Nanostructured oxide semiconductors grown on fabric for wearable thermoelectric power generator with UV shielding

学 位 論 文 要 約

Summary of Doctoral Thesis

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Summary：

Clothing and textile materials are the elements that are almost always present and is customizable to each human being. In the last few years, the smart textiles feature such as stain resistance, antimicrobial, superhydrophobic/ super-hydrophilic, antistatic, sensors, power generators, electromagnetic/ ultraviolet interference shielding, wrinkles resistant, and shrink-proof abilities. Since the energy and environmental efficiency governance are becoming the demand, there is a need for alternate renewable energy conversion system that will reduce the greenhouse gases emission and improve the energy competence.

The eco-friendly renewable energy source for smart textile from various environmental origin such as photovoltaic (PV) utilizing the light source, thermoelectric (TE) employs temperature difference, piezoelectric (PE) proving kinetic energy from vibrations or shocks and radio frequency (RF) energy were accepting moving waves of electric and magnetic together. The ability of harvest energy from ambient sources enables the lifetime of battery-operated for wearable devices. The human body is a constant heat source, and typically a temperature difference exists between body skin and the environment. Even in a scenario where the wearer located in a dark

room or stationary or presence in air condition room, energy can be produced. Because the thermoelectric generates electrical power from heat flow across a temperature gradient, and it is based on the solid-state technology with the principle of Seebeck effect. As the heat flows from hot to cold, free charge carriers (electrons and holes) in the material are driven, and the resultant voltages. Similarly, depending on power generator size, place, and activity of human body is suitable for harvesting energy in the range of microwatts to hundreds of milliwatts.

The performance of wearable thermoelectric power generator (WTPG) material is closely related to the dimensionless figure-of-merit (zT), $zT=[(S2\sigma)/\kappa]$ T, where S represents as thermopower (Seebeck coefficient), σ represent as electrical conductivity, κ represent as thermal conductivity, and T is the temperature respectively. Since the advent of nanostructured power generation materials exhibits high zT owing to the maximization of power factor (S2σ) and reduction in κ. Throughout the literature, the nanometer-scaled crystalline structure can reduce κ by enhancing the boundary scattering of phonons, but it degrades the power factor, simultaneously. With the aim of bettering the power factor, an increment of thermopower is expected by tailoring the density of states through nano-structuration such as nanocomposites and superlattices and doping modulation.

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. 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 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.

In chapter 1, For high-efficient wearable power generator, we have investigated the ZnO nanostructures grown on cotton fabric (CF) as a novel flexible TE material. ZnO is inexpensive, easy fabrication, and available for textile due to non-toxicity for skin. 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. 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 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.

ZnO nanostructure has formed on the scoured CF by a two-step growth method consisting of a seed creation process followed by a nanostructure growth process. A typical solvothermal seeding process was as follows; 1 M of zinc nitrate hexahydrate was dissolved in 40 mL of deionized water under stirring. 2 M of hexamethylenetetramine was dissolved in 40 mL of deionized water, and this solution is added to the zinc nitrate hexahydrate solution to form ZnO. The similar experimental conditions were adopted for the molar ratio of zinc nitrate hexahydrate and hexamethylenetetramine from 1:1 to 2:1. The CF was immersed into ZnO solution for 1 h, and then it was ultrasonicated for 30 min. The mixture solution was transferred to the autoclave with the inner volume of 100 mL (TEFLON, F-1029-06) and the solvothermal seeding was carried out at 120 °C for 3 h. ZnO-seed-coated CF was collected and washed with distilled water to remove the excess reactants. Finally, the ZnO-seed-coated CF was placed in hot air oven at 50 °C for 1 h.

