

Green Synthesis of SBS /ZnO Doped Nano Composites Film for Strutural-Surface Morphology, Mechanical and Electrical Studies

Umme Salma and Nayeemuddin

Department of Mechanical Engineering, FoET Khaja Bandanawaz University, Kalaburagi, India

Email: nayeem499@gmail.com

This study reports the synthesis of SBS /ZnO -doped nano composites. SBS /ZnO -doped nano composites were prepared by solution cast polymerization of Styrene and Butadiene monomer in the presence of ZnO -doped with ammonium per sulfate (APS) as oxidant. Different concentrations of ZnO (10-50 wt %) metal oxides were incorporated into the SBS. The obtained final product was well characterized by means of PXRD, SEM, AFM, TEM. FTIR, and XRD results shows the presence of ZnO particles in SBS. The morphology of the obtained product shows the porous and agglomerated particles which are due to large amount of gas evolution during the synthesis method. The present study demonstrates that the prepared samples are quite useful for mechanical and electrochemical storage applications

Keyword: Styrene, Butadiene, XRD, FTIR, SEM, AC and Mechanical.

1. Introduction

In recent years alternative renewable energies obtained by solar cells have attracted much attention due to exhaustion of other conventional energy resources especially fossil based fuels and due to global warming they caused [1]. The 21st century is an information age. Information science and technology have penetrated into all areas of our social life and have profoundly influenced and changed the global economic structure and people's production and lifestyle. The information age is based on intelligence, all of this is inseparable from the collection and processing of data, so this is also the era of sensors. Sensors have been extensively researched in the fields of wearable electronics [2], health care [3] and smart terminals [4], including rapidly evolving technology areas such as artificial intelligence (AI) and Internet of Things (IoT) technology, as sensors enable context awareness and data collection, it plays a vital role in AI and IoT application. So the pressure sensor, as an important sensing element among various electronic devices, is of more and more interests, as revealed by recently research. For the above technology to play a better role in human life, there are strict requirements for the

preparation of flexible pressure sensors with low-cost manufacture and over-all properties. Currently, a wide variety of sensor models have been proposed to prepare comprehensive properties pressure sensor, and it can be divided into capacitive [5,6], piezoresistive [7], piezoelectric [8], and triboelectric [9]. Among them, capacitive pressure sensor has become the focus of research because of its outstanding performance, such as high stability and short response time. In principle, the flexible capacitive pressure sensor is a type of traditional

Thus the synthesis of novel conducting polymers and study of their physical properties has been of prime importance. Aqueous electrochemical process is an environmentally friendly and efficient technique used to process conducting polymer. It is widely preferred because of its simplicity and it can be used as a one-step method to form polymer. It allows efficient control of the physiochemical properties of the coatings and It can also be easily scaled up for large scale production [2-4]. Conductive polymers have been the topic of the large number of investigations during last decades because of their unique properties such as mechanical strength, electrical conductivity, corrosion, stability and possibility of both oxidative and electrochemical synthesis. Hence PANI is useful in wide area of application: such as solar energy conversion, rechargeable batteries, electrochromic displays, electrochemical sensors, capacitors and active corrosion protector [5-6]. Due to ease of synthesis, processing environmental stability and low synthetic cost, so SBS is probably the most important industrial conducting polymer today [7-8]. The use of conducting polymers for photovoltaic applications has been reported [9]. Composites have become one of the most extensively studied materials all over the world, as they have shown to possess several technological applications. Further, composites composed of conducting polymers and metal oxides have opened many applications e.g. in drug delivery, conductive paints, rechargeable batteries, toners and smart windows etc. [10]. The present study especially aims to investigate Polystyrene and poly vinyl alcohol composites in order to obtain a new noble material which can be utilized for electrical applications. ZnO is a semiconducting material that has a direct wide band gap of 2.16 eV at room temperature. Indeed ZnO is a peculiar material that exhibits multiple properties that include piezoelectric, semiconducting, pyroelectric and photocatalytic activities. In the present paper, PANI/ZnO composites were prepared by solution cast polymerization of Polystyrene and Butadiene monomer with different doping concentrations of ZnO. All the composites have been analyzed using X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). The dc conductivity of these composites was studied as a function of temperature at different dopant concentrations [11].

