

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Recent Progress in Nanostructured Zinc Oxide Grown on Fabric for Wearable Thermoelectric Power Generator with UV Shielding

Pandiyarasan Veluswamy, Suhasini Sathiyamoorthy, Hiroya Ikeda, Manikandan Elayaperumal and Malik Maaza

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/intechopen.76672>

Abstract

Traditional materials for thermoelectric such as bismuth telluride have been studied and utilized commercially for the last half century, but recent advancements in materials selection are one of the principal function of the active thermoelectric device as it determines the reliability of the fabrication regarding technical and economic aspects. Recently, many researcher's efforts have been made to utilize oxide nanomaterials for wearable thermoelectric power generator (WTPG) applications which may provide environmental stable, mechanical flexibility, and light weight with low cost of manufacturing. In precise, fabric containing oxide metals have shown great promise as P-/N-type materials with improved transport and UV shielding properties. On the other hand, we have focused on ZnO nanostructures as a high-efficiency WTPG material because they are non-toxic to skin, inexpensive and easy to obtain and possess attractive electronic properties, which means that they are available for clothing with low-cost fabrication. To our observation, we are chaptering about the thermoelectric properties of ZnO and their composite nanostructures coated cotton fabric via the solvothermal method for the first time.

Keywords: ZnO, wearable device, UV shielding, nanocomposites, solvothermal method

1. Introduction

Turning textile fibers into progressively challenging and innovative product have seen manifold development in the last decade. The most promising characteristics of fibers drive the

development of a wide range of fibrous products enabling digital components and electronics to be embedded in them known as smart clothing or smart textiles or smart fabrics. Adopting the new technology of smart fabrics is advantageous since they are relatively lightweight, comfortable, soft, and biodegradable. The move towards function-focus fibrous structures in pavement and embankment reinforcement may seem more appropriate, it implies technological applications such as stain resistance, antimicrobial, superhydrophobic/ superhydrophilic, antistatic, sensors, power generators, electromagnetic/ultraviolet interference shielding, wrinkles resistant, and shrink-proof abilities.

Among modern perspective, the wearable devices used to monitor a variety of health and environmental measures are becoming popular, and those devices requires capable of functioning autonomously for extended periods without replacing or recharge of batteries, but it is not practically impossible or ineffective. Since time immemorial, technology focuses to decrease the power consumption of devices so that the battery lasts for years. It has been done long ago, e.g., in watches. Low power consumption devices are developing gradually and that today offers provide opportunities for yesterday's dreams [1–6].

The main drawbacks are to supply power stable and reliable to commercialize wearable devices, the efforts are being made to explore alternative energy sources for recharging of batteries is performed on a regular or occasional basis using the auxiliary power source of energy harvesting modules such as photovoltaic cells or thermoelectric devices, which are also known as renewable energies. The renewable energy sources, being clean energy sources, noiseless, have an extreme advantage over conventional energy resources from an environmental point of view. The photovoltaic cells are variable power supply, dependent on sunlight, which could lead to an energy shortage if too much of a region's power comes from photovoltaic cells. Therefore, photovoltaic cells fail to provide long-term autonomy sufficient power for portable devices. Fortunately, the thermoelectric devices have attracted much attention due to their ability of direct conversion of heat to electricity. The performance of thermoelectric devices is recycling wasted heat energy, lower production cost, scalability, long-lived power source, no side effects or harm, free from gas emission, easy to dispose and reliable source of energy [7–9] (**Figure 1**).

1.1. Motivation

The body heat from the human is one of the source to harvest energy, which produces electricity from tiny energies in the environment that is called thermoelectric (TE) power generator as shown in **Figure 2**. In this application, the power generator was designed in the form of textile, so-called wearable power generator (WPG). It is also made available in the form of curtain, tent, and umbrellas and therefore, it is useful not only for a daily life applications but for special applications such as natural disaster. TE materials have prominent aspects like reliability, environmental benignity, and easy incorporation into existing technologies. They can be used as long-life power sources and provide a long-lasting solution to the ever-growing demand for implantable medical devices. This increasing demands for lightweight, high flexible, stretchable, and washable presents critical challenges for the progress of WPG.

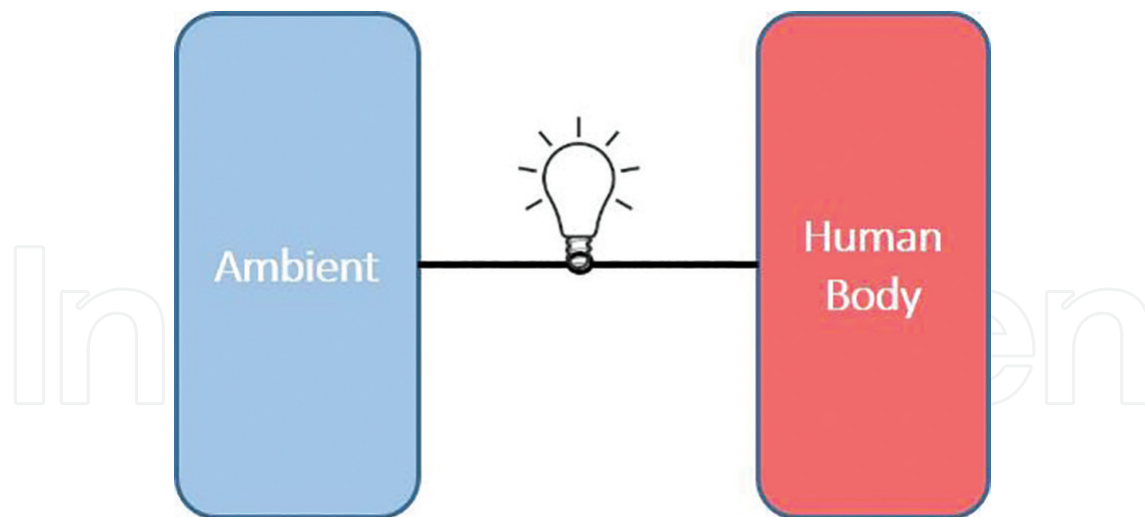


Figure 1. Commercial evolution of wearable thermoelectric devices.



Figure 2. Wearable power generation on human body.

1.2. History of wearable power generators

In 1821, the Thematron's technology developed watches at Centre Electronique Horloger (CEH) in Neuchatel, Switzerland. Basically, three different materials were used antimony, bismuth, and tellurium. The generators composed of two metal sheets: red one on the watch

back side (in contact with the wrist's skin) and a blue one at the top of the case (in contact with ambient air); it is based on "Seebeck effect" principle, which generates a voltage that supplies energy to the quartz caliber. They had very low conversion efficiency, and it could not hold the electrical load, thus the distribution was eventually stopped.

With not much achievement, several efforts followed, when finally, in the year 1988, Seiko developed another thermic watch; which was connected to a lithium-ion battery with a 10 months' power reserve. It has power saving mode, and it stopped when the watch was not being worn on hand to reduce energy consumption and save battery life.

In 2010, Skinny Player was designed by Chinese engineers Chih-Wei Wang and Shou-His Fu; the player with a preloaded album onto it and to listen music you would simply stick the player onto your body; By sticking the player, it would gain power from its flexible battery charging device; it is eco-friendly and sustainable way; major issues with the player is when intended to exercise, the body is hot and usually sweats, however it was stuck on a sweating body for a long time.

A tremendous achievement in the same year by Orange Power Wellies; Boots that converts heat from your feet into electrical power to charge your mobile phone; the battery gets charged by 12 hours of walking but still its remarkable significant that the amount of energy can be harvested from the normal human activity; in order to decrease the charging period we should try more active duties like dancing or running; then the device contains pairs of p-type and n-type semiconductor materials forming a thermopile.

In 2011, the first popular TE mobile developed by Nokia E-Cu designer Patrick Hilandom; the mobile would be able to heat-conductive charging system, being in your pocket and it creating a charger-free mobile phone future; the phone body is made up of copper on which are engraved heat sinks in the form of dried and cracked earth; basically, mobile phone chargers produce 51,000 tons of emission of energy in the environment, in addition to greenhouse gases.

In 2013, Fujifilm has developed the flexible polymer TE conversion module; it can able to generate milliwatt to microwatt power; it would be possible to operate the medium and low-temperature waste heat that surrounds us all in our daily lives; the power is generated by affixing a film substrate coated with organic materials on to a heating source, and the possible power can be generated in the temperature difference ambient and human body temperature of even 1°C.

In 2016, developed by Sam Shames in Embr Labs, Wristify is a heating and cooling bracelet that lets you make yourself comfortable by sending hot or cold pulses to a patch of skin on the wrist; it is more comfortable without changing your core temperature by focusing on the temperature at the skin, and sudden changing of the skin temperature can also notice immediately make you more comfortable.

1.3. Thermoelectric materials

The performance of WPG is essential to develop high-efficient flexible TE materials. Theoretically, the efficiency of TE power generator rises monotonously with increasing dimensionless figure of merit, zT which is given by $zT = (S^2\sigma)/\kappa T$, where S , σ , κ , and T denote the thermopower (Seebeck coefficient), electrical conductivity, thermal conductivity, and temperature

respectively. Henceforth, with the aim of improving the efficiency, an increase in Seebeck coefficient and a decrease in thermal conductivity are required. Traditional materials for TE such as bismuth telluride have been studied and utilized commercially for the last half century, but recent advancements in materials selection are one of the principal function of active TE device as it determines the reliability of the fabrication regarding industrial and economic aspects [10].