At the second step or solvothermal growth of ZnO nanostructure, 80 mL of deionized water contained 1 M of zinc nitrate hexahydrate and 2 M of hexamethylenetetramine. The mixed solution was transferred into the autoclave, and the solvothermal growth was carried out at 120 °C for 9 h. The autoclave could cool to the room temperature; then the fabric was taken out from the solution and rinsed with deionized water three times. Then, it was rinsed with ethanol thrice. Finally, the product was dried at 50 °C for 1 h. The similar growth process was adopted for the series of experiments with molar ratio of zinc nitrate hexahydrate and hexamethylenetetramine 1:2, 1:1, 2:1 and after this, they are termed as Z1CF (1:2), Z2CF (1:1) and Z3CF (2:1), respectively.

Conclusion on this chapter, the solvothermal method was employed to grow ZnO nanostructures on the surface of cotton fabric. The extraordinary enhancement of UV shielding efficiency of the modified fabric was obtained. The UPF value of the fabric with ZnO composite nanostructure was 183.84 which was 25 times higher than that of bare cotton fabric. The reasonable well dispersion condition of ZnO denser contributed to exceptional UV blocking. The PF of the coated fabric made by the ZnO composite nanostructure (nanorods and nanosheets) was 22 μW/m.k2, which was much larger than that of the nanosheets or nanorods. Considering that, the enhanced performance of ZnO composite nanostructure is due to the excellent grain connectivity and superior crystallinity of the sample.

In chapter 2, nanocomposites consisting of homogeneous and uniform dispersion of nanoparticles in the polymer matrix lead to higher TE properties. Moreover, polymers having crystalline with amorphous structure or polymers with nanoparticle interfaces create boundaries that scatter phonons, thus ensuring low thermal conductivity. The selection criteria of antimony (Sb) based on the following properties; it is electrical and thermal conductivity are lower than most metals conductivities, N type dopant for semiconductor industry, best thermoelectric materials at room temperature, due to existence of minimum in lattice thermal conductivity [25]. Similarly, for silver it has semiconductor intermetallic compounds which will have unexpectedly low thermal conductivity which leads to improved thermoelectric properties, P type dopant for semiconductor industry, it is stable in air with highest electrical conductivity. There are no available reports, which describe the influence of Sb-/Ag- ZnO-composite on cotton fabric using the solvothermal method for application on WPG [26]. The interaction of Sb-/Ag- ZnO with textile material would make major difference in thermopower. In this study, we modified cotton fabric with Sb-/Ag- ZnO-composite by in situ solvothermal growth technique at low temperature to develop flexible n-type and p-type TE material. In the present work, ZnO and its composites were prepared by solvothermal methods and its structural, morphological, electrical and thermoelectric properties were studied.

Conclusion on this chapter; In this study, a simple, versatile, and effective approach for the development of ZnO/ Sb-/ Ag-/ ZnO-composite on cotton fabric prepared by solvothermal method was described. It was demonstrated that the coating of ZnO/ Sb-/ Ag-/ ZnO-composite can convert an insulator, a cotton fabric into a conductive fabric. The existence of nanostructures on the fabric surface caused an excellent UV shielding property in the Ag-ZnO-Composite fabric, as was demonstrated by an UPF value of 83.96. Additionally, the coated fabric showed good I – V characteristics with rectifying behavior of conductivity. Furthermore, we have investigated the thermopower of the coated fabric, which attributes to the intergranular crystal structure of Ag-ZnO composite, possessing the highest value of 471.9

μ/K. It is concluded that the nanocomposites, having a higher thermopower and UV shielding, is a better candidate for wearable device applications.

In chapter 3, among various energy harvesting techniques, the thermoelectric has been proven able to harvest energy from human body at a high efficiency and large output power density. Comparing with other energy harvesting approach, the thermoelectric energy is nearly independent to the weather and working environment. Moreover, it is facile to be designed into fabric due to its simple structure and huge materials choices. In this work, rGO-deposited cotton fabric is synthesized by a new non-toxic method and the functional properties are studied.

