action. Notably, the change of phase from a clear brownish solution to the jelly-form evidences the aggressive capping action signifying the construction of the complex networking of Sn^{4+} cation. As time progress, more Sn^{4+} cation be capped by the hydroxyl groups. Later, the reduction Sn^{4+} to Sn^0 occurs, and the SnO_2 NPs is obtained after it has been calcined.

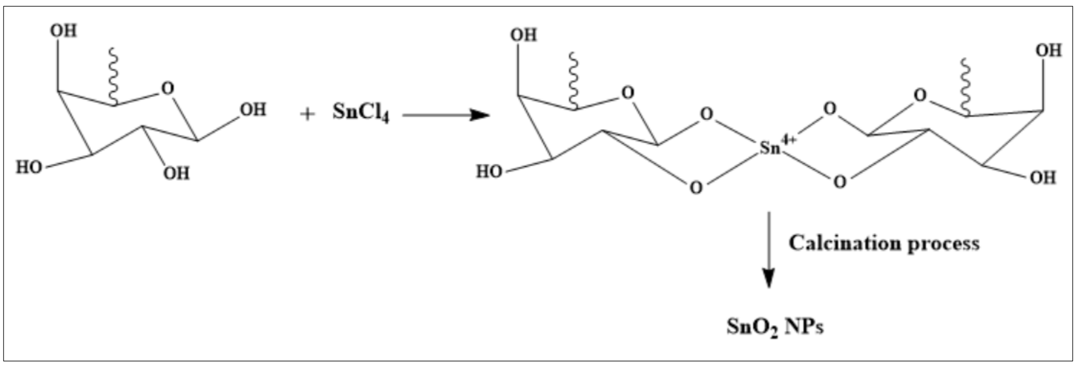

Figure 2. Plausible reaction mechanism for the synthesis of SnO_2 NPs

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3.2. Fourier-transform Infrared (FTIR) Analysis

The elucidation of biomolecules within pandan and soybean extracts has been affirmed through Fourier-transform infrared (FTIR) spectroscopy analysis. For pandan, the FTIR spectrum, as depicted in Figure 3(a), showcases a broad transmittance band spanning the range of 3514 to 3106 cm^{-1}, indicative of the presence of hydroxyl (OH) groups. This is succeeded by a pronounced transmittance peak at 2924 cm^{-1}, which signifies the stretching vibrations of the CH group. Additionally, the characteristic stretching vibrations of the CH_3, carbonyl (C=O), and carbon-carbon double bond (C=C) functional groups are distinctly observed at 2841, 1730, and 1635 cm^{-1}, respectively. The vibrational stretching of the C-OH group is identified at 1464 cm^{-1}. Furthermore, a notable transmittance peak at 1244 cm^{-1} signifies the presence of the C-O group, with the region from 1125 to 1009 cm^{-1} corroborating the existence of the ether (C-O-C) group. Lastly, the stretching vibrations attributed to the =CH group, associated with aromatic compounds, are identified within the range of 927 to 732 cm^{-1} (Ali & Hawa, 2017).

Conversely, the FTIR spectrum of untreated soybean, presented in Figure 3(b), confirms the presence of functional groups, particularly those associated with carbohydrates. A broad transmittance band observed at 3375 cm^{-1} denotes the stretching vibrations of the OH group. The presence of methylene (-CH_2) and methyl (-CH_3) groups, indicative of aliphatic saturated hydrocarbons (C-H), is evidenced by transmittance bands at 2929 and 2843 cm^{-1}, respectively, arising from asymmetric and symmetric stretching vibrations. A sharp band at 1624 cm^{-1} corresponds to the stretching vibrations of the carbonyl (C=O) group. Additionally, the peaks at 1418 and 1240 cm^{-1} are attributed to the stretching of OCH_2 and CH aromatic groups, respectively. The bending vibrations of the NH group are indicated by the peak at 1148 cm^{-1}, while the peak at 1063 cm^{-}1 is representative of the C-O stretching pattern. Finally, the region spanning 723 to 560 cm^{-1} is associated with the CH_2 stretching vibrations (Woumbo et al., 2021).