1.4. Nanostructuring an efficient approach

As a resolution of this purpose, the nanostructured materials are expected to enhance the Seebeck coefficient because of a carrier confinement effect and to lower the thermal conductivity because of an increase in the boundary scattering in phonon transport. The selection of the material has a significant role in the fabrication of high-performing TE materials. Owing to its flexible nature, conducting polymers (CPs) are favorable materials for the practical TE applications. Because of their high flexibility, environmental stability, and facile synthesis, they have the potential for use on human skin. However, most of the CPs such as polyaniline, polypyrrole, and poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS) are expensive and require complex treatments to achieve good electrical conductivity. Hence efforts have been made to find an alternative for fabricating flexible TE materials and composite materials have recently been attracting more and more attention since they possess many advantages including high thermopower, easy process-ability, and cost-effectiveness. Recently, many researcher's efforts have been made to utilize oxide nanomaterials for WPG applications that may provide environmental stable, mechanical flexibility, and lightweight with low cost of manufacturing [11–13].

1.5. Conflicting wearable power generator

Human skin as one of its charge-collectors, converts muscle movements into enough power for small electronics which requires optimization of a variety of conflicting properties. At the same time, it should enhance the performance of the material and increase the zT for which characteristics such as high electrical conductivity, lower the thermal conductivity and a high thermopower (Seebeck coefficient) are required. The three parameters are strongly interdependent each other to makes the enhancement of zT highly challenging. Sometimes the nanomaterials coated fiber bond is not the strongest, so it wears down and wears off through use and another challenge, which is related conductive fibers is erosion over time. Various techniques have been considered owing to maximum performance in TE materials; a few examples of manipulation are described in the following sections [14–17].

1.5.1. Optimization of power generation on human body

Human body releases the thermal energy of about 2.4 to 4.8 watts, but more can be achieved by placing at different parts of the body. The ideal positions are indicated in **Figure 3**. Similarly, the body heat trapping power may be enhanced by physical activity involved as shown in **Table 1**. Note, however, that energy harvested from the user may require considerable settings in position of the body. Most of the times it provides better expected results [18–22].

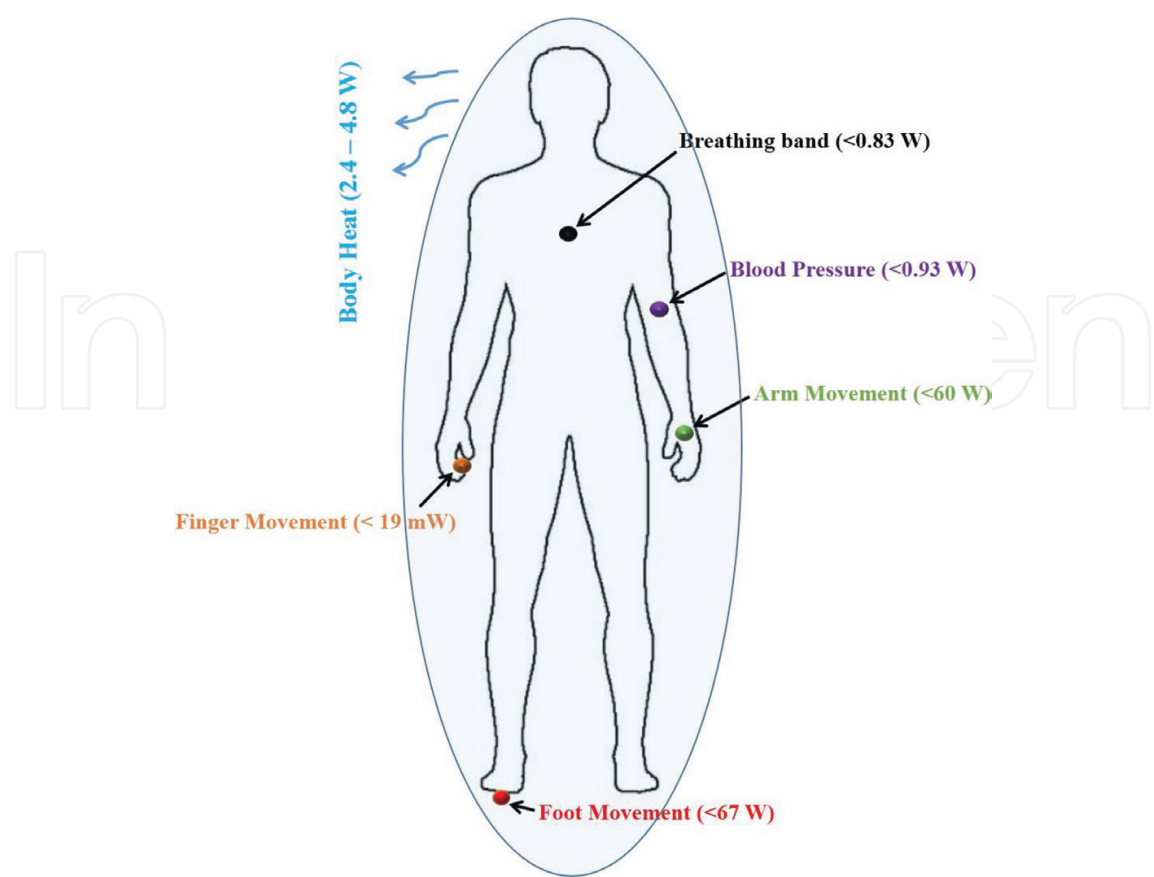


Figure 3. WPG recovery from body in different places.

1.5.2. Optimization of coating techniques

On the other hand, we have focused on ZnO and rGO nanostructure composites as a high-efficiency WPG material because they are non-toxic to skin, inexpensive, available easily and possess attractive electronic properties, making them available for engineered clothing with low-cost fabrication. Up-to-date, several coating methods have been used to grow ZnO and rGO films for tuning its size and morphology, such as sol–gel method, solvothermal synthesis, chemical precipitation, microwave method, sonochemical route, chemical vapor deposition, vapor-phase method, sputtering, and electrochemical. Among these techniques, the solvothermal method is a promising method to synthesize nanostructures with high purity and isometric crystallization. As well as it improves a surface’s strength and durability. Furthermore, a variety of nanostructures such as nanorods, nanoneedles, nanotube, nanosheets, nanoflakes,

Activity	Sleeping	Sitting	Standing	Conversation	Eating	Driving	House keeping	Swimming	Running
Watts	81	93	116	128	128	163	175	582	1048
Kilo cal/ hr	70	80	110	110	110	140	150	500	900

Table 1. Power enhancement by movement of body.

nanodiscs, and nanoflowers can be obtained by solvothermal method. In precise, fabrics containing ZnO and rGO have shown great promise as N-type and P-type materials with improved transport and UV shielding properties [23–26].

1.5.3. Optimization of composites

The thermopower can be enhanced in the presence of chemical composition and crystallinity of thermoelectric materials at nano-inclusion via engineering of multicomponent nanomaterials (nanocomposites), it has proven which can reduce the lattice thermal conductivity by promoting the phonon scattering at grain boundaries and simultaneously it enhances the power factor due to electron filtering at grain boundaries [27–30].

2. Materials fabrication

2.1. Scouring process

Scouring is an important treatment stage of cotton fibers for reducing the amount of impurities such as oils, wax, gums, fatty materials, natural coloring. The absence of impurities produce the fabric more hydrophilic for achieving uniform nanomaterials coating as shown in **Figure 4** before and after scouring process. The complete scouring process as shown below [31];

The development of nanomaterials is closely linked to the following synthesis process.

2.2. Sol-gel synthesis

Sol gel approach began with inorganic ceramic materials at early mid 1800's and especially fabrication of metal oxides. In a typical sol gel reaction process [32], the reactants involve conversion of monomers into a colloidal solution then it reacts as the precursor for an integrated network. The deposition of sol gel solution produces the coatings on the cotton fabric by dipping and followed by heat treatment to form an amorphous or crystalline coatings as shown in **Figure 5** (a – d).

2.3. Microwave approach

Since in 2000, the Microwave-assisted approach is known to transform electromagnetic energy into heat for the ultra-fast synthesis of chemical reactions using microwave irradiation [33]. It has homogeneous, rapid with deep internal heating as resultant produce high yield and lower quantities of side products, purifications of yield are easier, reactions are more reproducible, and the reaction temperature is accurate but it not reproducible with conventional heating. The cotton fibers microwave assisted synthesis has established with producing nanostructures to influence both side distribution of fibers effectively as shown in **Figure 5** (g–h).

