OPTICAL FEATURES OF NANOFIBROUS SCAFFOLDS COMPRISING ZINC STANNATE, FABRICATED THROUGH ELECTROSPINNING*

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Abstract

This study employed a sol-gel method to prepare zinc stannate nanopowder using zinc and tin chloride. Subsequently, zinc stannate nanofibers were synthesized on fluorine-doped tin oxide (FTO) glass substrates through an aqueous solution of zinc stannate and polyvinyl alcohol (PVA) using electrospinning. Natural dyes extracted from barks (Caesalpinia pulcherrima, Prunus domestica, Tamarindus indica, Pterocarpus macrocarpus) were utilized as photosensitizers in dye-sensitized solar cells (DSSCs). The natural dye solutions and zinc stannate nanofibers' optical properties, including absorption wavelengths and energy band gaps, were analyzed using Ultraviolet-Visible (UV-Vis) spectroscopy for DSSC photoelectrodes. The study observed significant variations in absorption wavelengths and energy band gaps. This environmentally friendly and cost-effective approach aims to enhance the efficiency and durability of zinc stannate nanomaterials for energy generation.

Keywords: Zinc Stannate Nanofibers, Sol-gel Method, Electrospinning Method, and UV-Vis.

Introduction

Increasing energy conversion efficiency is a great challenge to overcome in the market entrance of DSSCs. To realize this objective, modifications have been made to the components of the DSSC, as well as to their manufacturing processes. Several methods have been used for producing nanofibers, including electrospinning, melt or solution blowing, phase separation, self-assembly, and template synthesis (M. Afshari, et al.,2017). The electrospinning performance is an option to increase the efficiency of DSSCs, because the resultant nanofibers increase the contact area, garnering a greater absorption of solar energy. Electrospinning is the technique that uses a strong electric field to produce polymer nanofibers from a polymer solution or polymer melt (F. Huang, et al., 2012). In this work, a summary of the components of DSSCs is made, as well as its process. A brief review of the electrospinning technique and its usage in the manufacture of DSSC is discussed, presenting an updated comparison of electrospun compounds and their efficiency, and providing the basis for the progress in the manufacture and design of DSSCs. In the DSSCs study, nanofibers play a major role in obtaining maximum efficiency. Moreover, the nanofibers prepared via electrospinning have a high surface area-to-volume ratio, high porosity, and a unique web structure that are crucial to energy conversion and storage (X. Shi, et al.,2015). General DSSCs have a dye nanofibers coating sandwiched between two conducting glass plates in the existence of an electrolyte. The nanofibers have shown great potential for DSSC applications. This is because the electrospun nanofibers have excellent electrical conductivity and a large surface area to volume ratio, which permits improved penetration of viscous polymer gel electrolytes and provides a higher specific surface area than nanoparticles. It has been shown that replacing nanoparticulates with one-dimensional nanoarchitectures can improve charge transport by reducing the scattering of free electrons from the grain boundaries of the interconnected nanoparticles. As one-dimensional nanostructures provide a more direct pathway for charge collection, we can expect that electron transport in nanofibers would be significantly faster than in nanoparticles (N. Canever, et al.,2017). Several different shapes and sizes of micron and nanoscale fibers can be fabricated from various classes of polymers. Electrospinning offers a straightforward way to produce long polymer fibers with

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diameters in the range of 40– 2000 nm (S. Ramakrishna, et al.,1996). The basic components of DSSCs primarily consist of transparent conducting oxide glass substrates, dye, photoanode, electrolytes, and counter electrodes (S. N. Karthick, et al.,1996). Potoanode plays two roles in dye adsorption and electron transport media. Photoanode is grown on the surface of Transparent Conducting Oxide (TCO), and mesoporous semiconductor metal-oxide nanoparticles (R. Qohhar, et al.,2020). In the photoanode of a DSSC, morphology, and structure play a very important role in the performance of electron transport Several studies have been carried out for the development of photoanodes with materials with one-dimensional morphology. Therefore, nanofiber compounds are a very promising option for use in DSSC (J. G. López-Covarrubias, et al.,2020). The photoanode contains a metal oxide semiconductor deposited on the surface of a transparent conductive oxide substrate. The transparent conductive oxide allows the collection and transfer of electrons to an external circuit. A high electron transport rate is required to reduce the electron-hole recombination rate and enhance conversion efficiency (L. T. Yan, et al.,2012). Usually, fluoride-doped tin oxide is used as the transparent conductive oxide; this is due to its excellent electrical conductivity, optical transparency, and 75% transmittance. The dye sensitizer in the DSSC is responsible for absorbing the light generated from the electron current through photoexcitation and is thus fixed to the photoanode. The role of the photoanode material itself is very crucial in achieving higher light harvesting, proper dye loading, uninterrupted electron transport or diffusion, ultrafast injection of photoelectron, and lowering the recombination reactions (P. P. Das et al.,2016).

