Self Powered Nanopiezoelectric Device Based on ZnO Nanorod Array on Flexible Conjugated Copolymer Hybrid

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Abstract: ***Harvesting energy directly from the environment is one of the most effective and promising approaches for powering nanodevices. In this study, nano piezoelectric devices based on ZnO nanorod array/conducting polymers are fabricated for wearable power generation application. To replace the inorganic rigid indium-tin oxide (ITO) conducting coating commonly used in the nanogenerator devices, a series of flexible polyaniline-based conducting copolymers underlying the ZnO nanorod arrays has been synthesized with improved electric conductivity by the copolymerization of aniline and 3,4-ethylenedioxythiophene (EDOT) monomers in order to optimize the piezoelectric current collection efficiency of the Devices. Although the efficiency and durability of harvesting materials such as piezoelectric nanowires have steadily improved, the voltage and power produced by a single nanowire are insufficient for real devices. The integration of large numbers of nanowire energy harvesters into a single power source is therefore necessary, requiring alignment of the nanowires as well as synchronization of their charging and discharging processes. As an innovative and much improved step towards achieving a high-power-output, an ac nanogenerator based on vertically or laterally aligned ZnO nanowire arrays based on a hydrothermal method is proposed.It is to synthesize ZnO nanorod arrays on polyaniline-based conducting polymer coatings with different electric conductivities.***

Keywords: ZnO nanorod, copolymer, nano piezo electric device, 3,4 ethylenedioxythiophene (EDOT)

1. Introduction

Energy has been essential in building up modern society. Some energy can be seen, but most does not have a visible form. Energy is defined in several ways such as mechanical, electrical and chemical. All of these definitions are based on where energy is stored. Energy is stored everywhere. Heat, electricity, dynamic, chemical, photo and biomass forms of energy are all stored differently but these can be converted from one to the other. Among many types of energy, electricity is the most common used form for modern devices because it is easy to convert to other types. The energy obtained from the

vibration is converted to electrical energy. Mechanical energy surrounds us in our daily life, taking the form of sonic waves, mechanical vibrations and impacts, air flow, friction, hydraulic and ocean waves, all available around the clock. A novel ZnO nano piezoelectric device based on a hydrothermal method to synthesize ZnO nanorod arrays on polyaniline-based conducting polymer coatings is proposed here. A periodic, low-frequency, uniaxial strain is applied to the ZnO nanowires by an external mechanical action to create a piezoelectric potential along the nanowires ,which results in an alternating electrical output.

2. Literature Survey

Sheng Xu et al reported the vertical and lateral integration of ZnO nanowires into arrays that are capable of producing sufficient power to operate real devices[1].Recently Yu-Ping Lee et al demonstrated nanopiezoelectric devices based on ZnO nanorod array/conducting polymers for fabrication of wearable power generation application[2]. Extensive studies of ambient vibrations from different sources in the environment ranging from milling machines to commercial aircraft have been reported[3,4].By the discovery of its particular optoelectronic[5–7], piezoelectric [8-10], and biocompatible[11–13] properties, which grant this nanomaterials great possibility in electronics[10–18], biomedical devices [19–21], and power generation application [22–27].Especially, the piezoelectric property of ZnO nanorods makes this versatile material for nanotechnology applications, which include piezoelectric field-effect transistors [28–30] and diodes. ZnO nanorods can be used to generate rectifying piezoelectric current, which results from their combined semiconducting and piezoelectric characteristics upon the application of external forces, such as pushing, bending, vibration or rolling force, etc. Wang et al [8] reported the study of converting the mechanical energy in nanoscale into electrical energy by applying a dragging force on the ZnO nanowire arrays, therefore establishing the method of nanogenerators (NGs) for collecting mechanical energy. Thereafter, in the field of nanopiezotronics there have been various attempts to implement and utilize the semiconducting/coupled piezoelectric properties of ZnO nanostructure for novel application. ZnO nanowires are unique in their suitability not only for the fabrication of nanosensors but also for scavenging mechanical energy. One creative initiative is to use ZnO nanowires, alone, to build an integrated nanopower–nanodevice system that is self-driven, with no battery or external power source. The most challenging task in achieving this aim is probably the creation of an energy-scavenging unit that works over a range of frequencies.