Conclusion, the rGO deposited cotton fabric was successfully prepared by hydrothermal method. XRD and Raman spectrum confirmed the presence of rGO on the surface of the cotton fabric. The FESEM images indicated that the rGO-deposited cotton fiber had wrinkle-like wave structure. The UPF values of bare cotton and rGO deposited cotton fabric before and after laundering process were calculated as 7.83, 442.69 and 442.32, respectively. It is confirmed that the prepared material showed the excellent UV shielding property and good durability. The calculated Seebeck coefficient obtained from the linear approximation and larger value obtained.

In chapter 4, a facile sonochemical assisted hydrothermal growth of hierarchical ZnO nanostructures on carbon fabric demonstrated. Zinc nitrate hexahydrate and hexamine (HMT) were used as zinc source and the alkali source respectively. In the momentous morphological changes were obtained by tuning the zinc precursor concentration. When the zinc concentration increased, the ZnO nanorods/sheets became denser, and growth period indicated the morphological changes from rods to sheets nanostructure arrays under same growth temperature. Therefore, it is imperative to explore the new approach for the synthesis of ZnO nanostructures; well it works out to be an easier and economical process.

Conclusion, In this chapter, we have designed unique binder-free array-type

ZnO nanostructures grown directly on carbon fabric obtained by sonochemical assisted hydrothermal method. This approach allows ZnO nanostructures to grow effectively on carbon fabric in the absence of a template, catalyst or even a surfactant to inhibit growth and this method seems to be fast with reproducibility. With prolonged growth period, morphology changes from nanorods to nanosheets were observed. The FESEM images also confirm a significant difference in the morphology of the fabric before and after ZnO coating. EDX Mapping, XRD, XPS analyses were showed that there is a linear relationship between the coated layers of ZnO content and bare fabric. The UV protection value obtained by UV transmittance indicated excellent protective value for ZnO coated carbon fabric owing to their absorption. An enhancement of the thermopower was observed with ZnO coating due to the change in carrier concentration. This phenomenon is believed to be related with the formation of ZnO nanostructures on carbon fabric.

In chapter 5, Summary of the thesis, In this work, 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 rGO with various nanostructures such as nanorods, nanosheets, nanospheres, and nanoporous. 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 X-ray diffraction profile, Raman spectroscopy, X-ray photoelectron spectroscopy, field emission scanning electron microscopy with mapping, transmission electron microscopy, UV shielding properties and thermoelectric properties. Besides, two different composite (Sb and Ag) were used to study the efficiency of thermopower.

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. It revealed the highest UPF value of 183.84 and enhanced power factor of 22 μW/m.K2. Additionally, it is possible to observe that the connection between grains appears poorer in the case of ZnO nanorods, which resultant high resistivity. In ZnO nanosheets, boundary scattering of charge carrier is reduced in the thin film, and hence, its electrical resistivity is decreased. However, 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.

We have also employed two-step solvothermal method for ZnO composite with Sb-/ Ag- the coating on the cotton fabric. The growth process of ZnO is disrupted, when the Ag composites are introduced, and the growth process is again favored positive effect on the charge separation efficiency due to Ag have recombined with the Zn material. It possesses the P-type highest value of 471.9 μ/K thermopower because of intergranular crystal structure, which plays a significant role in charge transport, and the UV shielding value of 83.9. The rGO-coated fabric was successfully by the one-step hydrothermal method and improved the performance of this system by forming reduced graphene oxide on the fabric surface. The high UPF values measured as high as 442 and 32 μV/K of thermopower. Finally, carbon fabric used instead of cotton fabric to realize the difference of nonconducting and conducting fabric response towards UPF and thermopower, in this sonochemical assisted hydrothermal process involved to coat the ZnO nanostructures. Due to time duration, we obtained nanorods and nanosheets for 1h and 5h growth period respectively. The bare carbon fabric shows the UPF value of 28.62 and ZnO coated nanosheets UPF value of 201.75 due to denser coverage on carbon fabric. Similarly, ZnO coated carbon fabric about -0.04 ~ 0.054 μV/K and for bare carbon fabric it was found to be about 0.08 μV/K. It is significant to note that there was a change of carrier type from P-type to

N-type resulting due to the coating of ZnO on carbon fabric.