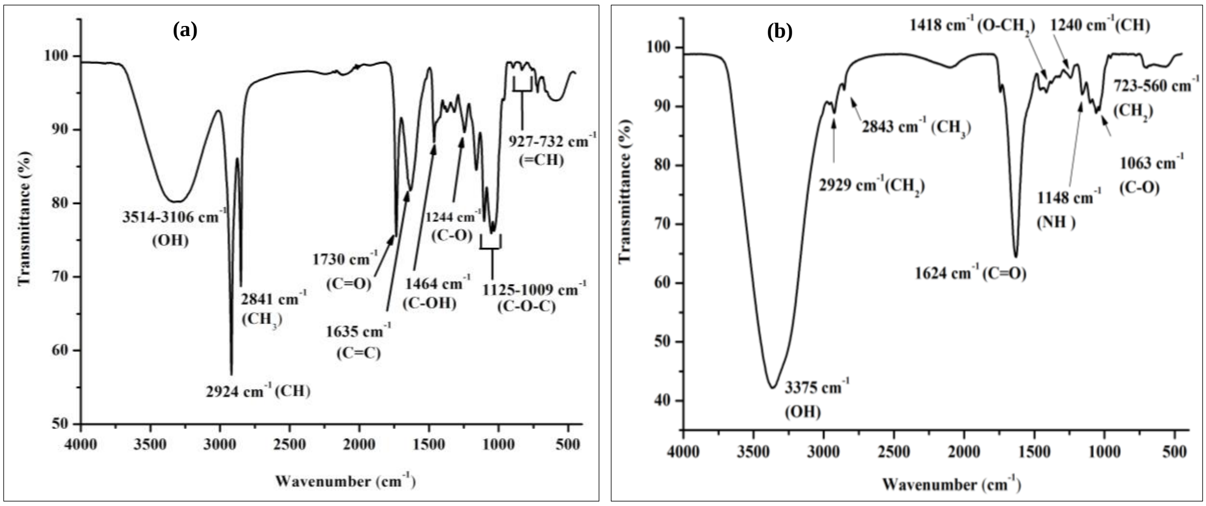

Figure 3. The FTIR spectrum for untreated pandan (a) and soybean (b)

The Fourier-transform infrared (FTIR) spectra of SnO_2 NPs synthesized from pandan and soybean extracts are illustrated in Figure 4 (a) and (b). The absence of peaks associated with the untreated pandan and soybean substantiates the effective capping and reduction processes facilitated by the biomolecules, culminating in the formation of SnO_2 NPs as evidenced in the FTIR spectra. This transformation is characterised by a transmittance band spanning 762 to 605 cm^{-1}, which signifies the stretching vibrations of the Sn-O-Sn linkage, corroborating the formation of SnO_2 NPs. Additionally, the detection of a distinct peak within the range of 1166 to 1073 cm^{-1} lends further support to the presence of SnO_2. Meanwhile, the observation of the carbon dioxide (CO_2) group within the spectral region of 1953 to 2210 cm^{-1} is deemed to be of minimal significance (Rahmi & Kurniawan, 2017; Buniyamin et al., 2023).