2. SYNTHESIS OF SBS

The synthesis of SBS was based on mixing liquid solution of styrene and Butadiene hydrochloride and APS at 32°C temperature, followed by taking part of SBS hydrochloride by filtration and drying. An equi-molar volume of Styrene and Butadiene and hydrochloride acid was dissolved in distilled water in a beaker to obtain 100 ml of solution. Similarly, ammonium persulphate (0.6M) was dissolved in 100 ml water. Both solutions were left 1 hour at room temperature and then mixed in a beaker, stirred with a mechanical stirrer and allowed to polymerize. After a day, the SBS films were collected on a filter, washed with 0.3 M HCl and acetone repeatedly. The SBS hydrochloride powder was then kept at 60°C for 24

hours[13].

2.1 SYNTHESIS OF SBS/ZINC OXIDE COMPOSITES

Synthesis of SBS–Zinc oxide nano composites were carried out by solution cast polymerization method. Styrene and Butadiene(0.3 M) was mixed in 0.3 M HCl and stirred for 15 min to form Styrene and Butadiene hydrochloride. Zinc oxide nanoparticles were added in the mass fraction to the above solution with vigorous mixing in order to keep the Zinc oxide homogeneously suspended in the solution. To this solution, 0.6 M of APS, which acts as an oxidizer was slowly added drop by drop with continuous mixing at ice temperature for 4 hours to completely polymerize. The precipitate was filtered, washed with deionized water and acetone, and finally dried in an oven for 24 h to reach a constant mass. The SBS-Zinc oxide composites were thus obtained containing 50wt % (i.e.50%weight percentage of zinc oxide) [13].

3. XRD ANALYSIS

Figure.1. X-Ray Diffraction were studies using Shimadzu-7000 diffractometer with Cu as the target (1.54 \AA) and nickel as the filter. Fig.1 Observed diffraction pattern of SBS. A broad peak centered at $2\theta = 25.53^\circ$ may be assigned to the scattering from the SBS chains at interplanar spacing which clearly implies the amorphous nature of SBS and it corresponds to diffraction planes (200) of pure SBS [13-14].

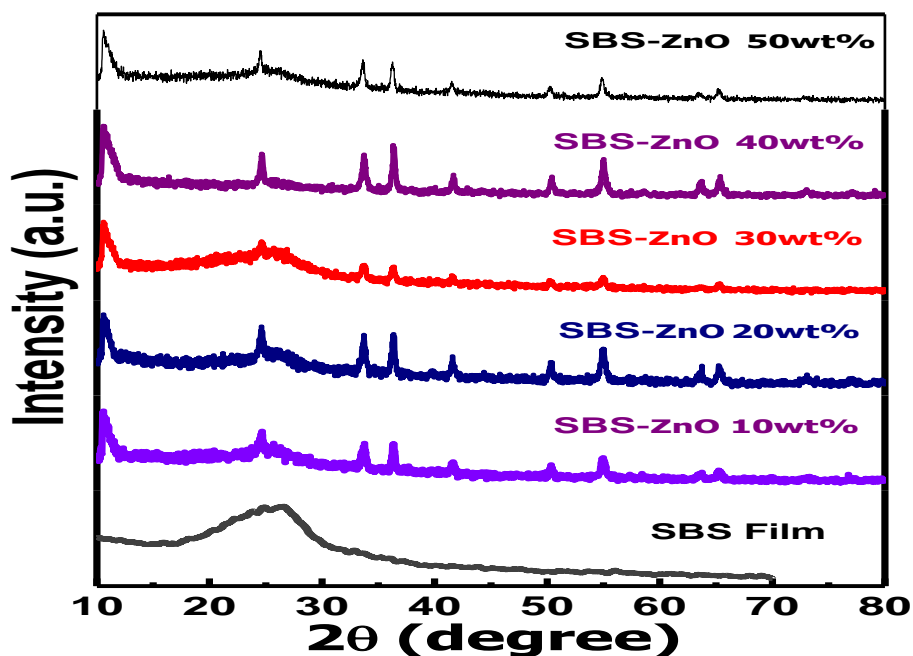


Fig.1. XRD Pattern of SBS doped zinc oxide nano film.