2.4. Coprecipitation method

In this process, the desired component is precipitated under the aqueous region to synthesize high purity and crystallinity without significant defects. As the novel method performed at room

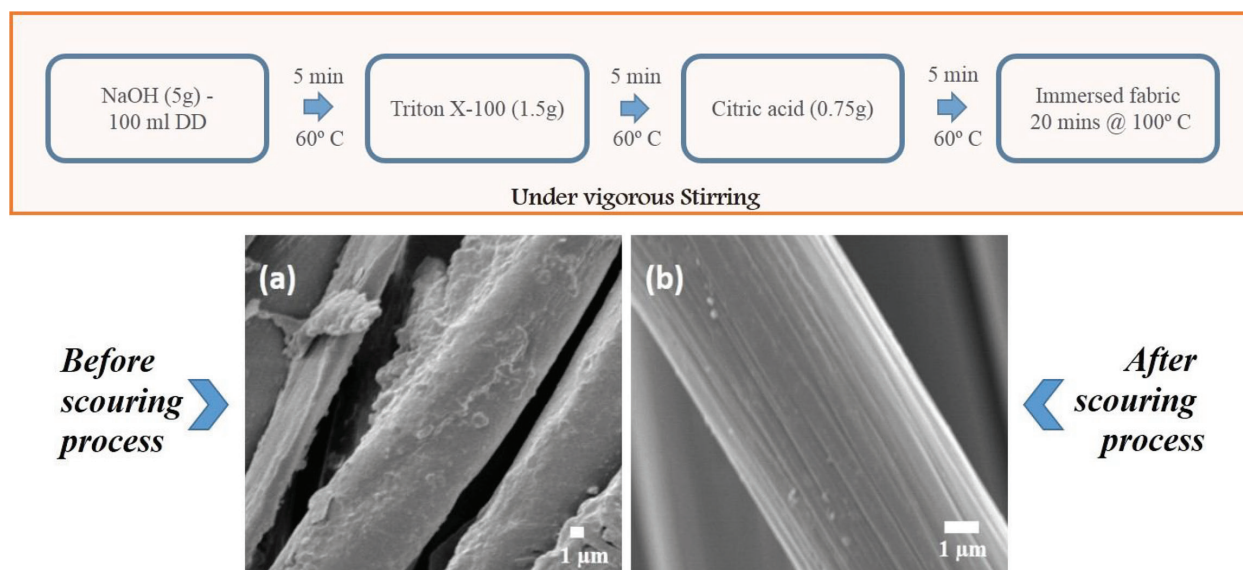


Figure 4. SEM image of cotton fabric (a) before and (b) after of scouring process.

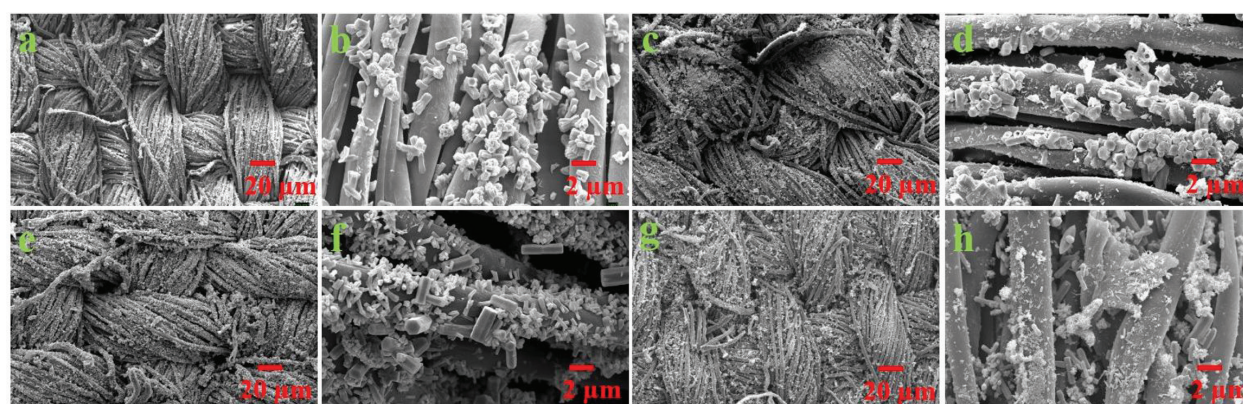


Figure 5. Coating method for cotton fibers (a–d) sol gel approach and (g–h) microwave approach.

temperature and suitable for quantifiable production because of its high yield, excellent repeatability, and low cost. Particularly, the metal hydroxides are precipitated from their precursor element because of low solubility, but the inclusion of alkaline solution can overcome it or raising the pH. For example, **Figure 6** (a–d) shows the coated cotton fabric nanostructures is done by the co-precipitation approach with the addition of amine groups and metal precursors [34].

2.5. Chemical bath deposition

Since from 1933, it was known that for solution growth method, and it adopts the simplest form of the concentrated solution which induces a solid phase to exsolve substrate mounting for thin films. Those yields are stable, adherent, uniform coatings with good reproducibility by a simple process [35]. To grow a denser nanostructure without seed layers are also possible but the precursor species tend to be very dilute within the solution during the deposition process and tailoring of chemical bath deposition is not possible without a clear understanding or control of mechanism. We could observe the coated nanostructures on cotton fiber as shown in **Figure 6** (e – h).

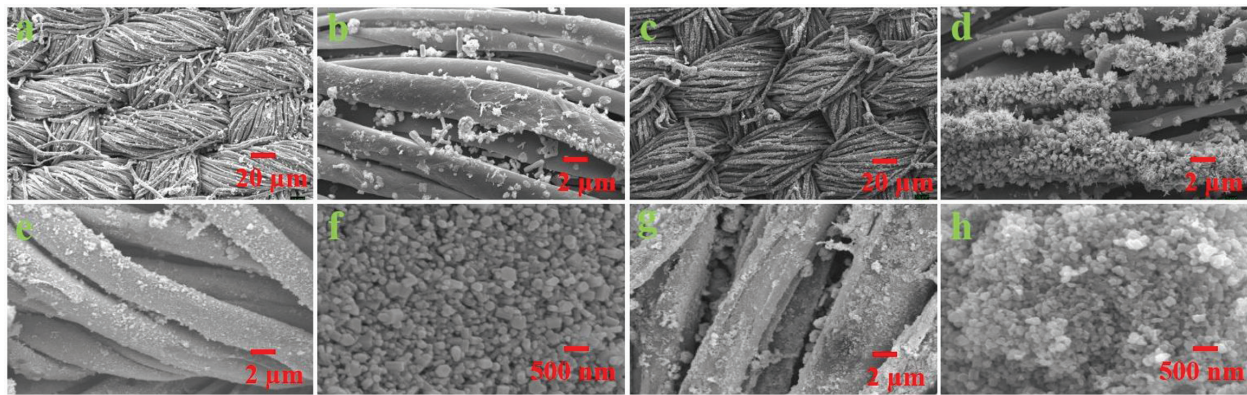


Figure 6. Cotton fabric deposited with nanostructures via (a) co-precipitation method and (b) chemical bath method.

2.6. Sonochemical synthesis

It is the effect of sound wave propagating in forming acoustic cavitation in liquids, resulting high temperature and pressure in a microscopic region of the sonicated process. The most notable effects are consequences of primary and secondary radical reactions it increases chemical activity through the formation of new species [36, 37]. The effects in processes may modification of surface morphology and particle size at high velocity interparticle collisions as shown in **Figure 7** (a–d).

2.7. Hydrothermal synthesis

In principle, hydrothermal technique refers to heterogeneous reactions in aqueous media above 100°C temperature and 1 bar pressure, these resulting powder needs no more high-temperature calcination and thus can avoid the nanoparticles from re-clustering (Oswald repining). The growth of nanomaterials is performed in an apparatus consisting of a steel

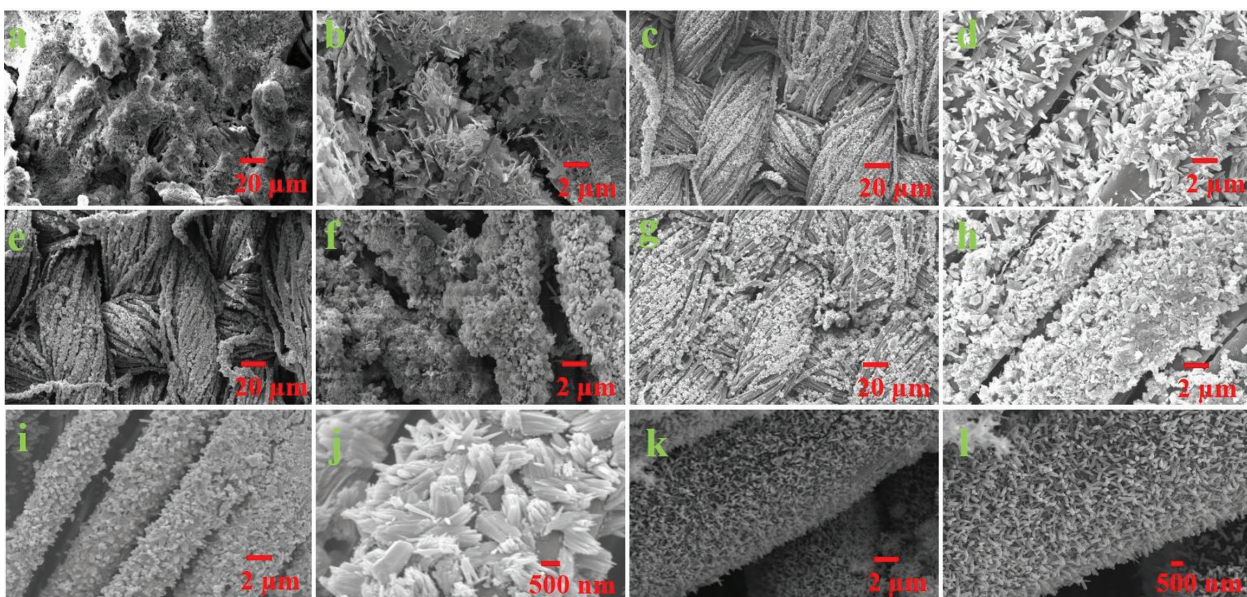


Figure 7. Different techniques involved for coating on cotton fibers (a–d) sonochemical, (e–g) hydrothermal, and (i–l) solvothermal method.

vessel with Teflon container innermost that sustained the pressure. The morphology and size of the nanoparticles could be tuned easily by operating temperature, pressure and time duration. Using hydrothermal synthesis for depositing metal oxide on the cotton fabric [38, 39] was shown in **Figure 7** (e–h).