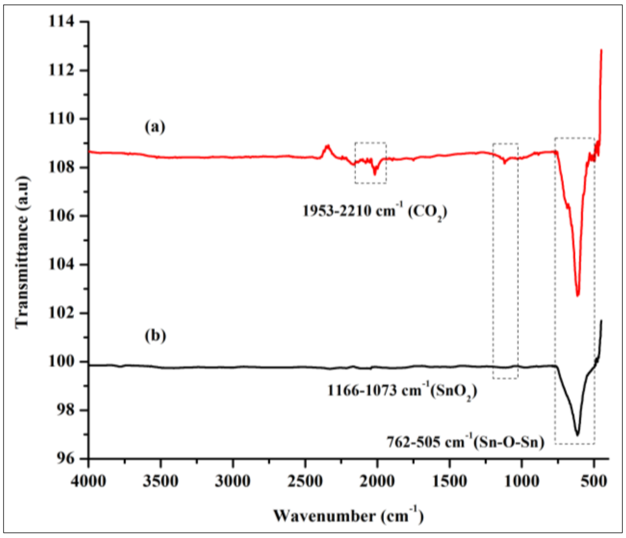

Figure 4. The manifestation of functional groups for SnO_2 NPs

3.3. X-ray Diffraction (XRD) Analysis

The analysis of XRD diffraction peaks is shown in Figure 5. The primary diffraction peaks of the SnO_2 NPs corresponding to (110), (101) and (211) planes with their respective 2θ angles at 27°, 34° and 51° is presented. These peaks can be attributed to the tetragonal rutile type structure as per JCPDS card no.01-077-0452, in complete agreement with previous reports (Kumari & Philip, 2015; Buniyamin et al., 2023; Ayeshamariam, 2013; Tammina et al., 2017). The crystalline size (D) of SnO_2 NPs was calculated using Scherrer's formula (Eq. 1):

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

in which D=Crystallite size (nm), λ= wavelength of the incident rays (1.54Å), k= Unknown shape factor, β= Full Width at Half Maximum value (radian) and θ= Position (radian), diffraction angle (Wicaksono et al, 2020).

The average crystallite size of SnO_2 NPs synthesized from pandan extract, as calculated using the previously referenced equation, is determined to be 10.6 nm. In comparison, SnO_2 NPs produced from soybean extract exhibit a marginally smaller average size, measuring at 9.6 nm. This variation in crystallite size underscores the efficacy of both biomolecule types that are the flavonoids and carbohydrate groups, as both capping and reducing agents within the synthesis process, evidenced by their contribution towards providing distinct diffraction peaks that affirm the formation of SnO_2 NPs. Although the crude extracts contain a variety of hydroxylated biomolecules, it is posited that only those hydroxyl groups attached to aromatic or cyclic structures partake in the capping mechanism. Specifically, hydroxylated flavonoids and carbohydrate groups are highlighted for their significant compatibility and contribution, likely attributed to their inherent stability. This strategic stabilization of Sn^{4+} ions by the hydroxylated biomolecule networks is pivotal in directing the nucleation and subsequent growth phases of the nanoparticles, thereby enhancing their crystallinity and structural integrity (Madkour, 2018; Singh et al., 2015; Makarov et al., 2014).

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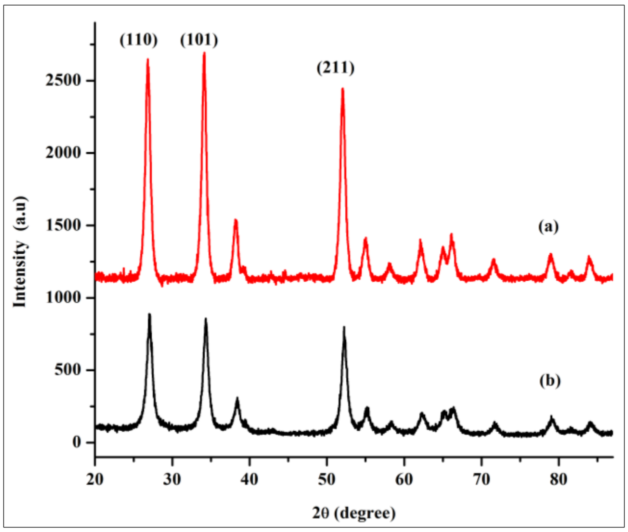

Figure 5. The diffraction peaks of SnO_2 NPs synthesized from pandan (a) and soybean (b)