Fig.1 Shows a broad peak at $2\theta=16^\circ$, 37° & 49.75° which has a sharp and well defined peak and it indicates good crystallinity of ZnO nano particles Fig.1.shows the intensity of diffraction peaks for SBS /ZnO composites and it is found to be lower than that for pure Zinc oxide particles. The peaks of pure zinc oxide particles are also present in SBS /ZnO composites. The amorphous background hump comes from the SBS [15].

4. SEM MICROGRAPH

The morphology of the materials was recorded using a scanning electron microscope (Hitachi table top, Model TM 3000) operated at an accelerating voltage of 15 kV. Fig.2(a) shows SEM micrographs of pure SBS. It can be seen from the figure that the pure SBS is poorly adsorbed on the surface with no ZnO particles. Fig.2(b) depicts the SEM micrographs of ZnO particles, It can be seen from the figure that the ZnO particles were agglomerated in nature and this agglomeration was due to trapping of Cu-O bonding.

As we concentration of ZnO increase the SEM micrographs show more and more number of particles deposited on the surface of SBS layer [16-18] (Fig.2(c-e)).

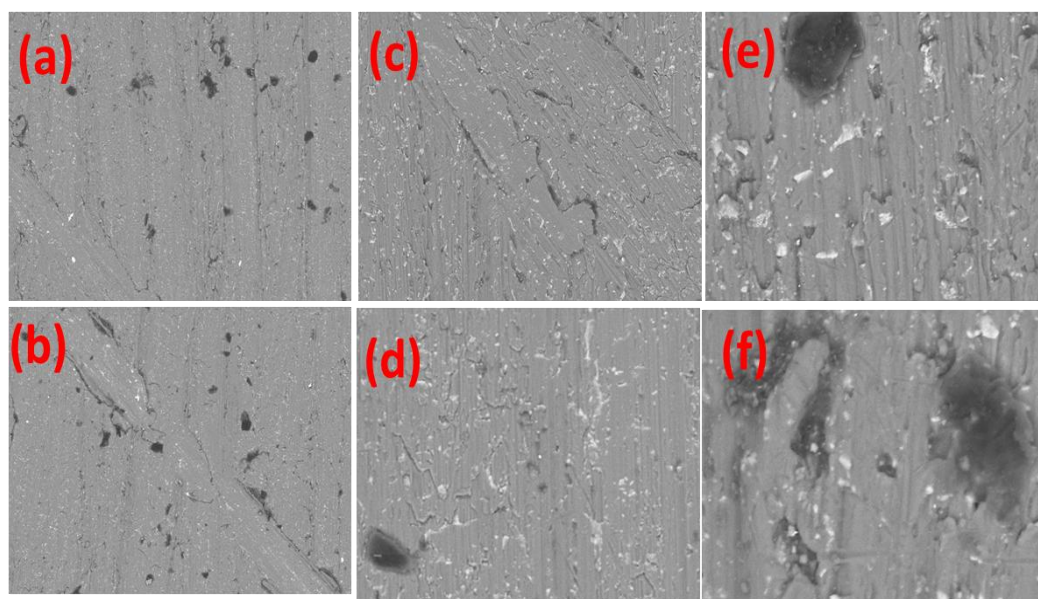


Fig.2. SEM Micrographs of (a) SBS, (b) Pure ZnO Particles & (c) SBS /ZnO (50 wt %) composites

5. TRANSMISSION ELECTRON MICROSCOPY (TEM)

It is evident from the figure that, the particles are in nano regime and which are in good agreement with the average particle size computed from the PXRD data. From micrographs of TEM, particles size was around 25nm. Fig.3 (a, b) and (c) Shows TEM image of SBS /ZnO (50 wt . %) composites [19-20].