Materials and Methods

Sample Preparation of zinc stannate nanopowders

Materials

In this research, Zinc Stannate, PVA, and distilled water were used as the starting materials to produce zinc stannate nanofibers, and distilled water was used as the dissolving solvent.

Methods

The synthesis method consisted of two steps: (1) The preparation of zinc stannate nanopowders was synthesized by the sol-gel technique, and (2) zinc stannate nanofibers were fabricated using the electrospinning method.

Cleaning Process of FTO Glasses

Fluorine-doped tin oxide glasses were used as transparent substrates, and the glass slides were cleaned as follows.

(1) Firstly, the FTO glass slides were cleaned with distilled water.
(2) They were taken and immersed in ethanol for 15 minutes and dried.
(3) And then, they were immersed in acetone for 15 minutes and dried.

Eventually, clean FTO glass slides were obtained. The space of (1cm×1cm) of FTO glass was used for the coated area, and the other area was masked by using a tape spacer, and they were ready to use for the photoelectrode.

Preparation of Natural Dye Extraction

In this research, samples were collected from the stem barks of Caesalpinia pulcherrima (Peacock Flower Tree), Prunus Domestica (Plum Tree), Tamarindus indica (Tamarind Tree), and P. macrocarpus (Padauk Tree). The natural dye solution from four different barks of the plants was extracted as sensitizers for dye-sensitized solar cells by using a simple and easy solvent extraction method. The obtained samples were washed with water to remove dust particles and then dried at room temperature in the dark for one week in the laboratory. The dried samples were chopped into small pieces. Dye solutions were extracted from different barks using ethanol as the extraction solvent. Then, 50 g of small pieces of bark samples were mixed with 70 ml of ethanol at room temperature. The mixtures were annealed at 80 °C for 45 min until the mixtures showed homogeneity in color. The solutions were carefully filtered with filter papers, and then the resulting filtrate was used as a natural dye sensitizer. All dye solutions were stored in the dark. Figure 1 describes the step-by-step preparation of four different dye solutions from bark samples.

Weighing **Mixed with solvents**

Annealing at low temperature

Filtering dye solutions

Figure 1 Step-by-step preparation of four different dye solutions from bark samples

Preparation of Zinc Stannate Nanofiber Electrode

In this research work, the photoanodes of zinc stannate nanofiber were prepared by using the Electrospinning method. The zinc stannate nanofiber was coated onto the FTO glass substrates by using the electrospinning method. Firstly, the viscosity is used to obtain the nanofibers. The solution used to produce nanofibers was prepared with PVA. Fibers were produced using five types of zinc stannate nanopowder at different temperatures. Zinc stannate nanopowder and solution are mixed and added to the beaker, and then stirred with a magnetic stirrer. The mixture was first heated at 80ºC with constant stirring until a transparent homogeneous polymer solution was formed. The electrospun Zn_2SnO_4/PVA nanofiber membranes were prepared using the electrospinning system. Then it was allowed to cool down to room temperature and was transferred to a syringe pump connected to a needle. A high voltage of 2.5 kV was applied between the tip of the needle and the grounded drum collector, which were fixed 8 cm apart. The PVA nanofibers were deposited onto a glass substrate, which was attached to the drum collector by an aluminum foil. The nanofiber membrane is deposited on the glass substrate. The zinc stannate nanofibers coated film was heated at 100℃ for 45 minutes and annealed at 450℃ for 1 hour. After annealing, the film was cooled down at room temperature, and a zinc stannate nanofiber photoelectrode was obtained. Then, the zinc stannate nanofiber photoelectrode was immersed in a dye solution for 24 hours, and the optical properties of the zinc stannate nanofiber photoanode were examined by Ultraviolet-Visible Spectroscopy.