2.8. Solvothermal synthesis

The phenomena of the solvothermal method are sol gel process followed by the hydrothermal approach, and they have involved two steps process for the crystallization process: crystal nucleation formation by sol gel process and subsequent growth rates by the hydrothermal approach. Particle size and morphology can be controlled by processing variables such as temperature, pH, precursor concentration and additives or surfactants. Thus, solvothermal synthesis allows for precise control over the size, shape distribution and crystallinity of metal oxide nanostructures on cotton fabric [40–43] as shown in **Figure 7** (i–l).

3. Wearable device measurements

3.1. Electrical measurements

A current–voltage (IV) characteristics is a relationship, exemplary representation of graph between the electric current through a material and the corresponding potential difference obtained. In the precise IV measurement, current/ voltage response can be measured while applying voltage/ current to obtain current versus voltage and resistance characteristics and power dissipated or generated can be determined from the IV curve by the resistive element [44–48]. **Figure 8** (a) shows the JASCO, CEP-25BX with which IV_ characteristics were monitored in this study.

3.2. Thermopower measurements

In general, the thermoelectromotive force determined by using probes that are directly connected to the samples, and the temperature difference is measured through thermocouples. Consequently, for a good measurement of thermopower (Seebeck coefficient), it is necessary to measure the thermoelectromotive force and temperature difference instantaneously at the same place, to make sure the probes in excellent thermal and electrical connection with the samples, and to have a high precision measurement device. There are two primary methods used to measure thermopower which is the integral and differential methods. The integral method typically used for analysis with large temperature difference, where one end of the sample is maintained at a constant temperature T_1 while the temperature of other end is varied in the temperature range of interest ($T_2 = T_1 + \Delta T$).

The fitting technique is used to estimate the thermopower on complete measured data set of measured thermoelectromotive force V (T_1 , T_2) as shown in **Figure 8** (b). The integral method succeeds in minimizing the influence of voltage offset. Since the applied temperature difference is large which will produce a large thermoelectromotive force. However, it is hard to maintain the temperature at one end of the sample due to the flow of heat from the high

temperature applied at the other end. Moreover, it is also difficult to obtain the proper fit for evaluating the thermopower from the measured data. In additionally, the differential method can operate from a small temperature difference is applied across the sample and it is maintained at the average temperature ($T = (T_1 + T_2)/\Delta T$). Then the thermopower is evaluated from the linear fit of thermoelectromotive force and temperature difference for several sets of data as shown in **Figure 8** (c). Hence, this evaluation of thermopower is valid for constant thermopower at average temperature. This technique is also effectively eliminating the offset voltages that arise from thermocouples in similarities and no equilibrium contact interfaces. In this study, the thermopower of samples is measured to be constant in the average temperature range, and a schematic representation of experimental setup shown in **Figure 8** (d).

There are two Cu plates were positioned side by side with a gap of ~ 1 mm. The sample for measuring placed across the gap, associate with both plates. A resistive heater was placed underneath the plate, and by controlling the heater current, a temperature difference could be produced in a plane parallel to the sample surface. A couple of probes and two K-type thermocouples were directly connected to the sample surface. The time evolution of the thermoelectromotive force was measured by a nanovoltmeter (Keithley 2182A) and simultaneously with the temperatures at the high- and low-temperature regions by a digital meter (Keithley 2700) equipped with a switching module (Keithley 7700) [49–52].

3.3. Ultraviolet ray shielding measurements

The human body have largest organ is skin, since in the beginning people desired to use sunscreen products to get beautiful and to prevent the skin burns from sun tan, without the risk towards change to burns. Now, it is necessary for all people to use sunscreen products because for the protection against ultraviolet (UV) radiation. The UV radiation is broadly divided into three distinct bands in order of decreasing wavelength and increasing energy. UVA (320–400 nm) has a longer wavelength; it penetrates skin through both the epidermis and dermis, UVB (290–320 nm) has an intermediate wavelength; these rays can be blocked by sunscreen, automobile glass, and windows but UVA is not filtered. UVC (200–290 nm) has a

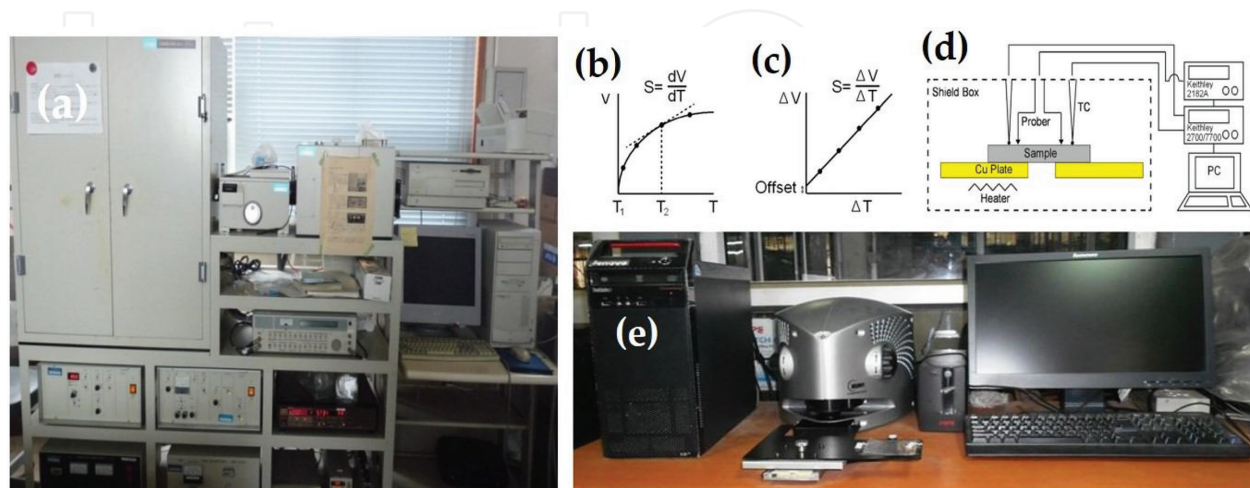


Figure 8. (a) JASCO, CEP-25X, illustration of integral (b) and differential (c) technique for measuring thermopower (Seebeck coefficient), (d) schematic representation of system for measuring the thermopower and (e) UV shielding measurement system.

shorter wavelength; it is effectively filtered by the atmosphere (Ozone layer) and is therefore not a forethought to be a considerable factor. Those imbalances can result in formation of wrinkles, hair loss, rashes, life-threatening cancers, and disorders in immune regulation.

UV protection factor (UPF) applications due to increasing global awareness on green/eco textile products and their market demand. Research has been intensified in the area of development of sustainable UV protective textile using plant extracts and other natural polymeric materials or biocompatible. The Ultraviolet ray shielding measurement was analyzed by UV scattering and absorption spectroscopy by Lapsphere UV1000F as shown in **Figure 8** (e). In the Australia/New Zealand standard AC/NZS 439:1996 method, Eq. (1) is used to determine,

$$UPF = \frac{\int_{290}^{400} E_{\lambda} \times S_{\lambda} \times d\lambda}{\int_{290}^{400} E_{\lambda} \times S_{\lambda} \times T_{\lambda} \times d\lambda} \quad (1)$$

where E_{λ} is the relative erythemal spectrum effectiveness, S_{λ} is the solar UV spectral irradiance, T_{λ} is the spectral transmittance of the specimen (incoming light that passes through the sample) and λ represents the wavelength (nm). Laundering durability of the treated fabric was measured in agreement with AATCC test method 61-2006 [53–55].

4. Fabrication of hierarchical ZnO nanostructures on cotton fabric

Various growth techniques of ZnO have been developed for tuning its size and morphology, such as sol–gel method, solvothermal synthesis, chemical precipitation, microwave method, sonochemical route, chemical vapor deposition, and vapor-phase method [56, 57]. Among these techniques, the solvothermal method is a promising method to synthesize ZnO nanostructures with high purity and isometric ZnO crystallization. Furthermore, a variety of nanostructures such as nanorods, nanoneedles, nanotube, nanosheets, nanoflakes, nanodiscs, and nanoflowers [58–61] can be obtained by solvothermal method. In applying the power generator to the textile, curtain, and so forth, the flexible TE material is required to have three principal functions of the superhydrophobic surface, ultraviolet (UV) shielding and high TE efficiency. Consequently, in this paper, we fabricated ZnO nanostructures on cotton fabric by the solvothermal method and characterized their UV shielding and thermoelectric properties. A facile solvothermal method was adapted to grow the mixed nanostructures like rods and sheets without any surfactant or amine additive. Due to the two-step process, the controlled growth and optimization of the ZnO mixed nanostructures, its functional properties were investigated [62].