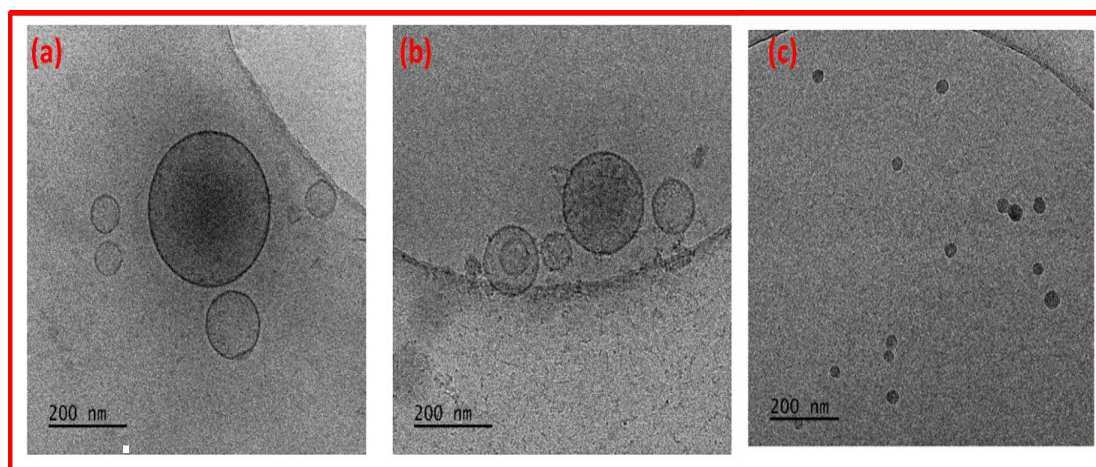


Fig.3. (a) TEM image, (b-c) HRTEM of SBS /ZnO (50 wt. %) composites

6. FTIR STUDIES

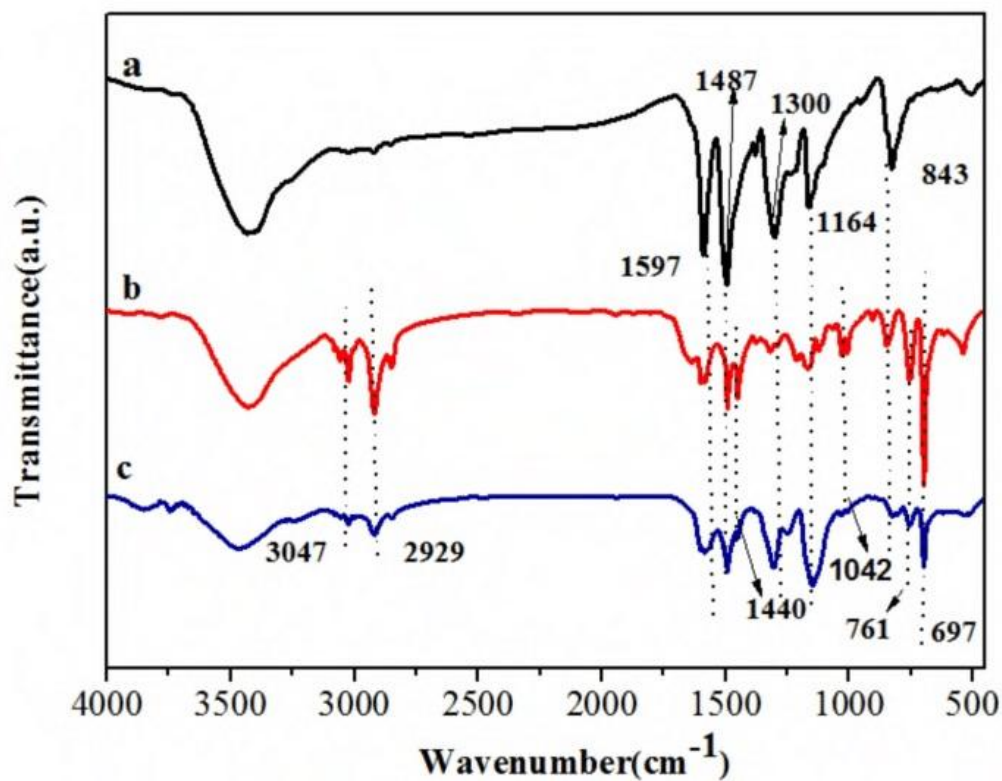


Fig.4. FTIR Spectra of (a) SBS, (b) Pure ZnO Particles & (c) SBS /ZnO 50 wt.% composites