Washed with distilled water

Immersed in ethanol (15 min)

Immersed in acetone (15 min)

Figure 2 Cleaning process of FTO Glasses and checking conductive side

(a) Electrospinning process

(b) As prepared electrospun nanofibers on FTO

Figure 3(a, b) Preparation of Zinc Stannate nanofiber photoanodes

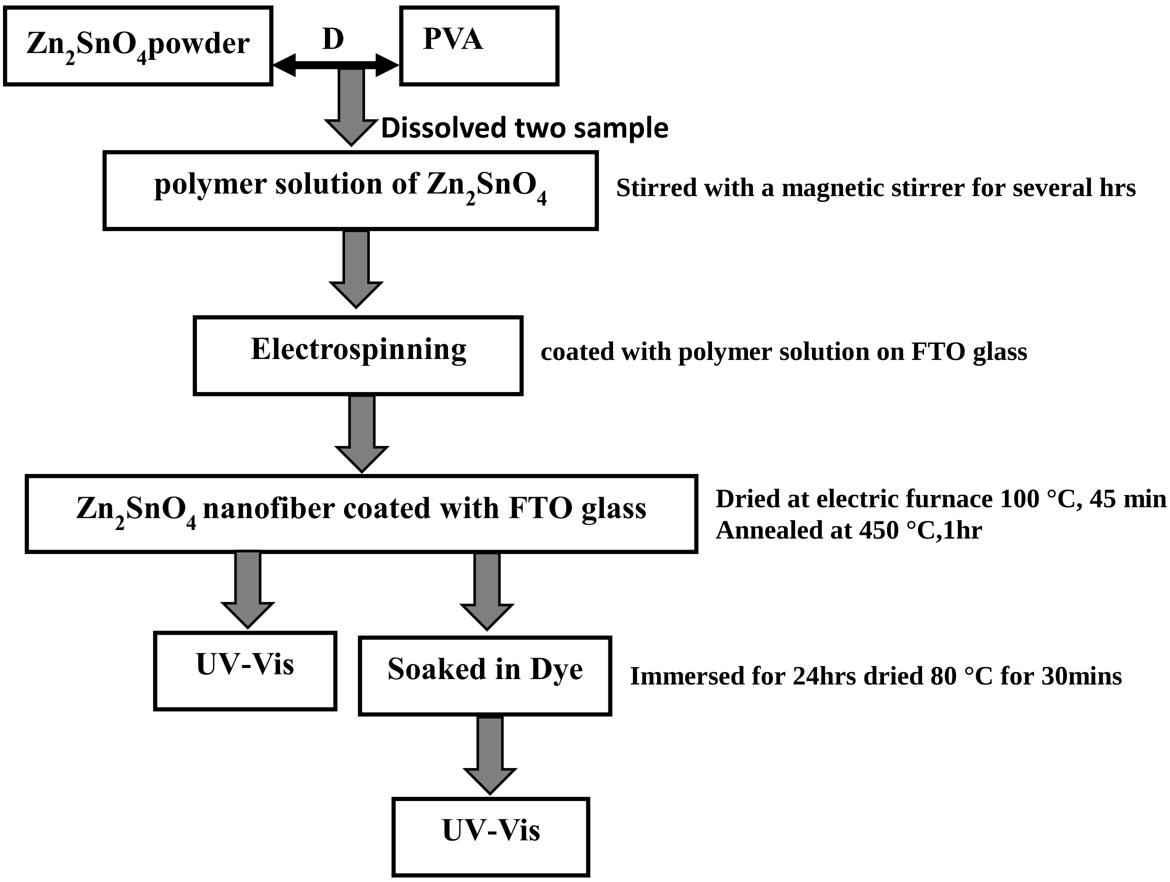

Figure 4 Block diagram of the preparation of Zinc Stannate nanofiber photoanode

Results and Discussion

UV-Vis Analysis of Zinc Stannate Nanofiber Photoanodes

The optical absorption property of the electrospun Zn_2SnO_4 nanofibers on FTO substrates was investigated using UV-Vis spectroscopy. Figure 5(a-e) showed the energy bandgaps using Tauc's electrospun Zn_2SnO_4 nanofiber photoanodes equation. The estimated energy bandgaps for Zn_2SnO_4 nanofiber photoanodes were 3.50 eV, 3.20 eV, 3.18 eV, 3.17 eV, and 3.14 eV for different temperatures, respectively. The energy bandgap of Zn_2SnO_4 nanoparticles ranges from 3.25 eV to 3.65 eV (D. L. Young et al.,2002; H. Zhu et al.,2016). But, in this study, the energy bandgaps of Zn_2SnO_4 nanofibers were narrowed from 3.50 eV to 3.14 eV due to the heat treatment, phase changes (powders to nanofibers), and incorporation of excess Zn into Zn_2SnO_4 crystal (M. A. Alpuche-Aviles et al.,2009). Although the optical absorption property of Zn_2SnO_4 remains controversial, the observed energy bandgap values of the electrospun Zn_2SnO_4 nanofibers photoanodes agreed well with previous reports. Table 1 listed the observed energy bandgaps and referenced energy band gaps.