In **Figure 9** shown the fabrication process of the ZnO nanostructures coating on cotton fabric by solvothermal method. To obtain the uniform and denser of ZnO coating on the cotton fabric surface, where the glass frame designed and manufactured for the small-scale screening of ZnO seed and growth conditions. The cotton fabric is treated by scouring process to eliminate the wax, fatty and other impurity materials. Pale white color of cotton fabric obtained after scouring process, surface of the fibers is smooth and it increased the surface area due to removal of unwanted materials. Two step process have been involved like seed creation and growth process, the end product apparently found that ZnO nanostructures with high density and high aspect ratios coatings obtained. The morphology images of **Figure 10** (a1 & a2) show high density and

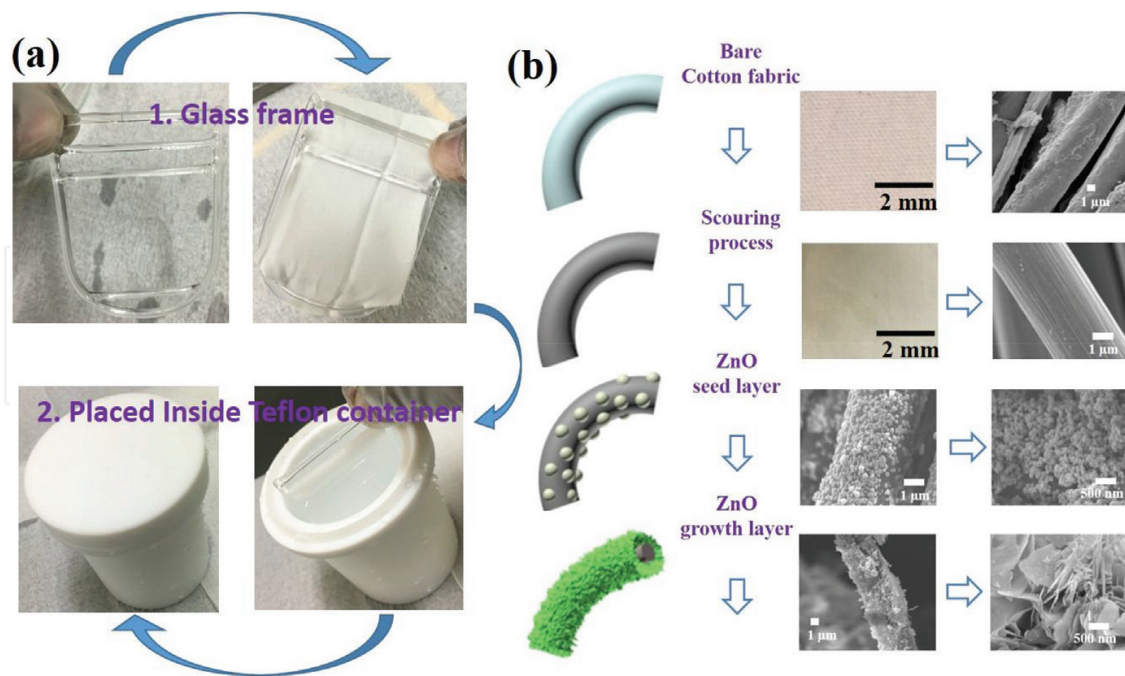


Figure 9. (a) Growth technique (b) fabrication process of ZnO nanostructures coated on cotton fibers.

uniformly aligned nanorods without any preferred orientation, which means ZnO nanorods grow preferably on c-axis direction towards the surface of each fibrous. Thus, the nanorods grew along the [002] direction. The nanosheets are shown **Figure 10** (b1 & b2), which represents the overlapped layer by layer as seen in image. Moreover, thickness of nanosheets is around to be 4 nm. **Figure 10** (c1 & c2) reveals the crumbled nanosheets with shrunk edges on nanorods.

These structural changes happening due to the concentration of zinc nitrate: hexamine as given in **Table 2**. When the growth solution of nanoparticles the OH^- anions and Zn^{2+} cations were released, which leads to the immediate precipitation of $\text{Zn}(\text{OH})_2$ units. Successively ZnO nanostructures were made by the solvothermal of $\text{Zn}(\text{OH})_2$ units at extended reaction temperature and time. In self-assembling of nanoparticles takes place in the growth solution, hexamine act as a capping agent or stabilizer and building block. In the meantime the presence of ZnO seed

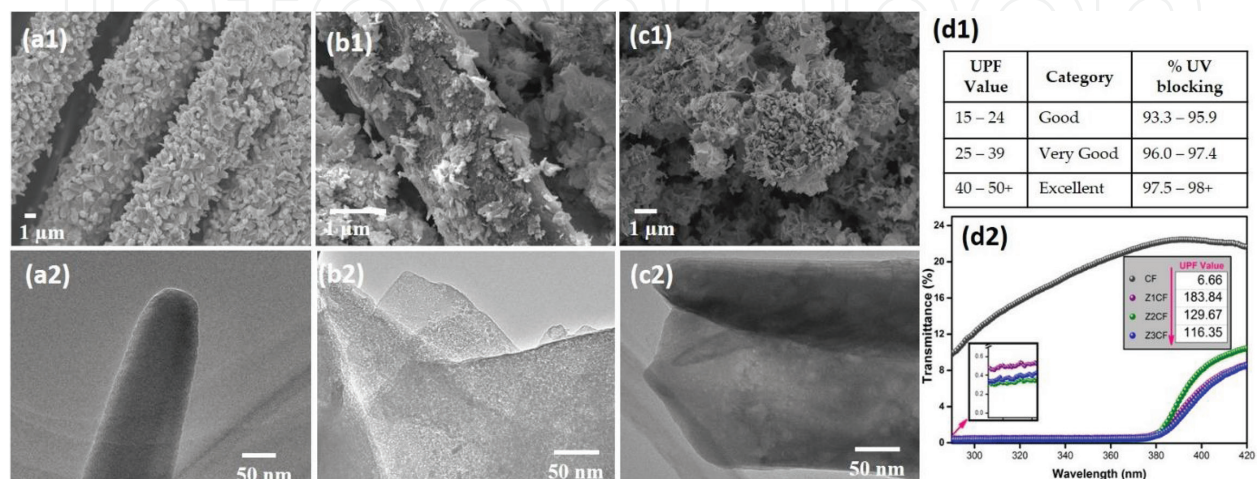


Figure 10. (a–c) morphology image of ZnO growth layer fibers and (d) UV shielding spectra.

S. no	Materials		Nanostructures
1	Zinc nitrate 1 molar	Hexamine 2 molar	Nanorods
2	Zinc nitrate 1 molar	Hexamine 1 molar	Nanosheets
3	Zinc nitrate 2 molar	Hexamine 1 molar	Nanosheets crumpled Nanorods

Table 2. Possible ZnO nanostructures.

Sample	Conduction type	Carrier concentration n (10^{19} cm^{-3})	Resistivity ρ ($\Omega\text{-cm}$)	Mobility μ ($\text{cm}^2/\text{V-s}$)	Seebeck coefficient S ($\mu\text{V/K}$)	Power factor PF ($\mu\text{W/m.K}^2$)
Z1	n	0.05	0.15	81.1	45	13
Z2	n	2.1	0.02	13.7	6	1.4
Z3	n	1.5	0.04	11.5	28	22

Table 3. Thermoelectric properties at room temperature.

layer can minimize the energy barrier and the lattice divergence at heterogeneous nucleation site of the growth layer. When amine group presence of high concentration, it encourages the growth oriented along the c-axis. Whereas if the amine group in equal concentration, c-axis oriented growth direction leads to longitudinal and lateral direction. In other case, subsequent growth formation which would coalescence of crumpled with shrinkage edges of nanosheets surrounded on nanorods. Ultraviolet (UV) ray protection values and description are shown in **Figure 10** (d1). UV transmittance curve of the before and after coating of ZnO on cotton fabric is shown in **Figure 10** (d2). The before coating of ZnO showed 6.66 which is poor protection against UV radiation, but coated nature which is greatly improved the blocking of UV radiation.

Thermoelectric properties at room temperature are shown in **Table 3**, when oxygen vacancy occurs the Seebeck coefficient indicates n-type conduction. The Z1 resistivity and mobility are higher in nanorods compare with Z2 & Z3 nanostructures which is related to the poorer connection between grains. In Z2 as a thin film it reduce electrical resistivity and also the boundary scattering of charge carrier. However Z3, when the nanorods surrounded by nanosheets possess the intergranular electron transport is expected to be easier than nanorod, which explains the lower value of the electric resistivity qualitatively.

5. Incorporation of ZnO and their composite nanostructures on cotton fabric

Material selection has a significant role in the fabrication of high TE performing materials. The conducting polymers are promising to its flexible nature and favorable for the TE applications. However, most of the conducting polymers are expensive and required complex synthesis procedure to achieve high electrical conductivity [63–65]. So the efforts have to be made for finding an alternative for fabricating flexible materials of TE applications and composites have recently been appealing more consideration such as thermopower, easy process ability, cost effective,

and long life span [66–68]. Similar to the previous section here also two step solvothermal method for ZnO and their composite nanostructures on cotton fabric have been employed. The fabrication process of the ZnO nanocomposite coated cotton fabric represented in the **Figure 11**.

As we discussed the amine group concentration in previous session, similarly higher concentration of hexamine longer nanorods are obtained as shown in **Figure 12** (Z1) and when hexamine decreases the nanorods dramatically decreases as shown in **Figure 12** (Z2). However, Sb composite ZnO influences the orientation of nanorods towards the surface of the fibers. **Figure 12** (SZ1 & SZ2), high density Sb/ZnO composite formed on the fiber surface with intertwining into a cluster. **Figure 12** (AZ1 & AZ2) exhibits the absents of nanorods and initiate the 3D network architectures growth of nanosheets assembled with lots of interspaces/ intermesh with each other's [69, 70].