3.4. UV-Visible Diffuse Reflectance (UV-DRS) Analysis

Ultraviolet-diffuse reflectance spectroscopy (UV-DRS) analysis was undertaken to evaluate the reflectance properties inherent in the nanoparticles, aimed at elucidating their enhanced surface-to-volume ratio, which is instrumental in augmenting light scattering and optimizing light harvesting capabilities (Xinjuan et al., 2013). The resultant reflectance spectrum, as illustrated in Figure 6, exhibits a reflectance value of 82% for SnO_2 NPs synthesized from pandan extract (a) and 76% for those derived from soybean extract (b). The absorption edges of both specimens are positioned within the visible light spectrum, specifically at 599 cm^{-1} and 699 cm^{-1}, respectively. This positioning denotes the threshold wavelength beyond which the capacity to attain optimal reflectance is constrained, highlighting the spectral efficiency of the synthesized SnO_2 NPs in light absorption and reflection (Buniyamin et al., 2023).

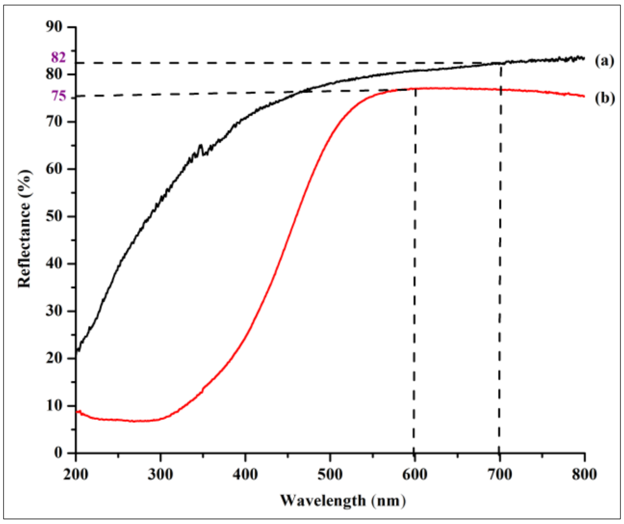

Figure 6. The reflectance percentage plotted from the analysis of UV-DRS

Upon obtaining the reflectance results, the Kubelka-Munk function (Equation 2) was utilised to transmute the reflectance values into band gap energy estimations (Senthilkumar et al., 2012). This process entailed graphing the square of the Kubelka-Munk function values against the photon energy and extrapolating the linear portion of the resultant plot, as depicted in Figures 7(a) and (b). This methodological approach facilitates a quantitative assessment of the optical band gap energy, providing insights into the electronic structure and photonic properties of the synthesized materials.

$$F(R) = (1-R)^2 / 2R = k/s \qquad (2)$$

The determined energy band gaps for SnO_2 NPs synthesized from pandan and soybean extracts are 4.86 eV and 3.45 eV, respectively. These values render the nanoparticles suitable for utilization in photocatalytic reactions, a finding that is in alignment with earlier research (Buniyamin et al., 2023). Notably, the SnO_2 NPs generated through the mediation of pandan extract exhibit an energy band gap that surpasses the typical range for bulk SnO_2, conventionally acknowledged to be around 3.6 eV. This elevation in the energy band gap is presumably due to an increased defect density which is associated with electrical conductivity, thereby leading to an expansion of the band gap value (Zulfiqar et al., 2017). While the energy band gap of SnO_2 NPs derived from soybean closely aligns with the theoretical expectation of 3.45 eV, a minor reduction may be observed. Such a variation could be ascribed to a series of factors including the limitations in carrier concentration, the presence of unoccupied electronic states, and the emergence of homogeneous oxygen vacancies (Ayeshamariam et al., 2014; Yang et al., 2017). The elucidation of these energy band gaps offers an optimistic perspective for the application of SnO_2 NPs, synthesized from both pandan and soybean, in photocatalytic processes. This optimism is predicated on the potential for these nanoparticles to facilitate the generation of high levels of photo-induced electrons and holes.