3. Problem Definition

In this study, I propose a novel ZnO nanopiezoelectric device based on a hydrothermal method to synthesize ZnO nanorod arrays on polyaniline-based conducting polymer coatings with different electric conductivities and as an innovative and much improved step towards achieving a high-power-output, a.c. nanogenerator based on vertically (VING) or laterally(LING) aligned ZnO nanowire arrays in which there are solid bonds/contacts between the electrodes and the ends of the nanowires. To replace the commonly used indium-tin oxide (ITO) conducting coating in the nanogenerator devices, a series of the conducting polymer coatings underlying the ZnO nanorod array has been synthesized by the copolymerization of 3,4-ethylenedioxythiophene (EDOT) and aniline at different monomer compositions in order to optimize the piezoelectric current collection efficiency of the devices for the new all wet chemical coating processes.

ZnO nanorod array based on flexible conjugated copolymer hybrids

Nanopiezoelectric devices based on ZnO nanorod array/conducting polymers are fabricated for wearable power generation application. To replace the inorganic rigid indium-tin oxide (ITO) conducting coating commonly used in the nanogenerator devices, a series of flexible polyaniline-based conducting copolymers underlying the ZnO nanorod arrays has been synthesized with improved electric conductivity by the copolymerization of aniline and 3,4-ethylenedioxythiophene (EDOT) monomers in order to optimize the piezoelectric current collection efficiency of the devices. It is found that significantly higher conductivity can be obtained by small addition of EDOT monomer into aniline monomer solution using an in-situ oxidative polymerization method for the synthesis of the copolymer coatings. The highest conductivity of aniline-rich copolymer is 65 S/cm, which is 2.5 times higher than that for homopolymer polyaniline coating. Subsequently, ZnO nanorod arrays are fabricated on the polyaniline-based copolymer substrates via a ZnO nanoparticle seeded hydrothermal fabrication process. The surface morphology, crystallinity, orientation, and crystal size of the synthesized ZnO nanorod arrays are fully examined with various synthesis parameters for copolymer coatings with different monomer compositions. It is found that piezoelectric current generated from the devices is at least five times better for the device with improved electric conductivity of the copolymer and the dense formation of ZnO nanorod arrays on the coating. Therefore, these results demonstrate the advantage of using flexible –conjugated copolymer films with enhanced conductivity to further improve piezoelectric performance for future wearable energy harvesting application based on all wet chemical coating processes.

Deposition of ZnO Seed Layer on Polyaniline-Based Copolymer Coating

In order to ensure the fabrication of well-organized ZnO nanorod arrays on the surface of the synthesized conducting copolymer coatings, prior to the hydrothermal synthesis method for ZnO nanorod fabrication, a seed layer of crystalline ZnO nanoparticles needs to be deposited on the conducting copolymer coatings. The procedure for depositing the ZnO seed layer on polyaniline-based copolymer coating by a spin-coating method. A hydrothermal fabrication process was used for fabricating ZnO nanorod arrays on a seed coated copolymer film substrate. The surface morphology of ZnO nanorod array/polyaniline-based copolymer coatings was analyzed by using field scanning electron microscopy (FESEM)