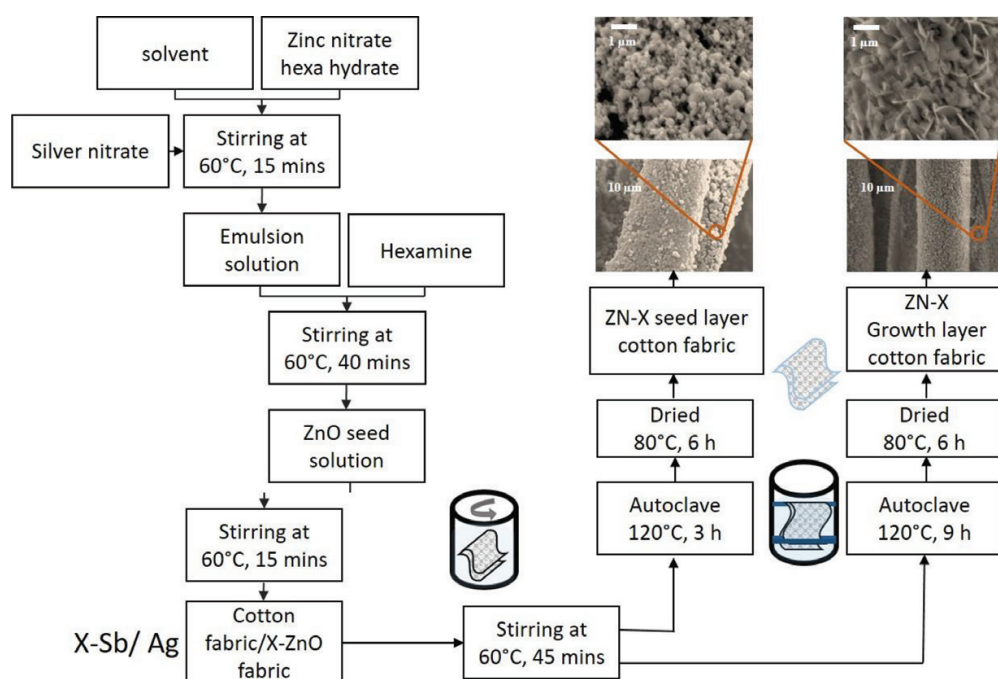


Figure 11. Fabrication process of the nanocomposite coated cotton fabric.

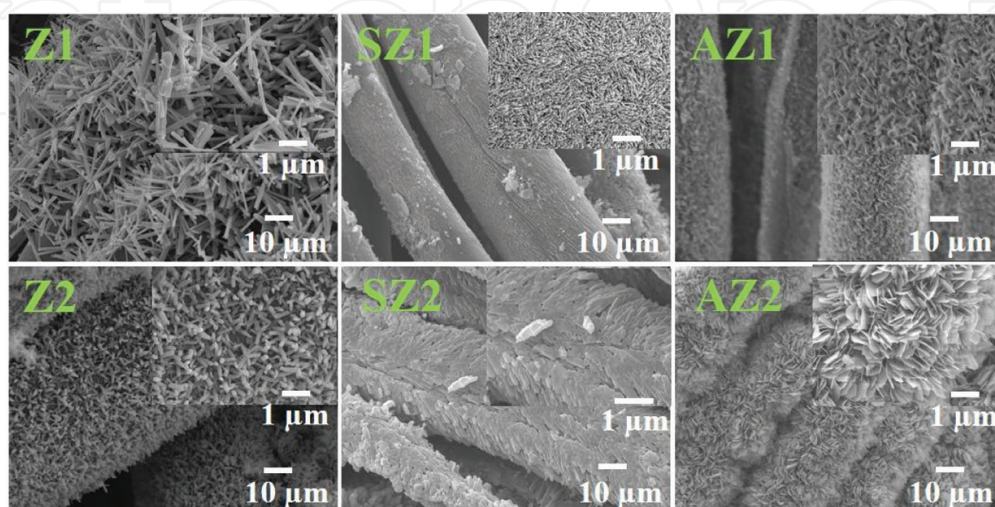


Figure 12. Morphology image of ZnO and its composite growth layer fibers.

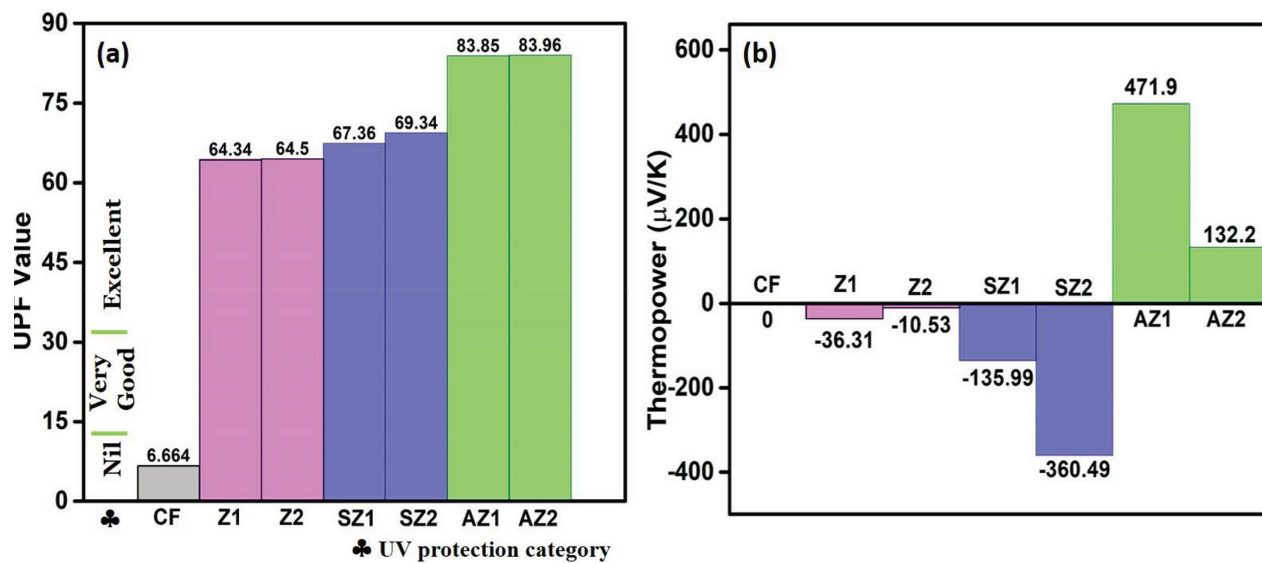


Figure 13. (a) UV shielding effect and (b) Thermopower of before/after coating of cotton fabric.

The UV shielding effect of ZnO and its composite have shown in **Figure 13 (a)**, bare fabric shown poor shielding response of 6.664 and coated of above 64 which means it is excellent for UV shielding performance. **Figure 13 (b)** shows the thermopower of coated cotton fabric. The ZnO coated fabric depict from -36.31 to $-10.53 \mu\text{V/K}$ of longer to shorter nanorods as it higher concentration to low concentration of hexamine. Thus, the longer nanorods have possibility of connect with each other's which contribute the electron transport easier than in the other case. The ZnO growth process disrupted, while the Sb composite introduced growth towards the surface of the fiber although the thermopower increases from -135.99 to $-360.49 \mu\text{V/K}$ due to Sb incorporation into the Zn site. Similarly, when Ag composite led to favor the recombined with Zn material that may cause the positive effect on the charge separation efficiency of 471.9 to $132.2 \mu\text{V/K}$. It plays an important role in charge transport and intergranular crystal structure.

6. Conclusion

In this chapter, we focused on wearable thermoelectric power generator since the performance of the device is recycling wasted heat energy, lower production cost, scalability, long-lived power source, no side effects or harm, free from gas emission, easy to dispose of and reliable source of energy. Herein, we have adopted the solvothermal method for the coating ZnO and its composite with various nanostructures such as nanorods, nanosheets, nanospheres, and nanowalls. The seed creation and growth condition, the concentration of precursors, growth time, have been systematically studied. The as-synthesized fabric sample of functional properties was analyzed by field emission scanning electron microscopy, transmission electron microscopy, UV shielding properties and thermoelectric properties. Besides, two different composite (Sb and Ag) were used to study the efficiency of thermopower.

Author details

Pandiyarasan Veluswamy^{1,2*}, Suhasini Sathiyamoorthy³, Hiroya Ikeda²,
Manikandan Elayaperumal^{4,5} and Malik Maaza⁴

*Address all correspondence to: pandiyarasan@yahoo.co.in

1 Department of Electronics and Communication Engineering, Indian Institute of Information Technology Design and Manufacturing, Chennai, India

2 Research Institute of Electronics, Shizuoka University, Hamamatsu, Japan

3 Department of Electronics and Communication Engineering, SRM University, Chennai, India

4 UNESCO-UNISA Africa Chair in Nanosciences/Nanotechnology Laboratories, College of Graduate Studies University of South Africa (UNISA), Pretoria, South Africa

5 Department of Physics, Thiruvalluvar University College for Arts and Science (TUCAS), Thiruvalluvar University, Vellore, India

References

- [1] Gilsoo C, Seungsin L, Jayoung C. Review and reappraisal of smart clothing. *International Journal of Human-Computer Interaction*. 2009;**25**(6):582-617. DOI: 10.1080/10447310902997744
- [2] Shuhui L, Jianying H, Zhong C, Guoqiang, Yuekun L. A review on special wettability textiles: Theoretical models, fabrication technologies and multifunctional applications. *Journal of Materials Chemistry A*. 2017;**7**:31-55. DOI: 10.1039/c6ta07984a
- [3] Gokulraja TS, Kadarkaraithangam J, Vimal KM, Pandiyarasan V, Ikeda H, Karthikeyan K. Excellent floating and load bearing properties of superhydrophobic ZnO/copper Stearate nanocoating. *Chemical Engineering Journal*. 2017;**320**:468-477. DOI: 10.1016/j.cej.2017.03.052
- [4] Pandiyarasan V, Archana J, Pavithra A, Ashwin V, Navaneethan M, Hayakawa Y, Ikeda H. Hydrothermal growth of reduced graphene oxide on cotton fabric for enhanced ultra-violet protection applications. *Materials Letters*. 2017;**188**:123-126. DOI: 10.1016/j.matlet.2016.11.047
- [5] Sennoga T, Jie Z, Yuying Y, Bo L. A comprehensive review of thermoelectric technology: Materials, applications, modelling and performance improvement. *Renewable and Sustainable Energy Reviews*. 2016;**64**:698-726. DOI: 10.1016/j.rser.2016.07.034
- [6] Zheng XF, Liu CX, Yan YY, Wang Q. A review of thermoelectrics research – Research developments and potentials for sustainable and renewable energy applications. *Renewable and Sustainable Energy Reviews*. 2014;**32**:486-503. DOI: 10.1016/j.rser.2013.12.053