7. DC CONDUCTIVITY OF SBS /ZNO COMPOSITES

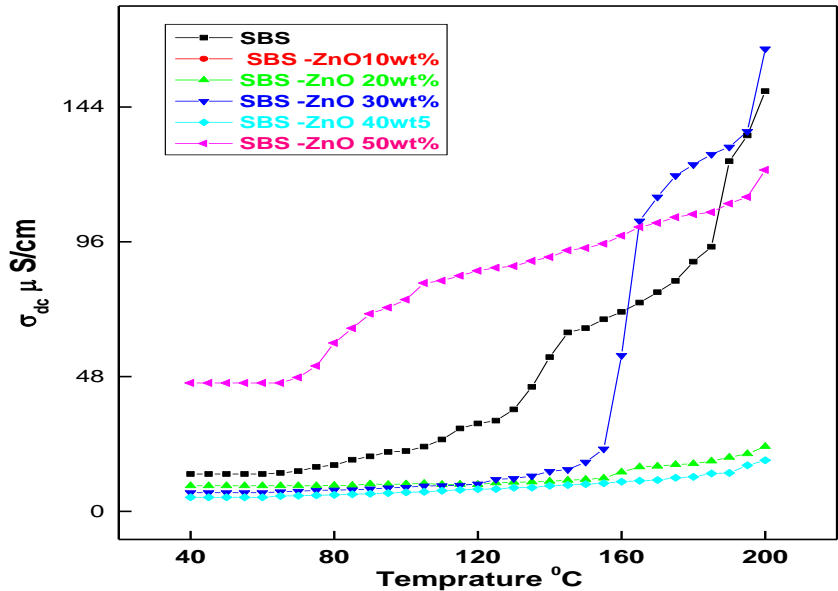


Fig.5. DC Conductivity of SBS zinc oxide nano film composites.

The dc conductivity of the SBS /ZnO O composites was studied by using Keithley 6514 electrometer. The plot of dc conductivity of SBS and SBS /ZnO composites with temperature dependent are shown in Fig.5. The conductivity is found to increase as a function of increase in temperature. This increase in conductivity with temperature is the characteristic of “thermal activated behavior”. The increase in conductivity could be due to increase of efficiency of charge transfer between the polymer chains and the dopant with enhancement in temperature. The thermal curing effects of the alignment of polymer chain, which leads to the increase of conjugation length possibly also brings about increase in the conductivity of the composites [17-22].

8. AC Conductivity of SBS /ZnO composites

Fig.6 shows the variation of ac conductivity as a function of frequency for SBS /ZnO O composites for (10 to 50wt %) performed in RT. It is observed that σ_{ac} remains constant up to 104 Hz. SBS /ZnO 40 wt % composites shows high conductivity due to interfacial polarization and concentration of charge carriers enhanced. However, in case of pure SBS and other composites with SBS conductivity is comparatively high. The conductivity of PANI/ZnO composites increases due to the distribution of ZnO particles in Pure SBS [15-22].

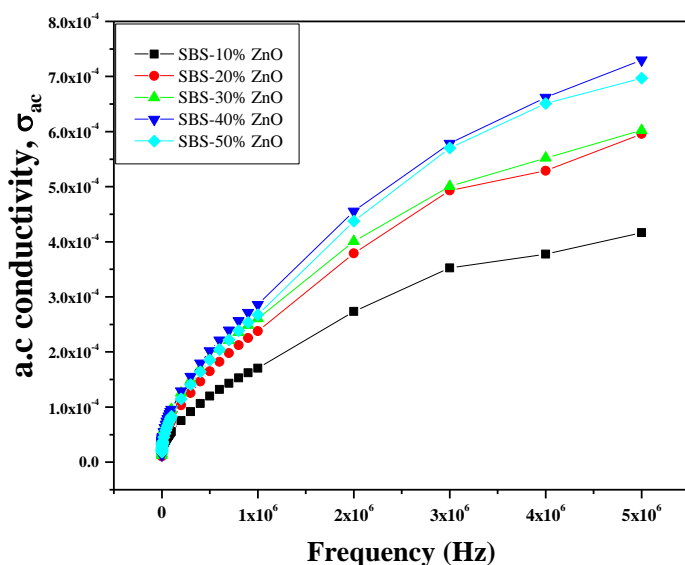


Fig.6. AC Conductivity of SBS zinc oxide composites.

