Full paper

Human-motion interactive energy harvester based on polyaniline functionalized textile fibers following metal/polymer mechano-responsive charge transfer mechanism

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ABSTRACT

Our experimental output opens up a new vision by proposing mechano-responsive charge transfer mechanism (MRCTM) to π-conjugated polymers in the field of human-motion interactive energy harvester. Doped polyaniline (d-PAN) has been used to functionalize conducting textile fibers (f-CTFs) and integrated with our proposed design for wearable power plant. Each f-CTF generates current by patting, bending, or even soft touching. Localized force deformation at the metal/polymeric interface layer with direct visualization of charge distribution pattern has been extensively studied by atomic force microscopy. The integrated arrays of f-CTFs produce a peak power-density of ~0.6 Wm⁻² with output current-density of ~22 mA m⁻² and can power at least 10 white LEDs of 2.5 W. The procured energy from f-CTFs is capable of charging a commercial 10 μF capacitor to 3 V in 80 s and powering portable electronic devices. The prototype energy harvester stably shows the same performance after more than 100 thousand times of patting, bending or twisting.

1. Introduction

In 21st century, technology is emerging more stylish and smarter, with the new generation paying more for trendy and fashionable wearable gadgets, whereas essential sectors like health and defence demanding for ultra-advanced, flexible smart technology for more prosperity [1–7]. Wearables are emerging as part of a growing trend to move data analysis and communication from the electrical device directly to the body. More than ever, technologists are using a combination of sensors, machine learning and big data analysis to provide consumers more data about their bodies and lives [8–10]. This emerging field of technology will have a dramatic impact on human-machine interaction. Compared with the rapid growth of wearable technology like fitness tracker, smartwatch, GPS tracker and other categories, smart clothing represents less than 1% of the global wearables market [1,11,12]. According to a recent survey of 2407 consumers in developed and emerging markets of wearable technologies, public awareness is at a minimum level regarding smart clothing and e-textile products [11]. Therefore, recent research trend in flexible electronics demands an increasing popularity in ‘Smart e-clothing’, prospecting a larger global market in the near future. Moreover, the tremendous development of portable electronics urgently demands for sustainable, smart wearable energy sources that can spontaneously provide electrical power to the daily used smart electrical products. This is now one of the biggest technical challenges also. Looking at the lack of expansion and adoption in this category, the vision of our scientific output is towards increasing competitiveness in the field of smart fiber-based innovative technical textiles, mainly for energy applications - answer of alternative sustainable energy power plant! Our newly prototyped design of human-motion interactive energy harvester based on polymer functionalized free-standing textile fibers will bring to bear a vast variety of fields, from direct weaving in clothing system to inserting into different kind of daily usage articles like sofa, bed, car seat, chair, carpet etc. Considering existing huge garment industries, this human-motion interactive textile power harvester will start a new era, which can also promote a new business strategy in other essential industry sectors, such as health care and defence.