Table 1. Observed energy bandgaps and referenced energy bandgaps

Samples	Temperatures	E_g (this study)	E_g (references)
Zn_2SnO_4 nanofibers	500 °C	3.50 eV	3.25 – 3.67 eV [11,12]
	600 °C	3.20 eV	
	700 °C	3.18 eV	
	800 °C	3.17 eV	
	900 °C	3.14 eV	

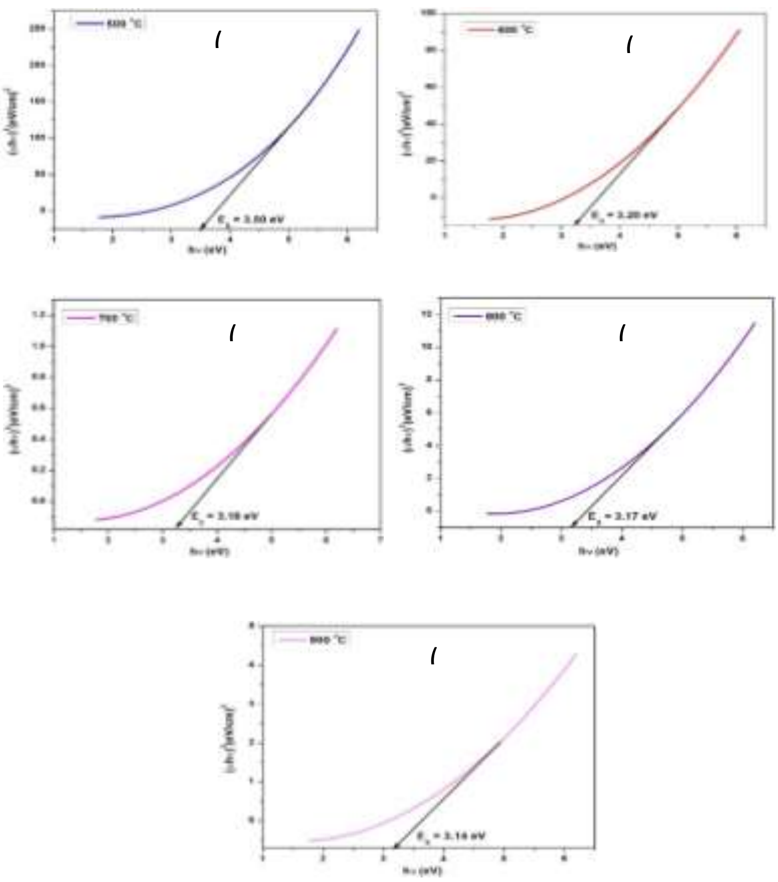

Figure 5(a-e). UV-Vis analysis of electrospun Zn_2SnO_4

UV-Vis Analysis of Dye-soaked Zinc Stannate Nanofiber Photoanodes

The energy bandgaps of natural dyes with ethanol solvent were 2.05 eV for Padauk, 2.83 eV for Peacock flower, 2.91 eV for Plum, and 2.56 eV for Tamarind trees, respectively. In this study, these natural dye sensitizers were adsorbed on zinc stannate nanofiber photoanodes, and the optical properties of dyes-soaked nanofiber photoanodes were investigated using UV-Vis spectroscopy. Figures 6(a-e), 7(a-e), 8(a-e), and 9(a-e) showed the energy bandgaps of dyes-soaked nanofiber photoanodes. According to the results, the energy bandgaps of dye-soaked zinc stannate nanofiber photoanodes were well matched with the standard energy bandgap values of zinc stannate. Although some of the samples had wider energy bandgap values, most were suitable for the usage of dye-sensitized solar cell applications. The energy bandgap values of all dye-soaked nanofiber photoanodes were tabulated in Table 2.