Three-dimensionally integrated VING

The key to a self-powered nanosystem is the fabrication of a nanogenerator that provides high output voltage and power Polyaniline-based conductive copolymer coatings, on which Vertical ZnO nanorod arrays were grown A layer of polymethyl-methacrylate (PMMA) was spin-coated onto the nanowires to fully wrap them from top to bottom largely improving the stability and mechanical robustness of the entire structure, and also preventing possible short-circuiting between the substrate and the top electrode. Oxygen plasma etching was performed, leaving behind fresh and clean tips on the nanowires. A piece of silicon wafer coated with a 300-nm-thick platinum film was then placed in direct contact with the nanowires creating a Schottky contact at the interface. The working principle of the VING lies in the coupling of piezoelectric and semiconducting properties. The presence of a Schottky contact at least at one end of the nanowires is essential for the operation of the VING. The output voltage and current could be greatly enhanced by linearly integrating a number of VINGs. Theoretical calculations have shown that, within the elastic linear mechanics regime, the output voltage of a single nanowire is linearly proportional to the magnitude of its deformation. The ZnO nanowires in the VING were all connected in parallel between the two electrodes. Undoubtedly, as we increase the pressing force acting on the nanowires, their deformation becomes larger, and the output voltage will linearly scale up. It must be noted that a large fraction of the applied stress was consumed in overcoming the elasticity of the packaging material (1–2 mm in thickness) around the VING. The magnitude of the output voltage also depended on the straining rate at which the stress was applied The output signals of the VING were stable over a long period of time.

High-output flexible LING

A single nanowire-based nanogenerator on a flexible substrate can be driven by the mechanical agitation present in our living environment including that resulting from human or animal motion.It is essential to enhance the output power by integrating contributions from multiple nanowires. Because the diameter of a nanowire is much smaller than the thickness of the substrate film, all the nanowires on a substrate are subjected to a pure tensile strain when the substrate is stretched. Each active nanowire works as a ‘charging pump’, and is independent of the other nanowires as the substrate is bent and released. If the charging and discharging processes of many nanowires could be synchronized, the output a.c. voltages could be added constructively resulting in a high output voltage. Several factors have to be considered when integrating the outputs of many nanowires. First, there should be a Schottky contact at least at one side of the nanowires . Second, the contacts at the two ends should be robust enough that the mechanical deformation can be effectively transmitted from the electrodes to the nanowires. Third, all the nanowires should have the same crystallographic orientation to ensure that the polarities of the generated piezoelectric potentials are aligned. The nanowires therefore need to be rationally grown, directly on the substrate, rather than by chemical assembly. Finally, all of the nanowires must be stretched and released in a synchronized manner, so that the piezoelectric potentials generated by all of them are in the same direction and occur at the same time resulting in an enhanced output voltage. The first step was to grow crystallographically aligned nanowires parallel to the substrate using Polyaniline-based conductive copolymer coatings, on which Lateral ZnO nanorod arrays were grown. A thick layer of gold was then deposited using an aligned mask technique to connect the tips of the nanowires with the gold electrode so that the nanowires were robust to mechanical deformation without there being any loose contacts A periodic external force was used to deform the flexible substrate so that the nanowires experienced a cyclic stretching–releasing deformation process. A push to the middle of the substrate by the linear motor resulted in a tensile strain across all the rows of the nanowires constructed on top of the substrate , creating a macroscopic piezoelectric potential resulting from the crystallographic alignment of the nanowires. Integrating more ZnO nanowires, improving the interconnection of the electrodes and nanowires, and increasing the strain or straining rate are all important targets for enhancing the output voltage and current of the LING.

Like the VING, increasing the strain is an effective way to achieve a high output voltage and current.The output voltage has been greatly enhanced by lateral integration, but the output current is rather limited, which is probably attributable to the following factors. First, the orientational alignment of the as-grown lateral nanowires was not perfect and only a fraction of them were in contact with the gold electrode Second, the bonding between the gold and ZnO was not very solid, and could become loose during repeated mechanical stretching cycles.

4. Conclusion

ZnO nanorod arrays on various polyaniline-based conducting copolymer coatings and utilized the coupled piezoelectric-semiconducting properties of ZnO nanorods and improved charge-collection performance of the conducting copolymer coatings. The active piezoelectric hybrid coatings could be produced by sequential solution-based manufacturing processes of coating conducting polymers, ZnO nanoparticle seeds, and hydrothermal synthesis of ZnO nanorod arrays, facilitating future wearable application based on all wet-chemical methods. The enhancement in the measured conductivity for the copolymer coatings with a small addition of EDOT monomer into aniline might be due to the minor monomer inhibition effect on the copolymerization rate, which enhances the molecular weight of synthesized conductive copolymer coatings. In addition, the reduction in the copolymerization rate ensured the formation of uniform film surface with less defects, leading to an enhancement in the subsequent growth of dense and well-organized ZnO nanoarrays with better crystallinity for piezoelectric performance improvement. The vertical and lateral nanowires were in full contact at both ends. Using the crystallographic alignment of the nanowires, a macroscopic piezo-potential is created when the nanowires are subjected to a uniaxial compressive or tensile strain, which drives a transient flow of electrons in the external circuit. This demonstrates the great potential for layer-by-layer three-dimensional integration in applications where a dynamic compressive stress/straining is available, such as in shoe pads, vehicle tyres and under carpets or floors. Experimental observation has shown that ZnO nanowires are robust and fatigue-free. Therefore, a layer-by-layer integration of LINGs is possible for fabricating three-dimensional energy harvesters that have a high enough output to power small electronic devices.