9. MECHANICAL STUDIES

Figure.7. shows the polymer films is Initially, PS-PVDF exhibits a lower tensile strength and a higher elongation at break that reflects its flexibility due the hydrophilic nature of the SBS /ZnO , which is related to the existence of the hydroxyl groups in the polymer backbone, which contribute to water absorption competent to raise the open volume among the polymeric chains. In doing so, the relieve of progress of polymeric chains with admiration to each other is spectacularly enhanced. In packaging, a plasticizer is a substance further to materials to impart flexibility, workability, and elongation. The plasticizer to the film is to overcome the film brittleness caused by extensive intermolecular force and 50 wt % shows the more stronger then remaining films.The prepared new ductile materials, The below graphs shows Strain – Strain relation SBS /ZnO NCs with different ratios (10-50) NCs.

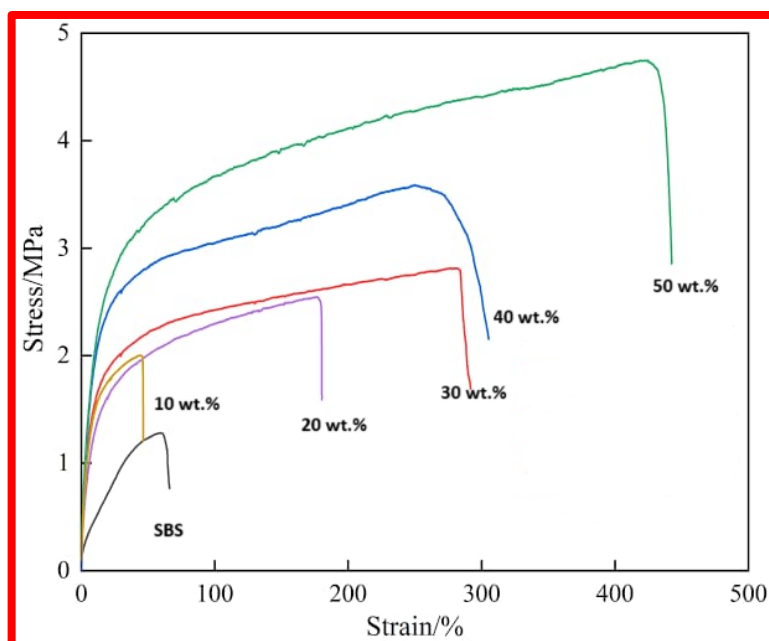


Fig.7. Mechanical studies of SBS zinc oxide composites.

10. CONCLUSIONS

Pure and SBS /ZnO composites were successfully prepared by in-situ polymerization technique. The composites showed high crystalline nature with no impurity peaks. The surface morphology of the composites were studied by means of SEM and the results showed agglomeration of particles. variation of ac conductivity as a function of frequency for SBS /ZnO O composites for (10 to 50wt %) performed in RT. The increase in AC and DC conductivity could be due to increase of efficiency of charge transfer between the polymer chains and the dopant with enhancement in temperature. SBS /ZnO 40 wt % composites shows high conductivity due to interfacial polarization and concentration of charge carriers enhanced. All these results together reveal that the synthesized composites can be used in the field of electrical applications.

References

- [1] Song JK, Son D, Kim J, Yoo YJ, Lee GJ, Wang L, et al. Wearable force touch sensor array using a flexible and transparent electrode. *Adv Funct Mater* 2017;27(6). 1605286.
- [2] Nie B, Li X, Shao J, Li X, Tian H, Wang D, et al. Flexible and transparent strain sensors with embedded multiwalled carbon nanotubes meshes. *ACS Appl Mater Interfaces* 2017;9(46):40681e9.
- [3] Li T, Luo H, Qin L, Wang X, Xiong Z, Ding H, et al. Flexible capacitive tactile sensor based on micropatterned dielectric layer. *Small* 2016;12(36):5042e8.
- [4] Wang R, Jiang N, Su J, Yin Q, Zhang Y, Liu Z, et al. A Bi-sheath fiber sensor for giant tensile and torsional displacements. *Adv Funct Mater* 2017;27(35). 1702134.
- [5] Chen X, Parida K, Wang J, Xiong J, Lin MF, Shao J, et al. A stretchable and transparent nanocomposite nanogenerator for self-powered physiological monitoring. *ACS Appl Mater Interfaces* 2017;9(48):42200e9.