During the last decade, some research groups have reported on mechano-responsive energy harvesters, mostly based on either triboelectric [13–18] or piezoelectric [19–24] platform. Among them, very few reports are solely on textile fiber based energy harvesting system.
Triboelectricity is a phenomenon of contact electrification mechanism where two different kinds of material become electrically opposite charged if rubbed against each other. Static polarized charges arise on the materials surfaces due to the friction, and their separation by the back electrode (charges can flow through the back electrode of the material to the external circuit) creates a potential difference which further generates current. Usually in this mode, dielectric to dielectric and conductor to dielectric types of different materials are being used [25–27]. But herein, we report the noble observation of mechanical force stimulated energy harvesting from conjugated polymer, applied to free-standing textile fibres for human-motion induced wearable power energy source. In 2016, initially we have reported polyaniline as a stress-induced energy harvester [28]. These \( \sigma \)-conjugated polymers are fascinating materials with a unique combination of hard (metal like) and soft (organic like) matter which can be exerted to convert mechanical-stimuli to electrical potential energy [29–31]. It is not surprising that stimuli-responsive polymeric materials that exhibit a desired output (the response) upon being subjected to a specific input (the stimuli such as chemicals, heat, light, electricity, stress etc.) are evolving nowadays into an attractive class of smart materials which can be designed for different application fields ranging from camouflage systems to artificial muscles, human-motion interactive motor and drug delivery [32–34]. However, comparatively few polymers have been developed to respond in a useful way to mechanical stress. In that context, we consider this input-output relationship as an energy transduction process through converting mechanical energy to electrical energy. The core idea behind this is to initiate a mechano-responsive charge transfer mechanism (MRCTM) and energy-transfer process in a \( \sigma \)-conjugated polymer at the organic-metal interface layer [28]. The common building blocks of \( \sigma \)-conjugated polymers are mainly carbon atoms, scheme with alternating single and double bonds. The conjugation is a result of \( sp^2 \) hybridized carbon atoms, yielding three covalent s-bonds (i.e. localized \( \sigma \)-bonds) that form strong chemical bonds. The remaining \( p \) orbital is free to overlap with the corresponding \( p \) orbital of an adjacent carbon (i.e. \( \sigma \)-bond), formally leading to one unpaired electron per carbon that is delocalized over the molecule \( \sigma \), in the case of polymers, that allows carrier mobilities over large segments of the polymeric chain. The HOMO (valence band) and LUMO (conduction band) of \( \sigma \)-conjugated polymers are generally derived from occupied \( \sigma \)-bonding orbitals and unoccupied \( \pi^* \)-antibonding orbitals, respectively. Polyaniline (PANI) [35,36] encompasses a family of conjugated polymers where the nitrogen atoms connect six-membered carbon rings of benzenoid or quinoid character. However, conjugation is not sufficient to make it conductive until mobile charge carriers are introduced into the electronic system through doping. With primary and secondary doping, PANI shows an interesting feature [37,38] with plenty of mobile charge carriers, which can be tunable for desired electro-mechanics [39–41].

Very recent a few works have been reported on PANI based mechno-responsive energy harvesters [42,43] in which the authors have coated the 2D substrates like carbon mat or cotton piece with polyaniline. Moreover, those groups have obtained their best results for devices with additional triboelectric layers of PVDF or PTFE. But in the present report we have functionalized each individual textile fiber with d-PANI and designed them for harvesting mechno-responsive energy using purely electrode/d-PANI/electrode system. Our device is basically working on free standing d-PANI functionalized fibers (which can be considered as a 3D system) and the electrode was wound surrounding each functionalized fiber. This unique design of our system practically has the huge opportunity to increase the pressure contact area with increasing efficiency and can be further adopted easily into any form of garments or incorporated into any flexible/weearable systems.

2. Results and discussions

Herein, we have functionalized conductive fibers (commercial silver coated thread with 400\( \mu \)m diameter) by hydrochloric acid doped polyaniline (d-PANI) nanostructure. Fig. 1a shows the field emission scanning electron microscopic (FESEM, Carl Zeiss Auriga Crossbeam microscope) image of a d-PANI functionalized conducting textile fiber (f-CTF). Center inset of Fig. 1a shows the zoom in on d-PANI layer and the upper inset image shows the normal view of an f-CTF. The corresponding EDS elemental mapping (using Oxford XMax 150) of uncoated CTF and f-CTF is shown in Fig. S2 and Fig. S3 respectively (supporting information). The thickness of the d-PANI layer is approximately 400–450 nm over 400-\( \mu \)m diameter conductive fiber, which is uniformly coated with our optimized wet chemical method. Details of synthesis have been described in experimental section. The cross-sectional FESEM image of f-CTF has been shown in Fig. S4 in the supporting information.

2.1. Investigation on localized mechno-responsive charge transfer mechanism (MRCTM)

Before exhibiting the mainstream approach of measuring human-motion interactive current harvesting from f-CTFs, we have first explored the localized charge transfer mechanism at the metal-conjugated polymer (i.e. d-PANI) layers based on free-standing textile fiber by atomic force microscopy (AFM) technique. The most unavoidable primary requirement to any device performance depends on the interface dynamics of the materials which is very relevant given that a new unexpected phenomenon may occur and may dramatically change materi-