References

[1] Yu-Ping Lee et al ,"Nanopiezoelectric Devices for Energy Generation Based on ZnO Nanorods/Flexible-Conjugated Copolymer Hybrids Using AllWet-Coating Processes" Micromachines 2020.

[2] Sheng Xu et al, Self-powered nanowire devices, nature nanotechnology Vol 5,| May 2010 366 .

[3] S. Roundy, P. Wright, and J. Rabaey, "A study of low level vibrations as a power source for wireless sensor nodes," Computer Communications, vol. 26, pp. 1131–1144, 2003.

[4] S. Lee, and B. Youn, "A new piezoelectric energy harvesting design concept: multimodal energy harvesting skin," IEEE Transactions on Ultrasonics, Ferroelectrics, and Frequency Control, vol. 58, pp. 629-645, March 2011.

[5] Rajendar, V.; Dayakar, T.; Shobhan, K.; Srikanth, I.; Rao, K.V. Systematic approach on the fabrication of Co doped ZnO semiconducting nanoparticles by mixture of fuel approach for antibacterial applications. Superlattices Microstruct. **2014**, 75, 551.

[6] Dingle, R. Luminescent transitions associated with divalent copper impurities and the green emission from semiconducting zinc oxide. Phys. Rev. Lett. **1969**, 23, 579.

[7] Kumar, B.; Kim, S.-W. Energy harvesting based on semiconducting piezoelectric ZnO nanostructures. Nano Energy **2012**, 1, 342

[8] Wang, Z.L.; Song, J. Piezoelectric nanogenerators based on zinc oxide nanowire arrays. Science **2006**, 312, 242.

[9] Wang, X.; Zhou, J.; Song, J.; Liu, J.; Xu, N.; Wang, Z.L. Piezoelectric field e_ect transistor and nanoforce sensor based on a single ZnO nanowire. Nano Lett. **2006**, 6, 2768.

[10] Chang, C.-J.; Lee, Y.-H.; Dai, C.-A.; Hsiao, C.-C.; Chen, S.-H.; Nurmalasari, N.P.D.; Chen, J.-C.; Cheng, Y.-Y.; Shih, W.-P.; Chang, P.-Z. A large area bimaterial sheet of piezoelectric nanogenerators for energy harvesting:Effect of RF sputtering on ZnO nanorod. Microelectron. Eng. **2011**, 88, 2236.

[11] Salehi, R.; Arami, M.; Mahmoodi, N.M.; Bahrami, H.; Khorramfar, S. Novel biocompatible composite (chitosan–zinc oxide nanoparticle): preparation, characterization and dye adsorption properties. Colloids Surf.B Biointerfaces **2010**, 80, 86.