Table 2. Energy bandgaps comparison between dyes and dye-soaked photoanodes

Dyes	Zn_2SnO_4	E_g (dyes)	E_g (dye-soaked photoanodes)
Padauk	500 ºC	2.05 eV	3.19 eV
	600 ºC		3.15 eV
	700 ºC		3.33 eV
	800 ºC		3.27 eV
	900 ºC		3.74 eV
Peacock	500 ºC	2.83 eV	3.73 eV
	600 ºC		3.89 eV
	700 ºC		3.32 eV
	800 ºC		3.48 eV
	900 ºC		3.74 eV
Plum	500 ºC	2.91 eV	3.16 eV
	600 ºC		3.23 eV
	700 ºC		3.09 eV
	800 ºC		3.08 eV
	900 ºC		2.95 eV
Tamarind	500 ºC	2.56 eV	3.08 eV
	600 ºC		3.06 eV
	700 ºC		3.14 eV
	800 ºC		2.94 eV
	900 ºC		3.01 eV

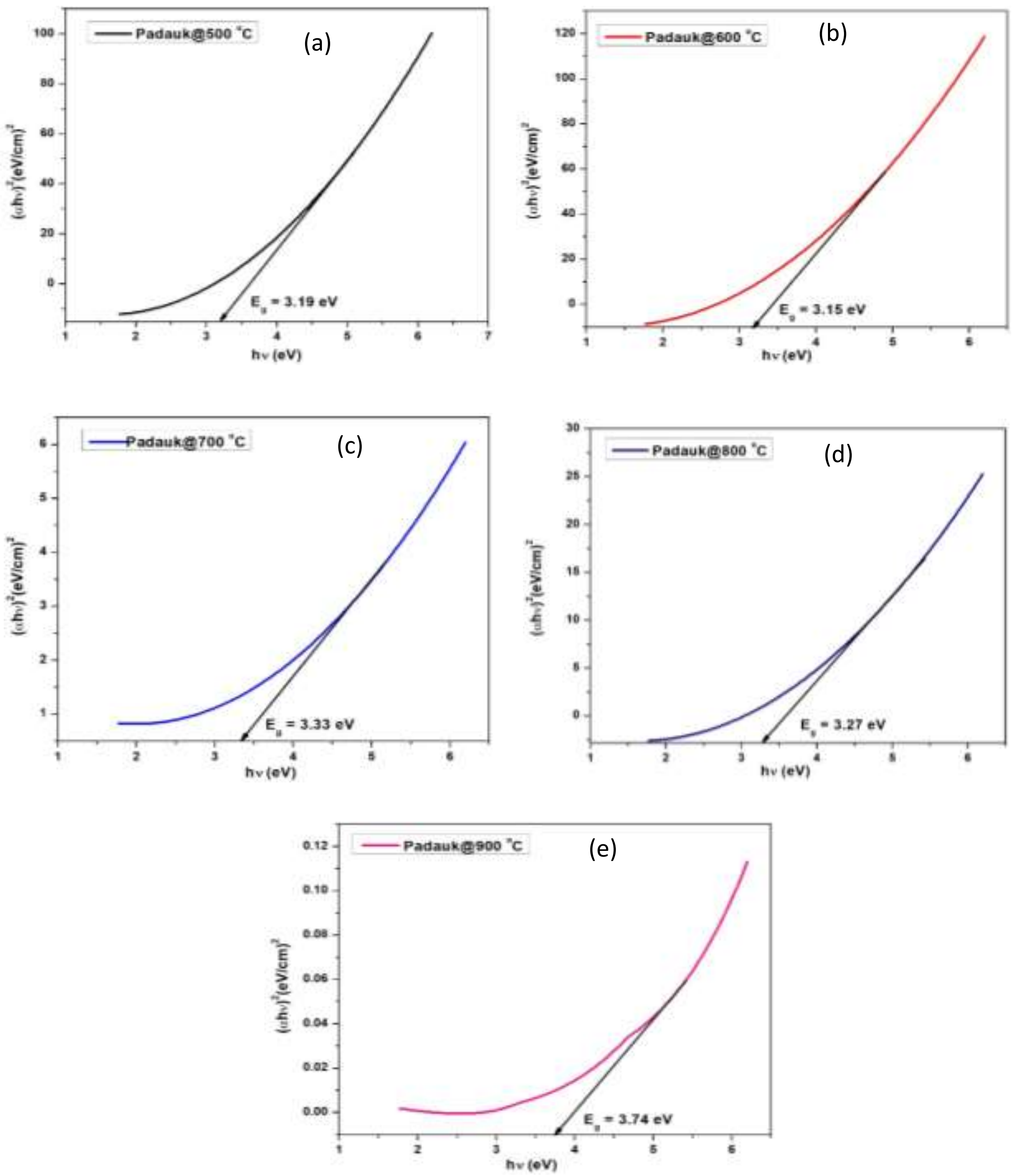

Figure 6(a-e). Energy bandgaps for Padauk dye-soaked nanofiber photoanodes

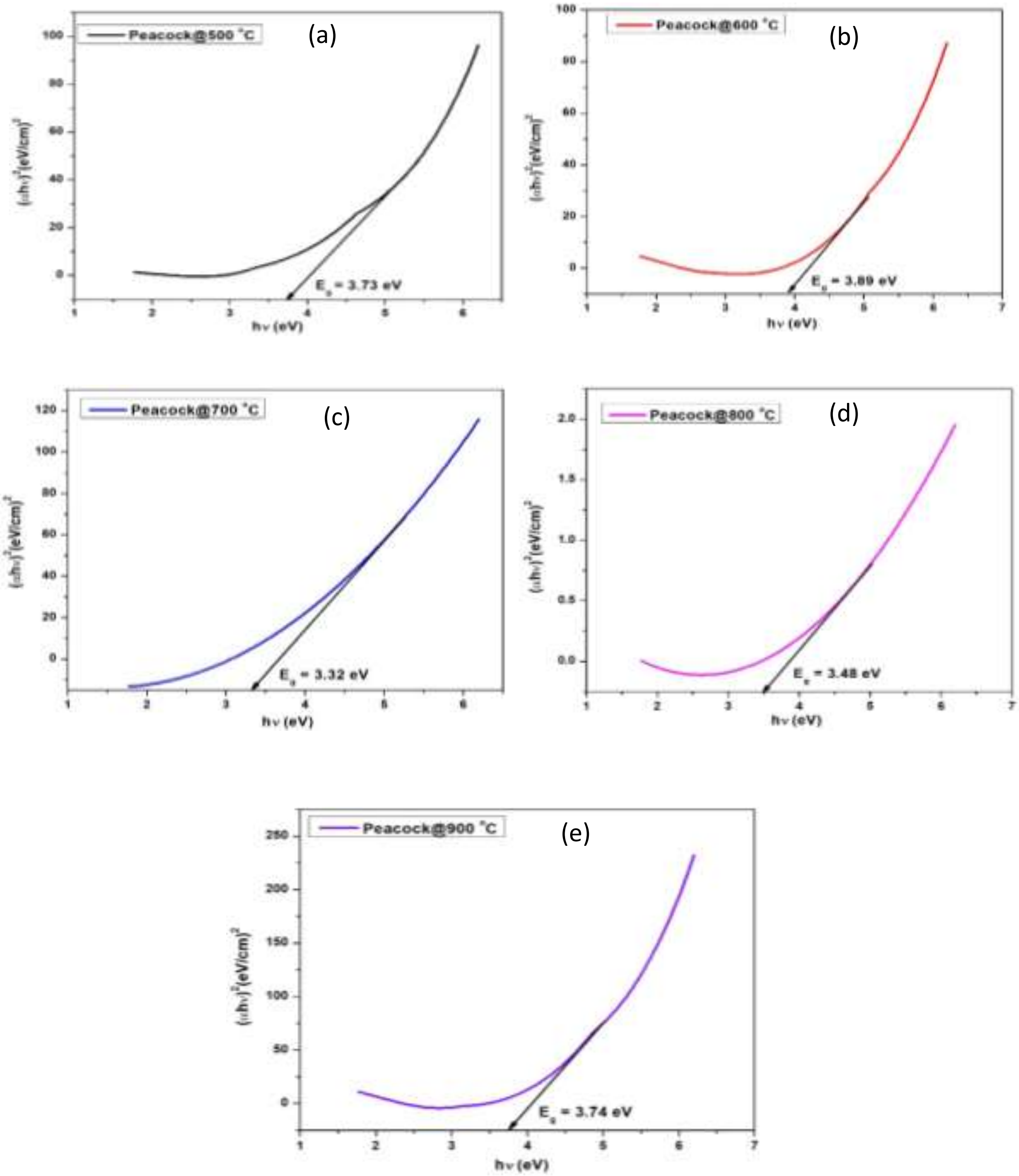

Figure 7(a-e). Energy bandgaps for Peacock flower dye-soaked nanofiber photoanodes