![Fig. 1. Localized study of mechno-responsive charge transfer mechanism (MRCTM) on d-PANI functionalized textile fiber (f-CTF). (a) FESEM image of d-PANI functionalized layer on a textile fiber. Center inset shows the higher magnification of d-PANI nanostructure and top inset shows the normal view of f-CTF. (b) Schematic illustration of AFM based characterization on MRCTM. (c) Output current response from d-PANI surface for typical three different contacting forces of 8, 12 and 16 mN delivered by AFM probe. Each applying force conferring for 1s which shows that the output current increases with increasing applying forces. (d) Schematic illustration (not in scale) on probable systematic investigation on MRCTM: d-PANI layers arranged with uniform molecular networks at undisturbed condition → localized stress delivered by the top electrode to the d-PANI layer → molecular networks contracted → generating Fermi level pinning due to increasing localized charge carrier density → initiating a charge transfer mechanism from nearest energy level of metal electrode (SDCC electrode) → yielding current generation → stress releasing → causing molecular networks stretching → creating decrease in localized charge density → Fermi level de-pinning → charge carriers tunnels from nearest polymeric energy level or back electrodes.](image-url)
als properties and result in new useful functionalities such as electronic memory effects [44] etc. Henceforth, as many nanomaterials procure their applications in nanoelectronics, characterizations of localized electronic transport mechanism through the interface of material are not only pursued in fundamental science but also of widespread practical need.

In this work, we have used conductive AFM (c-AFM) [34,39] and electrostatic force microscopy (EFM) [45,46] technique for a detailed investigation on nanoscale localized probe induced mechanosensitive effect through direct visualization of electrical mapping of d-PANI layer. Metal coated AFM nanoprobe was used to impart localized stress on the d-PANI layer deposited on conductive textile thread, as shown with schematic in Fig. 1b. Fig. 1c exhibits a systematic investigation of mechano-responsive current output for three different forces applied through the AFM probe in contact mode without applying any electrical bias, with a retaining time of 1 s for each. The electrical response is increasing according with the increment of applied force. This nature can be exerted as the pumping of mobile charge carriers from d-PANI to nearest energy level of stress delivered metallic electrode. The following is our phenomenology that can be explained by charge transfer mechanism in the conjugated polymer system, dealing with the mechanoresponsive effect of output current which is illustrated as MRCTM in Fig. 1d.

In MRCTM, actually two electrodes act differently during stressing and stress-releasing, depending on the metal/polymer interface layer formation. The “back electrode” act as a static electrode where the d-PANI layer is deposited, and in this case the metal/polymer interface is formed chemically. The other electrode (i.e. top electrode) acts as a stress-deliverer, charge-collector (SDCC) electrode, for which a metal/polymer interface is transiently created upon the application of a stress by the electrode to the d-PANI layer. When the mechanical force is exerted into the polymeric surface through any chosen point by the SDCC electrode, the molecular structure at that point experiences a mechanical deformation, which leads to a localized squeezing between molecular chains (schematic as shown in stress-developed condition). As we stated initially that the d-PANI exhibits a metallic character (degenerate medium with the Fermi energy level in delocalized states due to disorder), typically the mobile ions (charge carriers arise due to π-π antibonding) become over crowded in that deformed area, which will possibly give rise a localized Fermi energy level pinning. Therefore, the localized mechanical stress creates a tiny non-uniform energy state, which is further initiating a charge transfer mechanism between the SDCC electrode and the d-PANI layer. Now, it is interesting that the mobile charges from the Fermi level in d-PANI system jump into the nearest available energy level, i.e the energy level in the SDCC electrode, not to the back electrode which is far away from the stressed area. Therefore, during stress the SDCC electrode, which will embed a stress on the d-PANI layer, will actively take part in the charge transfer mechanism through the metal/polymer transitory interface layer. This nature is quite equivalent to the energy pumping by mechanical stimuli which generates a flow of electrons through the polymer/metal interface layer, therefore giving rise to a current. Now, when the stress is released, the squeezed polymeric chain becomes unfettered again, causing localized Fermi level depinning with scarcity of charge carriers (schemed as shown in stress-released condition), and creating a localized nonuniform electrostatic field. The scarcity of charge carriers in the stressed region is further balanced by the energy transfer from the nearest energy level between the d-PANI layers from neighbour polymeric chains through hopping conduction mechanism. Additionally, some of the charges are also transferred from the back electrodes on which the d-PANI is functionalized.

