Zinc oxide nanowire-parylene nanocomposite based stretchable piezoelectric nanogenerators for self-powered wearable electronics

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Abstract. Sustainable flexible micro power supplies for wearable and mobile electronics is a strategic field in today's energy research, which could offer a viable solution to provide the energy required by microsystems. In this interest, we report a facile, cost-effective and industrially scalable process flow for the fabrication of a high performance stretchable piezoelectric nanogenerator (SNG) on polydimethylsiloxane (PDMS) substrate. The present proposed fabrication process is substrate independent. The proof-of-concept is shown by fabricating SNGs on bank cards, free standing PDMS and on silicon substrates. The active layer of the present SNG device is realized by encapsulating ZnO nanowires (NWs), synthesized by hydrothermal method, in parylene C polymer matrix. The SNG devices exhibit excellent performance with peak power density of ~0.7 μW/cm² under a 13 N vertical compressive force at 5 Hz. The obtained electricity from the SNG is used to drive electronic devices such as liquid crystal displays (LCDs) without employing any storage unit, implying the device significance in the field of consumer electronics.

1. Introduction
Wearable systems and flexible electronics have gained extensive research interest recently, as they enable a range of applications including health monitoring, military and prosthetics [1,2]. The stable real-time operation of electronic devices on the wearable systems pretty much depends on the energy, which is currently supplied through standard batteries which have limitations, such as large size and weight, non-flexibility, and finite reservoir of available charges. To be effective, especially for above mentioned applications where portability is necessary, it is critical for wearable systems to be energy autonomous. Smart nanogenerators (NGs) for harvesting energy sources including solar, thermal and mechanical energy have been intensively investigated for the realization of autonomous electronic systems. Solar energy, for example, is one of the important green energy sources for energy autonomous electronic systems such as electronic skin [1]. However, solar cells application to power wearable systems may have limitations such as non-availability of light (at night and/or indoor). Converting thermal energy using pyro- and/or thermoelectric generator can be an interesting solution to power bulky electronic systems but face serious limitations to drive micro-/nanosystems, as it is difficult to have large temperature difference across thin devices and thus the output power is very low. Alternatively, kinetic/mechanical energy is a power source that is ubiquitous and can be a
potential solution to supply green energy for the development of autonomous electronics and has potential to be fabricated over fully flexible and stretchable platform [3].

Mechanical energy harvesting systems that can be realized on highly flexible, stretchable and foldable substrates, and further the possibility to transfer them on any surface topology, could be used for the development of energy autonomous wearable systems. For example, piezoelectric NGs (PENGs) have been used to scavenge body movements to power micro-/nano devices [3]. Since the first demonstration of the PENGs in the scientific domain in 2006 [4], they have been developed and evolved in a variety of configurations. Flexible PENG device structures, such as vertically integrated NG (VING) [5,6], laterally integrated NG [7], and/or nanocomposite generators (NCG)[8] have been demonstrated using diverse piezoelectric nanomaterials. Each device configuration has its advantages and limitations in terms of the average power generated, ease of integration into the devices and stretchability. In this work, we exploit advantages of both VING and NCG device prototypes and developed a facile, cost-effective and industrially scalable process flow for the fabrication of high performance, mechanically robust, stretchable nanogenerator (SNG) on PDMS substrate.

2. Experimental work

2.1 Zinc oxide nanowire synthesis

The ZnO NWs are synthesized at around 90 °C on ZnO thin-film (deposited by sputtering) coated PDMS substrate by the hydrothermal process, as reported elsewhere [9]. The reaction nutrients i.e. equimolar ratio (50 mM) of zinc nitrate hexahydrate (30 ml) and Hexamethylenetetramine (30 ml) and 5 mM polyethylenimine (1 ml) in DI water are added. The substrates are immersed face down in a Teflon lined stainless steel autoclave reactor and placed in a preheated convection oven for 6 hours.

2.2 SNG characterization test-bench

The experimental test bench is a mechanical shaker equipped with an actuator arm. The amplitude and frequency of the shaker are controlled via an Agilent 33 250A function generator and a LDS PA100E power amplifier is used to drive the shaker. The actuator arm is attached to the reciprocating shaker platform at one end and a height adjustable screw is inserted through it at the opposite end. To avoid excessive damage to the SNGs during testing, the screw tip is also insulated by soft styrene–butadiene rubber. The SNGs are then firmly fixed onto a solid aluminium block using double sided adhesive tape. The screw tip is positioned over the active region of the SNG, without making contact.