- [7] Weber J, Potje-Kamloth K, Haase F, Detemple P, Volklein F, Doll T. Coin-size coiled-up polymer foil thermoelectric power generator for wearable electronics. *Sensors and Actuators A*, DOI: 10.1016/j.sna.2006.2006;**132**, **04**:325, 054-333
- [8] Francisco S, Amin N, Daryoosh V, Mehmet CO. Designing thermoelectric generators for self-powered wearable electronics. *Energy Environmental Science*. 2016;**9**:2099-2113. DOI: 10.1039/C6EE00456C
- [9] Vladimir L, Ruud JMV. Wearable electronics self-powered by using human body heat: The state of the art and the perspective. *Renewable and Sustainable Energy*. 2009;**1**: 062701. DOI: 10.1063/1.3255465
- [10] Aranguren P, Astrain D, Rodriguez A, Martinez A. Experimental investigation of the applicability of a thermoelectric generator to recover waste heat from a combustion chamber. *Applied Energy*. 2015;**152**:121-130. DOI: 10.1016/j.apenergy.2015.04.077
- [11] Sungmook J, Jongsu L, Taeghwan H, Minbaek L, Dae-Hyeong K. Fabric-based integrated energy devices for wearable activity monitors. *Advance Materials*. 2014;**26**:6329-6334. DOI: 10.1002/adma.201402439
- [12] Veena M, Omer O, Susasn T, David W. Flexible technologies for self-powered wearable health and environmental sensing. *Proceeding of the IEEE*. 2015;**108**:665-681. DOI: 10.1109/JPROC.2015.2412493
- [13] Francioso L, Pascali CD, Farella I, Martucci C, Creti P, Siciliano P, Perrone A. Flexible thermoelectric generator for ambient assisted living wearable biometric sensors. *Journal of Power Sources*. 2011;**196**:3239-3243. DOI: 10.1016/j.jpowsour.2010.11.081
- [14] Wei W, Peining C, Sisi H, Xuemei S, Huisheng P. Smart electronic textiles. *Angewandte Chemie International Edition*. 2016;**55**:6140-6169. DOI: 10.1002/anie.201507333
- [15] Tony V, Courtney H, Joseph R, Nicholas K, Chao H, Pasindu G, David E, Rutvik J, Yanliang Z. High-performance and flexible thermoelectric films by screen printing solution-processed nanoplate crystals. *Scientific Reports*. 2016;**6**:33135. DOI: 10.1038/srep33135
- [16] James D, Henry G, Steven M, Michael M, Shanshan Y, Feiyan L, Eric B, Brinnae B, Bongmook L, Veena M, Young Z, Omer O, Jason S, John M, David P and Alper B: Low power wearable systems for continuous monitoring of environment and health for chronic respiratory disease. *IEEE Journal of Biomedical and Health Informatics*. 2016;**20**:1251-1264. DOI: 10.1109/JBHI.2016.2573286
- [17] Deepa M, Zuoqian W, Paul KW, James WE. Printed flexible thermoelectric generators for use on low levels of waste heat. *Applied Energy*. 2015;**155**:587-592. DOI: 10.1016/j.apenergy.2015.07.066
- [18] Ziyang W, Vlandimir L, Paolo F, Chris VH. Realization of a wearable miniaturized thermoelectric generator for human body applications. *Sensors and Actuators A*. 2009;**156**:95-102. DOI: 10.1016/j.sna.2009.02.028
- [19] Wei H, Gan Z, Xingsing Z, Jie J, Guiqiang L, Xudong Z. Recent development and applications of thermoelectric generator and cooler. *Applied Energy*. 2015;**143**:1-25. DOI: 10.1016/j.apenergy.2014.12.075

- [20] Zhisong L, Huihui Z, Cuiping M, Chang ML. Silk fabric-based wearable thermoelectric generator for energy harvesting from the human body. *Applied Energy*. 2016;**164**:57-63. DOI: 10.1016/j.apenergy.2015.11.038
- [21] Lymberis A, Paradiso R. Smart fabrics and interactive textile enabling wearable personal applications: R & D state of the art and future challenges. *IEEE EMBS Conference*. 2008;**2008**:5270-5273. DOI: 10.1109/IEMBS.2008.4650403
- [22] Seiichi D, Norifumi I, Yusuke I, Shoichiro I, Keisuke S, Muneaki O, Kenji S, Kentaro K. Stack-type thermoelectric power generating module with flexible section and using phase changes of low-boiling-point medium. *Energy Conversion and Management*. 2016;**127**:103-111. DOI: 10.1016/j.enconman.2016.08.040
- [23] Robert JS, Steven JW, Karuna SK. Theoretical limits of thermoelectric power generation from exhaust gases. *Applied Energy*. 2014;**133**:80-88. DOI: 10.1016/j.apenergy.2014.07.075
- [24] Patyk A. Thermoelectric generators for efficiency improvement of power generation by motor generators – Environmental and economic perspectives. *Applied Energy*. 2013;**102**:1448-1457. DOI: 10.1016/j.apenergy.2012.09.007
- [25] Minijeong H, Jonghwa P, Youngoh L, Hyunhyub K. Triboelectric generators and sensors for self-powered wearable electronics. *ACS Nano*. 2015;**9**:3421-3427. DOI: 10.1021/acsnano.5b01478
- [26] Tongcai W, Weiling L, Wei W, Shan-Tung T. Waste heat recovery through plate heat exchanger based thermoelectric generator system. *Applied Energy*. 2014;**136**:860-865. DOI: 10.1016/j.apenergy.2014.07.083
- [27] Chaoxing W, Tae Whan K, Fushan L, Tailiang G. Wearable electricity generators fabricated utilizing transparent electronic textiles based on polyester/Ag Nanowires/Graphene core-shell nanocomposites. *ACS Nano*. 2016;**10**:6449-6457. DOI: 10.1021/acsnano.5b08137
- [28] Matteo S, Alessandro C. Wearable electronics and smart textiles: A critical review. *Sensors*. 2014;**14**:11957-11992. DOI: 10.3390/s140711957
- [29] Franciso SP, Eduardo M, Manuel FM, Eduardo PT. Growth of vertically aligned ZnO nanorods using textured ZnO films. *Nanoscale Research Letters*. 2011;**6**:524. DOI: 10.1186/1556-276X-6-524
- [30] Pandiyarasan V, Suhasini S, Kalari HC, Omprakash M, Karthikeyan K, Tsunehiro T, Ikeda H. Morphology dependent thermal conductivity of ZnO nanostructures prepared via a green approach. *Journal of Alloys and Compounds*. 2017;**695**:888-894. DOI: 10.1016/j.jallcom.2016.10.196
- [31] Awais K, Mazhar HP, Muhammad M, Max W. A review on developments in dyeing cotton fabrics with reactive dyes for reducing effluent pollution. *Journal of Cleaner Production*. 2015;**87**:50-57. DOI: 10.1016/j.jclepro.2014.09.017
- [32] Manikandan E, Murugan V, Kavitha G, Babu P, Maaza M. Nanoflower rod wire-like structures of dual metal (Al and Cr) doped ZnO thin films: Structural, optical, and electronics properties. *Materials Letters*. 2014;**131**:225-228. DOI: 10.1016/j.matlet.2014.06.008