EFM technique was commenced further for visualization of mechano-responsive charge distribution pattern in the d-PANI layer through direct imaging of localized electric field gradient before and after stress developing on the sample surface. EFM has emerged as a powerful tool for exploring the nanoscale charge propagation dynamics through electrostatic mapping of the materials surface [45,46]. A constant dc bias has been applied between probe and samples surface, causing an EFM phase shift in the oscillation resonant frequency of the cantilever to monitor variations in the electrostatic field between sample and probe, corresponding to the different regions of the sample. Fig. 2a and b represent the mapping of localized charge distribution in the same region of d-PANI layer before and after applying the mechanical stress, respectively. The first image was scanned with tip lift-off height of 50 nm above the filament where the electrostatic field was acted using probe bias V_{Probe} = 3 V. In the next step, the mechanical stress was applied through the probe in the middle region (1 × 1 μm²) of the previous scanned area in contact mode. After that, again an EFM scanning was performed in the same region, keeping all the measuring data unaltered. Different colour contrast in the images which is basically a representation of EFM phase shift, can be attributed to dissimilarity of localized charge distribution pattern in the d-PANI layer. Fig. 2c and d shows the lateral and vertical line profiles of corresponding EFM mapping images. A gradual change in the surface charge distribution phase shift (Δφ) is observed and is maximized in the middle of the

![EFM and c-AFM study through direct visualization electrical image based on mechano-responsive effect. Visualization of localized electrostatic charge distribution image of d-PANI layer (a) before and (b) after stress has been applied through AFM nanoprobe in contact mode. Stress has been applied in the 1 × 1 μm² scanning area, middle of the 3.5 × 3.5 μm² of EFM images. (c) and (d) show the vertical (black dotted lines in EFM images) and lateral (white dotted lines in EFM images) line profile spectra of both electrostatic charge distribution images. A prominent phase shift (Δφ) has been observed before and after stresses which indicates an existence of mechano-responsive charge transfer mechanism. (e) Shows the scanning image of mechano-responsive electrical response effected by different external applied biased from 0 to 225 mV in steps of 25 mV. As the mechano-responsive output current is in negative polarity, a positive voltage is applied to oppose that current generation. (f) Corresponding plot of average electrical response with different bias. It has been noticed (pointed by dotted circle) that after applying 75 mV, the output current changes its polarity from negative to positive, indicating that mechano-responsive current harvesting is suppressed by the external voltage generating current.](image-url)

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stressed region, as a consequence of the charge flow from the un-stressed area of d-PANI layers to the stressed area after stress-releasing. Hence, this type of phase shift pattern in EFM mapping corroborates our MRCTM scheme.

To further demonstrate the visualization of the output current from d-PANI layer, we have also performed current mapping in contact mode with constant force embedding by the AFM probe but with different applied bias from 0 to 225 mV (Fig. 2e). As we have already noticed before, d-PANI surface generates negative current when the AFM probe scans its surface with force even without applying any external bias voltage (please see Fig. 1c). Under a positive bias, a prominent functional change in output current from negative to positive is observed. Due to the probe induced localized stress, mechano-responsive current harvesting from the d-PANI surfaces is negative, which is an evidence for yielding of negative voltage. To counteract the effect of mechano-responsive current harvesting, a gradual increment of positive external bias through the AFM probe has been introduced. Fig. 2f shows the average of output current for 0–225 mV in steps of 25 mV. It can be observed that the output current is negative until applying the positive bias of 75 mV, after which it is noticed that the output current is negligible (shown by the dotted circle), indicating that the mechano-responsive generating voltage is completely neutralized by the opposite external field (which is approximately 75 mV). Above this 75 mV external bias, the output current started to be positive, indicating an influence of external bias over the mechano-responsive current harvesting. This is a localized charge transportation dynamic studied by the conductive AFM mechanism, to correlate the mechano-responsive voltage with the external applied voltage.