3. Results and Discussions

The SNG device fabrication process is as follows: First, a thin PMMA layer (~ 100 nm) is spin-coated over a rigid substrate used as a sacrificial layer. Then, a ~250 μm thick PDMS layer, as a stretchable device substrate, is spin-coated (250 rpm, 100 rpm/sec and 15 sec). Subsequently, in a next step, the bottom electrode (Ti (100nm) / Pt (20nm)) and ZnO thin-film (50 nm) are sputtered over the cured PDMS. A low temperature hydrothermal process is used for the growth of vertically aligned ZnO NWs on various device substrates such as bank cards, free standing PDMS and Si substrates (Figure 1a-c). Following, the substrate with NWs is transferred into a chemical vapour deposition (CVD) system for the deposition of parylene C film (~600 nm). The decision of choosing parylene C as the encapsulation matrix has been made while considering its effectiveness of infiltration between the ZnO NWs, conformity and thickness controllability, and compatibility of this coating technique with flexible substrates [10]. The active area of the device is defined by depositing top metal electrode of ~ 100/400 nm Ti/Al layers using a shadow mask. Finally, the copper wires are connected to top and bottom electrodes using epoxy silver paste and the whole device is packaged in PDMS, to improve the robustness of the SNG device and to prevent any moisture and/or dust particle to stick onto the top metal. At the end, the complete device is lifted-off from the rigid substrates making it highly foldable, flexible and stretchable. A schematic of the final device structure is shown in Figure 1d. To confirm the parylene C infiltration and conformity, respectively in between and around the NWs, we captured
SEM pictures from a device fabricated on Si substrates. As shown in Figure 1e, NWs are completely encapsulated in parylene C film with high degree of infiltration between the NWs and conformity over the top surface of the NWs array.

**Figure 1.** Proof-of-concept for SNGs fabricated on: (a) bank cards, (b) free standing PDMS and (c) silicon substrates. The magnified image in each panel shows the as-grown ZnO NWs on respective substrates. (d) The final device structure and (e) SEM image after parylene C and metal deposition on NWs grown on silicon.

The fabricated SNG devices are characterized using a custom built test bench in order to assess their energy harvesting performance and the results are shown in Figure 2. Typical optical micrograph of the fabricated SNG device with an active area 1.2cm$^2$ (free standing PDMS after lifting-off the whole device from rigid substrate) is shown in Figure 2a. A schematic of the characterization system is shown in Figure 2b. The description of the test bench can be found in the experimental section. The energy harvesting performances of SNG devices are measured under different amplitudes of compressive force (6-13 N). It is well known that for PENG devices, the voltage generation is directly proportional to the applied stress (magnitude) and stress rate. The measurement results shown here are performed at fixed frequency of 5Hz. As seen from Figure 2c, the open circuit voltage ($V_{OC}$) amplitude increases from 3 to 9.1 V with the increase of compressive force amplitude from 6 to 13 N. The force sensitivity of the present device is $\sim0.7\pm0.1$ V/N at 5Hz. It is worth to mention that the observed output voltage signal may arise because of piezoelectric properties of parylene C polymer [11]. However, its piezoelectric coefficient ($d_{33} \sim 0.2$ pm/V) is 60 times lower than bulk ZnO ($d_{33} \sim 12$ pm/V) and further, poling step is needed to have any piezoelectric response from it [11]. It is to note that we have not applied any voltage bias to the SNG devices before or during the measurements. Therefore, we can rule out any contribution from parylene C to the observed piezoelectric response from the SNG device. The short-circuit current ($I_{SC}$) is also measured under vertical compressive force (with 13 N amplitude and 5 Hz frequency). The obtained output signal is shown in Figure 2d. A peak $I_{SC}$ of $\sim0.6$ µA is obtained from the SNG devices. To assess the impact of resistive loading on peak surface power density ($P_{max} = (V_{RL} \times I_{RL})/A$), we measure the device performances across a wide range of resistive loads ($R_L$), where $V_{RL}$ and $I_{RL}$ are the instantaneous peak voltage and current at a given resistive load respectively, and A is the device active area. The experimental data resulting from the various $R_L$ values can be found in Figure 2e. From Figure 2e, we can see that the SNG device can produce $P_{max} \sim0.7$ µW/cm$^2$ at the matched load of 8 MΩ. In terms of peak volume power density, the performance exhibited by the present SNG device ($\sim4$ mW/cm$^3$) is comparable to the state-of-the-art value for VING devices [12]. Furthermore, to demonstrate the potential utilization of the generated
electric output power, the SNG is further evaluated by connecting it to consumer electronic devices such as LCDs. For this, a larger area (~8 cm²) SNG device on bank cards is excited using a mechanical shaker by applying compressive forces with 13N amplitude. As shown in Figure 2f, many digits of a LCD screen can be driven without any external circuits, using the SNG only, implying the device significance in the field of consumer electronics energy supply.

Figure 2. Functional characterization of the fabricated SNG devices (active area ~1.2 cm²): (a) an optical image of the SNG on free standing PDMS. (b) Schematic of the custom-built test bench. (c) Output open circuit voltage w.r.t. applied compressive force. (d) The short circuit current w.r.t. time at constant amplitude (13N) and frequency (5Hz) of force. (e) Dependence of the output power density on the external load resistance and (f) optical image of the continuous display of LCDs driven by the SNG device.

4. Conclusions
In summary, we have demonstrated an industrially scalable process flow for the fabrication of high performance mechanically robust stretchable nanogenerators (SNG) on PDMS substrate. The SNG devices exhibit excellent performance with a high piezoelectric open circuit voltage of 9V, output short-circuit current density of ~0.5 µA/cm², and peak power density of ~0.7 µW/cm², under a 13N dynamic vertical compressive force at 5 Hz. The obtained electricity from the SNG device was used to drive LCDs without employing any storage unit. The results obtained from the fabricated SNG devices clearly demonstrate the interest of our novel fabrication process for the development of autonomous wearable electronics for personal health care and human-machine interfaces.

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