- [6] Han ST, Peng H, Sun Q, Venkatesh S, Chung KS, Lau SC, et al. An overview of the development of flexible sensors. *Adv Mater* 2017;29(33). 1700375.
- [7] Dong C, Fu Y, Zang W, He H, Xing L, Xue X. Self-powering/self-cleaning electronic-skin basing on PVDF/TiO₂ nanofibers for actively detecting body motion and degrading organic pollutants. *Appl Surf Sci* 2017;416:424e31.
- [8] Su B, Gong S, Ma Z, Yap LW, Cheng W. Mimosa-inspired design of a flexible pressure sensor with touch sensitivity. *Small* 2015;11(16):1886e91.
- [9] WangX, QueM, ChenM, HanX, LiX, PanC, et al. Full dynamic-range pressure sensor matrix based on optical and electrical dual-mode sensing. *Adv Mater* 2017;29(15).
- [10] Liu J, Wu W, BaiS, Qin Y. Synthesis of high crystallinity ZnO nanowire array on polymer substrate and flexible fiber-based sensor. *ACS Appl Mater Interfaces* 2011;3(11):4197e200.
- [11] Bae S-H, Lee Y, Sharma BK, Lee H-J, Kim J-H, Ahn J-H. Graphene-based transparent strain sensor. *Carbon* 2013;51:236e42.
- [12] Chen S, Zhuo B, Guo X. Large area one-step facile processing of micro structured elastomeric dielectric film for high sensitivity and durable sensing over wide pressure range. *ACS Appl Mater Interfaces* 2016;8(31):20364e70.
- [13] Joo Y, Byun J, Seong N, Ha J, Kim H, Kim S, et al. Silver nanowire-embedded PDMS with a multiscale structure for a highly sensitive and robust flexible pressure sensor. *Nanoscale* 2015;7(14):6208e15.
- [14] Zhang H, Liu N, Shi Y, Liu W, Yue Y, Wang S, et al. Piezoresistive sensor with high elasticity based on 3D hybrid network of Sponge@CNTs@Ag NPs. *ACS Appl Mater Interfaces* 2016;8(34):22374e81.
- [15] Wu S, Ladani RB, Zhang J, Ghorbani K, Zhang X, Mouritz AP, et al. Strain sensors with adjustable sensitivity by tailoring the microstructure of graphene aerogel/PDMS nanocomposites. *ACS Appl Mater Interfaces* 2016;8(37): 24853e61.
- [16] Chen X, Li X, Shao J, An N, Tian H, Wang C, et al. High-performance piezo electric nanogenerators with imprinted P(VDF-TrFE)/BaTiO₃ nanocomposite micropillars for self-powered flexible sensors. *Small* 2017;13(23). 1604245.
- [17] Ma Y, Zheng Q, Liu Y, Shi B, Xue X, Ji W, et al. Self-powered, one-stop, and multifunctional implantable triboelectric active sensor for real-time biomedical monitoring. *Nano Lett* 2016;16(10):6042e51.
- [18] Qian X, Cai Z, Su M, Li F, Fang W, Li Y, et al. Printable skin-driven mechano luminescence devices via nanodoped matrix modification. *Adv Mater* 2018;30(25):e1800291.
- [19] Pang Y, Zhang K, Yang Z, Jiang S, Ju Z, Li Y, et al. Epidermis microstructure inspired graphene pressure sensor with random distributed spinosum for high sensitivity and large linearity. *ACS Nano* 2018;12(3):2346e54.
- [20] WangJ, Jiu J, Nogi M, Sugahara T, Nagao S, Koga H, et al. A highly sensitive and flexible pressure sensor with electrodes and elastomeric interlayer containing silver nanowires. *Nanoscale* 2015;7(7):2926e32.
- [21] H. Peng, G.F. Ma, K.J. Sun, J.J. Mu, H. Wang, Z.Q. Lei, High-performance supercapacitor based on multi-structural CuS @ polypyrrole composites prepared by solution cast oxidative polymerization, *J. Mater. Chem. A* 2 (2014) 3303–3307.
- [22] Hajeelbaba K Inamdara, MVN Ambika Prasad, RB Basavaraj, M Sasikala, SC Sharma, H Nagabhushana, Promising red emission from functionalized Polypyrrole/CaTiO₃: Eu³⁺ nano-composites for photonic applications, *Optical Materials*, 88 (2019), 458-465