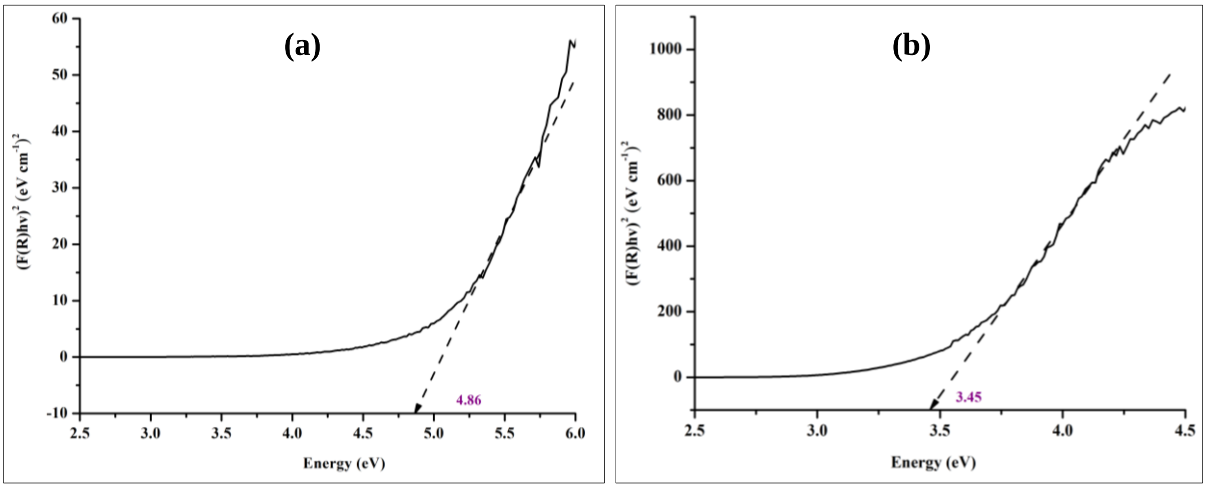

Figure 7. The energy band gap for SnO_2 NPs synthesized from pandan (a) and soybean (b)

4. CONCLUSION

In conclusion, the successful fabrication of SnO_2 NPs was accomplished using pandan and soybean extracts. The biomolecules within these extracts, particularly the flavonoids and carbohydrate groups, proved to be effective agents for the reduction and capping actions integral to the biosynthesis process. Although these biomolecules were not isolated in their pure forms, the employment of their crude extracts still efficiently facilitated the biosynthesis mechanism, leading to the production of pure SnO_2 NPs. This highlights the simplicity and efficacy of the method. The presence of key functional groups, specifically SnO_2 and Sn-O-Sn, was verified through Fourier-transform infrared (FTIR) spectroscopy. X-ray diffraction (XRD) analysis further elucidated the tetragonal rutile structure of the nanoparticles, with notable planes (110), (101), and (211) observed at 27°, 34°, and 51°, respectively. The derived band gap values of 4.86 eV and 3.45 eV for SnO_2 NPs from pandan and soybean, as determined by diffuse reflectance spectroscopy (DRS) analysis, highlight their potential efficacy in photocatalytic applications. Future research directions should encompass a thorough exploration of the scalability, stability, reproducibility, and longevity of the biosynthesized SnO_2 NPs, aiming to further elucidate their capabilities and cement a robust framework for their practical deployment in diverse settings. Additionally, investigating the use of isolated hydroxylated flavonoids and carbohydrate groups contrasting with this study reliance on crude extracts could provide valuable insights. Such an inquiry would facilitate a comparative analysis, shedding light on the precise impact of these bio-templates on the characteristics of the resultant SnO_2 NPs, thereby offering a clearer understanding of the biosynthesis process efficiency and potential enhancements.

Declaration of Interest

The authors declare that there is no conflict of interest in the current work.

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