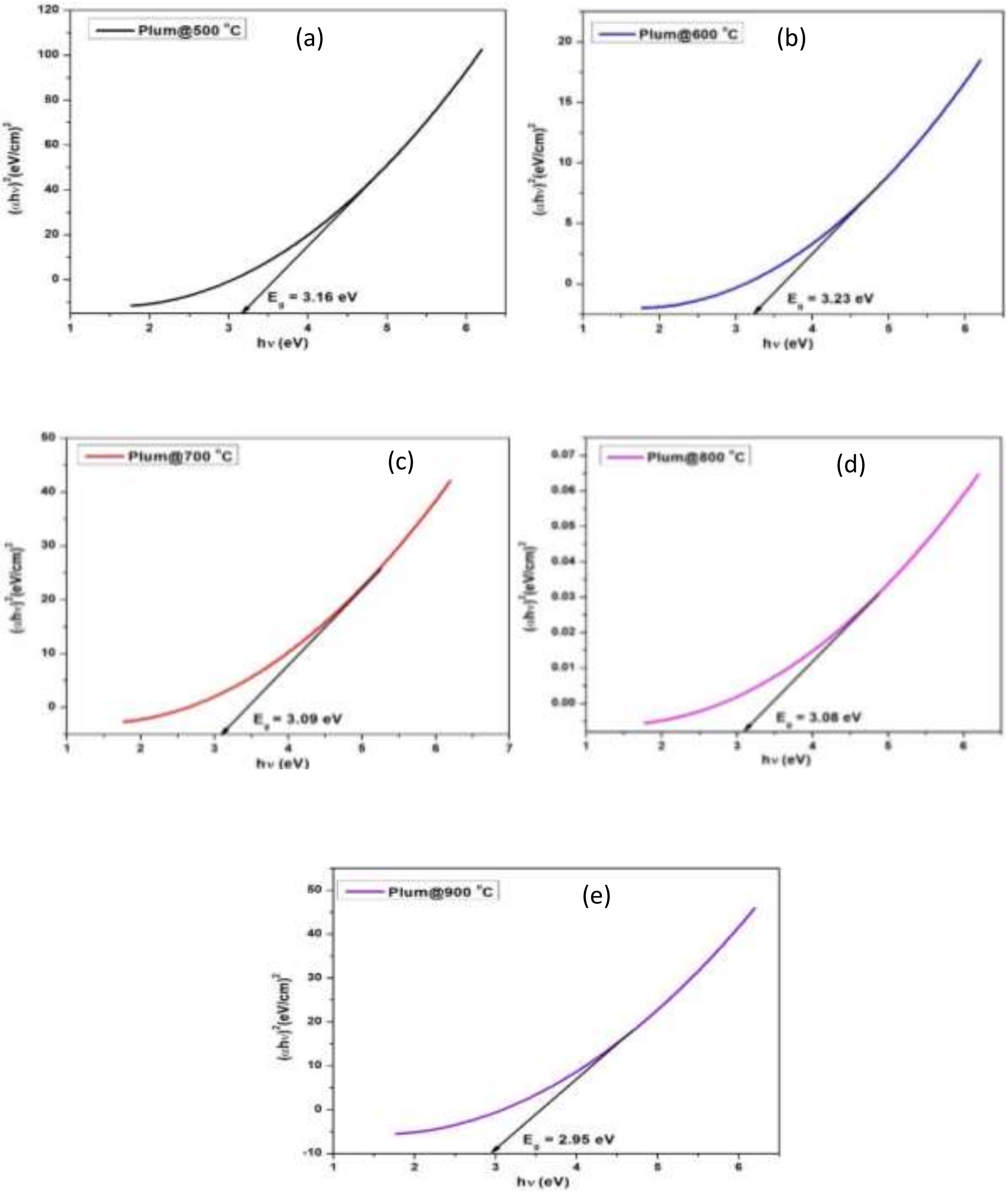

Figure 8(a-e). Energy bandgaps for Plum dye-soaked nanofiber photoanodes

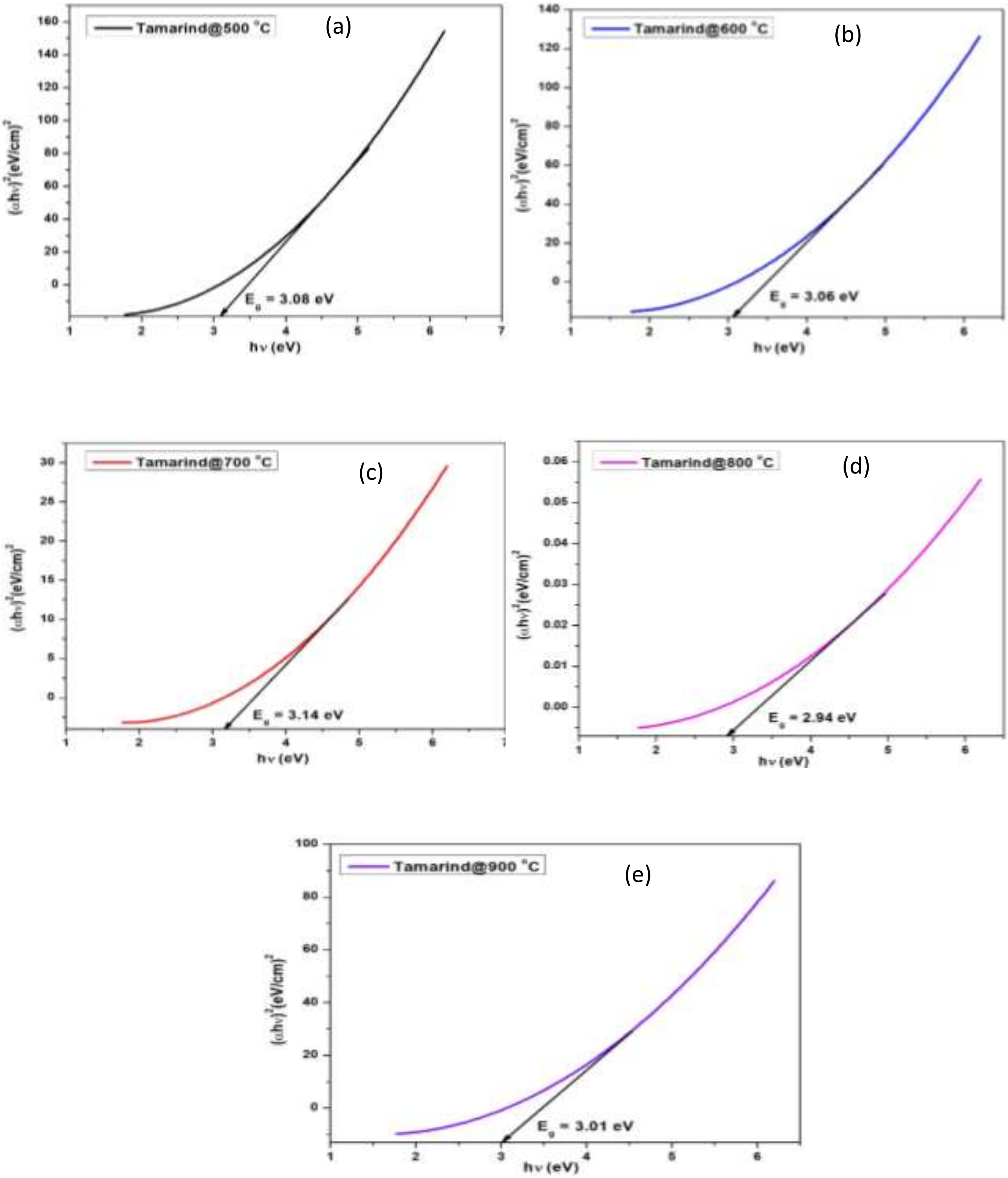

Figure 9(a-e). Energy bandgaps for Tamarind dye-soaked nanofiber photoanodes

Conclusion

Zinc stannate (Zn_2SnO_4) nanofibers exhibited decreasing optical band gap energies with rising temperatures: 3.50 eV at 500 ˚C, 3.20 eV at 600 ˚C, 3.18 eV at 700 ˚C, 3.17 eV at 800 ˚C, and 3.14 eV at 900 ˚C. These values align with optimal zinc stannate band gaps (3.2 - 3.7 eV). Dyes attached to Zn_2SnO_4 fibers showed absorption in the visible region (400 nm to 700 nm). Dye-sensitized solar cells (DSSCs) utilizing four tree bark natural dyes demonstrated solar energy conversion potential. UV-Vis spectroscopy studied the optical properties of dye solutions, revealing that higher dye concentration correlated with increased photon absorption. Four bark dye solutions had band gap energies of 2.05 eV, 2.83 eV, 2.91 eV, and 2.56 eV for ethanol solvents. Testing Zn_2SnO_4 nanofibers before and after dye soaking confirmed their applicability in DSSCs, with the Peacock dye showing particular promise for light absorption and charge-carrier transport. Extracted dyes proved effective, showcasing their potential for environmentally friendly, low-cost applications in light energy harvesting.

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