- [33] Ying J and Feng C. Microwave-assisted preparation of inorganic nanostructures in liquid phase. *ACS Chemical Reviews*. 2014;**114**:6462-6555. DOI: 10.1021/cr400366s
- [34] Kolthoff IM . Theory of coprecipitation. The formation and properties of crystalline precipitates. *Journal of Physical Chemistry*. 1932;**36**:860-881. DOI: 10.1021/j150333a008
- [35] Ngom BD, Mpahane T, Manikandan E, Maaza M. ZnO nano-disc by lyophilization process: Size effects on their intrinsic luminescence. *Journal of Alloys and Compounds*. 2016;**656**:758-763. DOI: 10.1016/j.jallcom.2015.09.230
- [36] Tina H, Majid M. A review on textile sonoprocessing: A special focus on sonosynthesis of nanomaterials on textile substrates. *Ultrasonic Sonochemistry*. 2015;**23**:1-10. DOI: 10.1016/j.ultsonch.2014.08.022
- [37] Hangxun X, Brad WZ, Kenneth SS. Sonochemical synthesis of nanomaterials. *RSC Chemical Society Reviews*. 2013;**42**:2555-2567. DOI: 10.1039/C2CS35282F
- [38] Kaviyarasu K, Manikandan E, Kennedy J, Maaza M. A comparative study on the morphological features of highly ordered MgO: AgO nanocube arrays prepared via a hydrothermal method. *RSC Advances*. 2015;**5**:82421-82428. DOI: 10.1039/C5RA15132E
- [39] Oliver SH, Karen JE, Daniel TB, Laura TM. Deep eutectic-solvothermal synthesis of nanostructures ceria. *Nature Communications* 2017:14150. DOI: 10.1038/ncomms14150
- [40] Kaviyarasu K, Fuku X, Mola GT, Manikandan E, Kennedy J, Maaza M. Photoluminescence of well-aligned ZnO doped CeO₂ nanoplatelets by a solvothermal route. *Materials Letters*. 2016;**183**:351-354. DOI: 10.1016/j.matlet.2016.07.143
- [41] Drik E, Hideto S, Yuji K, Hiroki S, Akira Y, Tsuguo F. Solvothermal growth of ZnO. *Progress in Crystal Growth and Characterization of Materials*. 2006;**52**:280-335. DOI: 10.1016/j.pcrysgrow.2006.09.002
- [42] Kaviyarasu K, Manikandan E, Kennedy J, Jeyachandran M, Maaza M. Rice husks as a sustainable source of high quality nanostructured silica for high performance Li-ion battery requital by sol-gel method- A review. *Advanced Materials Letters*. 2016;**7**(6):100-150. DOI:10.5185/amlett.2016.6059
- [43] Pimente A, Rodrigues J, Duarte P, Nunes D, Costa FM, Monterio T, Martins R, Fortunato E. Effect of solvents on ZnO nanostructures synthesized by solvothermal method assisted by microwave radiation: A photocatalytic study. *Journal of Materials Science*. 2015;**50**:5777-5787. DOI: 10.1007/s10853-015-9125-7
- [44] Mohana PS, Geetha A, Ramamurthi K, Pandiyarasan V, Ikeda H. Effect of pH and annealing temperature on the properties of tin oxide nanoparticles prepared by sol-gel method. *Journal of Materials Science: Materials Electronics*. 2018;**29**:658-666. DOI: 10.1007/s10854-017-7959-2
- [45] Saravanan L, Manivel RM, Prabhu D, Pandiyarasan V, Ikeda H, Therese HA. Perpendicular magnetic anisotropy in mo/Co₂FeAl_{0.5}/Si_{0.5}/MgO/mo multilayers with optimal Mo buffer layer thickness. *Journal of Magnetism and Magnetic Materials*. 2018;**454**:267-273. DOI: 10.1016/j.jmmm.2018.01.097

- [46] Merina PD, Jeyanthi RL, Pandiyarasan V, Das J. Exploration of Wedelia chinensis leafassisted silver nanoparticles for antioxidant, antibacterial and in vitro cytotoxic applications. *J. Journal of Food and Drug Analysis*. 2018;**26**:917-925. DOI: 10.1016/j.jfda.2017.07.014
- [47] Kennedy J, Murmu PP, Manikandan E, Lee SY. Investigation of structural and photoluminescence properties of gas and metal ions doped zinc oxide single crystals. *Journal of Alloys and Compounds*. 2014;**616**:614-617. DOI: 10.1016/j.jallcom.2014.07.179
- [48] Miller PH. The electrical conductivity of zinc oxide. *APS Physical Review Letters*. 1941;**60**:890. DOI: 10.1103/PhysRev.60.890
- [49] Hahn EE. Some electrical properties of zinc oxide semiconductor. *AIP Journal of Applied Physics*. 1951;**22**:855. DOI: 10.1063/1.1700063
- [50] Boor JD, Muller E. Data analysis for Seebeck coefficient measurements. *Review of Scientific Instruments*. 2013;**84**:065102. DOI: 10.1063/1.4807697
- [51] Andres S, Maria A, Shahed R, Gabriel C, Miguel AT, Torres JC. Diez: A thermoelectric by any other name... *Materials today*. 2012;**15**:P415. DOI: 10.1016/S1369-7021(12)70178-5
- [52] Zhi-Gang C, Guang H, Lei Y, Lina C, Jia Z. Nanostructured thermoelectric materials: Current research and future challenge. *Progress in Natural Science: Materials International*. 2012;**22**:535-549. DOI: 10.1016/j.pnsc.2012.11.011
- [53] Khan F, Pandiyarasan V, Sakamoto S, Navaneethan M, Shimomura M, Murakami K, Hayakawa Y, Ikeda H. Seebeck Coefficient of Flexible Carbon Fabric for Wearable Thermoelectric Device. *IEICE Transaction on Electronics*. 2018;**101**(5):343-346. DOI: 10.1587/transele.E101.C.343
- [54] Xue, Yin W, Jia ST, Ma JZ. UV-durable superhydrophobic textiles with UV-shielding properties by coating fibers with ZnO/SiO₂ core/ shell particles. *IOP Nanotechnology*. 2011;**41**:415603. DOI: :10.1088/0957-4484/22/41/415603
- [55] Omer KA, Tao Z. Review on : Developing UV protection for cotton fabric. *The Journal of the Textile Institute*. 2015;**11**:1-13. DOI: 10.1080/00405000.2017.1311201
- [56] Wang L, Zhang X, Li B, Sub P, Yang J, Xu H, Liu Y. Superhydrophobic and ultraviolet-blocking cotton textiles. *ACS Applied Materials and Interfaces*. 2011;**3**(4):1277-1281. DOI: 10.1021/am200083z
- [57] Sandeep KL, Hafeez YH, Pandiyarasan V, Ganesh V, Anish K, Ikeda H, Neppolian B. Enhanced Photocatalytic degradation and hydrogen production activity of in situ grown TiO₂ coupled NiTiO₃ Nanocomposites. *Journal of Applied Surface Science*. 2018;**449**: 790-798. DOI: 10.1016/j.apsusc.2018.02.136
- [58] Shanthi S, Poovaragan S, Arularasu MV, Nithya S, Sundaram R, Magdalane CM, Kaviyarasu K, Maaza M. Optical, magnetic and photocatalytic activity studies of Li, mg, Sr doped and undoped zinc oxide nanoparticles. *Journal of Nanoscience and Nanotechnology*. 2018;**18**:5441-5447. DOI: 10.1166/jnn. 2018.15442

- [59] Rai P, Kwak WK, Yu YT. Solvothermal synthesis of ZnO nanostructures and their morphology-dependent gas-sensing properties. *ACS Applied Materials Interfaces*. 2013;**5**:3026-3032. DOI: 10.1021/am302811h
- [60] Ayudhya SKN, Tonto P, Okorn M, Pavarajam P, Praserthdam P. Solvothermal synthesis of ZnO with various aspect ratios using organic solvents. *Crystal Growth. Designs*. 2006;**6**:2446-2450. DOI: 10.1021/cg050345z
- [61] Matinise N, Fuku XG, Kaviyarasu K, Mayedwa N, Maaza M. ZnO nanoparticles via *Moringa oleifera* green synthesis: Physical properties & mechanism of formation. *Journal of Applied Surface Science*. 2017;**406**:339-347. DOI: 10.1016/j.apsusc.2017.01.219
- [62] Pandiyarasan V, Suhasini S, Archana J, Navaneethan M, Majumdar A, Hayakawa Y, Ikeda H. Fabrication of hierarchical ZnO nanostructures on cotton fabric for wearable device applications. *Applied Surface Science*. 2017;**418**:352-361. DOI: 10.1016/j.apsusc.2016.12.202
- [63] Suhasini S, Greeshma G, Prashanth K, Kathirvel V, Saranya TS, Pandiyarasan V, Karolien DW, Ikeda H. Tailoring the functional properties of polyurethane foam with dispersions of carbon nanofiber for power generator applications. *Journal of Applied Surface Science*. 2018;**449**:507-513 DOI: <https://doi.org/10.1016/j.apsusc.2018.01.088>
- [64] Pandiyarasan V, Suhasini S, Faizan K, Aranya G, Majumdar A, Hayakawa Y, Ikeda H. Incorporation of ZnO and their composite nanostructured material into a cotton fabric platform for wearable device applications. *Journal of Carbohydrate Polymers*. 2017;**157**:1801-1808. DOI: 10.1016/j.carbpol.2016.11.065
- [65] Ming H, Feng Q, Zhiqun L. Towards high-performance polymer-based thermoelectric materials. *Energy & Environmental Science*. 2013;**6**:1352-1361. DOI: 10.1039/C3EE24193A
- [66] Mario C, Clara MG, Andres C. Review on polymers for thermoelectric applications. *Materials*. 2014;**7**:6701-6732. DOI: 10.3390/ma7096701
- [67] Mariappan P, Karthikeyan K, Jeyasubramanian K, Govindasamy M. Selective toxicity of ZnO Nanoparticles toward gram-positive bacteria and cancer cells by apoptosis through lipid peroxidation. *Nanomedicine: Nanotechnology Biology, and Medicine*. 2011;**7**:184-192. DOI: 10.1016/j.nano.2010.10.001
- [68] Junjie L, Xinfeng T, Han L, Yonggao Y, Qingjie Z. Synthesis and thermoelectric properties of hydrochloric acid-doped polyaniline. *Synthetic Metals*. 2010;**160**:1153-1158. DOI: 10.1016/j.synthmet.2010.03.001
- [69] Jiansheng W, Yimeng S, Wen-Bo P, Ling H, Wei X, Qichun Z. Self-assembled free-standing polypyrrole nanotube membrane as an efficient FTO- and Pt-free counter electrode for dye-sensitized solar cells. *ACS Applied Materials Interfaces*. 2014;**196**:173-177. DOI: 10.1021/am404265q
- [70] Olga B, Zia UK, Abdellah M, Slawomir B, Mats F, Magnus B, Xavier C. Optimization of the thermoelectric figure of merit in the conducting polymer poly(3,4-ethylenedioxythiophene). *Nature Materials*. 2011;**10**:429-433. DOI: 10.1038/nmat3012