[12] Dagdeviren, C.; Hwang, S.; Su, Y.; Kim, S.; Cheng, H.; Gur, O.; Haney, R.; Omenetto, F.G.; Huang, Y.; Rogers, J.A. Transient, biocompatible electronics and energy harvesters based on ZnO. Small **2013**, 9, 3398.
[13] Moussodia, R.-O.; Balan, L.; Merlin, C.; Mustin, C.; Schneider, R. Biocompatible and stable ZnO quantum
[14] Vispute, R.D.; Talyansky, V.; Choopun, S.; Sharma, R.P.; Venkatesan, T. Heteroepitaxy of ZnO on GaN and its implications for fabrication of hybrid optoelectronic devices. Appl. Phys. Lett. **1998**, 73, 348.
[15] Djuriši´c, A.B.; Ng, A.M.C.; Chen, X.Y. ZnO nanostructures for optoelectronics: material properties and device applications. Prog. Quantum Electron. **2010**, 34, 191.
[16] Choopun, S.; Vispute, R.D.; Noch, W.; Balsamo, A.; Sharma, R.P.; Venkatesan, T. Oxygen pressure-tuned epitaxy and optoelectronic properties of laser-deposited ZnO films on sapphire. Appl. Phys. Lett. **1999**,75, 3947
[17] Lim, J.H.; Shim, J.H.; Choi, J.H.; Joo, J.; Park, K.; Jeon, H.; Moon, M.R.; Jung, D.; Kim, H.; Lee, H.-J.Solution-processed InGaZnO-based thin film transistors for printed electronics applications. Appl. Phys. Lett. **2009**, 95, 012108
[18] Subramanian, V.; Bakhishev, T.; Redinger, D.; Volkman, S.K. Solution-processed zinc oxide transistors for low-cost electronics applications. J. Disp. Technol. **2009**, 5, 525.
[19] Wager, J.F. Transparent electronics. Science **2003**, 300, 1245–1246.
[20] Gruber, T.; Kirchner, C.; Kling, R.; Reuss, F. ZnMgO epilayers and ZnO–ZnMgO quantum wells for optoelectronic applications in the blue and UV spectral region. Appl. Phys. Lett. **2004**, 84, 5359.
[21] Huang, M.H.; Wu, Y.; Feick, H.; Tran, N.; Weber, E.; Yang, P. Catalytic growth of zinc oxide nanowires by vapor transport. Adv. Mater. **2001**, 13, 113
[22] Pauporté, T.; Lincot, D. Electrodeposition of semiconductors for optoelectronic devices: results on zinc oxide. Electrochim. Acta **2000**, 45, 3345.
[23] Premanathan, M.; Karthikeyan, K.; Jeyasubramanian, K.; Manivannan, G. Selective toxicity of ZnO nanoparticles toward Gram-positive bacteria and cancer cells by apoptosis through lipid peroxidation. Nanomed. Nanotechnol. Biol. Med. **2011**, 7, 184
[24] Xiong, H.-M.; Xu, Y.; Ren, Q.-G.; Xia, Y.-Y. Stable aqueous ZnO@ polymer core□ shell nanoparticles with tunable photoluminescence and their application in cell imaging. J. Am. Chem. Soc. **2008**, 130, 7522.
[25] Rasmussen, J.W.; Martinez, E.; Louka, P.; Wingett, D.G. Zinc oxide nanoparticles for selective destruction of tumor cells and potential for drug delivery applications. Expert Opin. Drug Deliv. **2010**, 7, 1063
[26] Gottschalk, F.; Sonderer, T.; Scholz, R.W.; Nowack, B. Modeled environmental concentrations of engineered nanomaterials (TiO2, ZnO, Ag, CNT, Fullerenes) for di_erent regions. Environ. Sci. Technol. **2009**, 43, 9216.
[27] Ho_mann, M.R.; Martin, S.T.; Choi, W.; Bahnemann, D.W. Environmental applications of semiconductor photocatalysis. Chem. Rev. **1995**, 95, 69
[28] Dai, Y.; Liu, W.; Formo, E.; Sun, Y.; Xia, Y. Ceramic nanofibers fabricated by electrospinning and their applications in catalysis, environmental science, and energy technology. Polym. Adv. Technol. **2011**, 22, 326.
[29] Lai, X.; Halpert, J.E.; Wang, D. Recent advances in micro-/nano-structured hollow spheres for energy applications: From simple to complex systems. Energy Environ. Sci. **2012**, 5, 5604
[30] Cheng, Y.Y.; Chou, S.C.; Chang, J.A. Development of flexible piezoelectric nanogenerator: Toward all wet chemical method. Microelectron. Eng. **2011**, 88, 3015

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