2.2. Human-motion interactive textile energy generatrix (HiTEX) device

To investigate the feasibility of d-PANI functionalized textile fibers for the application of smart wearable energy generator from human motion, we have integrated arrays of f-CTFs (each with 9 cm length) in parallel, after a sinusus stream weaving with another conducting textile fiber (with lesser diameter ~150 μm) to form a HiTEX, shown in Fig. 3b. The style of weaving is shown by the schematic diagram in Fig. 3a. The FESEM image shows the small portion of integrated f-CTF from HiTEX. There are two functional electrodes which are particularly designed for different purposes in HiTEX. The first electrode is the thinner conductive textile fiber (150 μm diameter) which was used to wrap the d-PANI functionalized fiber, acting as stress-deliverer; charge-collector (SDCC) electrode. The second electrode is the metallic layer of 400 μm diameter textile fiber, which was used for back electrode substrate, where the d-PANI has been functionalized, usually acting as ground electrode. We have discussed earlier that most probably this electrode acted as supply chain of mobile charge carriers, which are initiated to transfer from d-PANI layer to SDCC electrode.

On the human-motion interactive application platform, we have recorded open-circuit output voltage ($V_{oc}$) and short-circuit output current ($I_{sc}$) from our HiTEX device under stress induced/released sequences, generated by hand patting. Fig. 3c and d shows the output performance of HiTEX which has been determined by measuring single

**Fig. 3. Human-motion interactive textile energy generatrix (HiTEX).** (a) Shows the schematic with FESEM image of the knitted f-CTFs. (b) HiTEX designed by 16 f-CTFs, each with 9 cm length. The f-CTFs were covered with thin PDMS layers. (c) and (d) show the single period for motion-induced effect on open-circuit voltage ($V_{oc}$) and short-circuit current ($I_{sc}$) respectively. There are two states in output signals. One forward signal which is due to charge transfer at the stress-induced condition. Another is the reverse signal, which is due to stress-released condition. (e) and (f) show the $V_{oc}$ and $I_{sc}$ for different numbers of f-CTFs from 1, 2, 8 and 16, each f-CTF with 9 cm length. Inset shows the nature of increment of average $V_{oc}$ and $I_{sc}$ with the number of fibers integrated into HiTEX.
period of $V_{ac}$ and $I_{ac}$. A forward output signal ($V_{ac}$ or $I_{ac}$) is generated upon stressing the f-CTFs. This spontaneous forward voltage or consequently current has been produced due to mechanical stress impelled on the metal/d-PANI interface layer which will be commencing a charge transfer mechanism through the interface. As previously explained, this feature can be conceptualized by localized Fermi level pinning charge transfer initiator. In contrast, upon the releasing of mechanical stress, a reverse output signal is produced. This phenomenon can be explained by localized Fermi level depinning stage. As discussed below (Fig. 1d), after the releasing of mechanical stress, localized area in d-PANI layers became extended, creating localized Fermi level depinning, by scarcity of charge carriers, which are already transferred at the stress-induced period. Therefore, to get electrostatic stability, the charge will flow to the ruptured polymeric area by the back electrode or nearby polymeric energy level through tunnelling process. As the flow of this charge carrier due to scarcity is in opposite direction, it generates a voltage or a current in opposite polarity but, as expected, with a lower value. Also, this feature is much slower with irregular and less uniform value than the forward output signals.

Given that, HITEX is much slower with irregular and less uniform value than the forward output signals.

Real time videos of output voltage for the HITEX, responding to different forces of patting, bending and even to soft touch are shown (Supporting Video SV1, SV2, SV3, and SV4). Fig. 4a demonstrates that with the motion induced by patting on HITEX, the MRCTM charge density increases from 0 to 260 $\mu$C.m$^{-2}$ in 30 s against the commercial capacitor of 10 $\mu$F. Therefore, the amount of spontaneous charge transferred during the operation of MRCTM is approximately 20 $\mu$C.m$^{-2}$. The instantaneous power output ($W = F^2R$) was calculated from the output voltage against different loads. Fig. 4b shows the variation in peak current density and power density versus external loading resistance of the HITEX based on MRCTM. The current density decreases with the increased external load from 1 k$\Omega$ to 10 M$\Omega$, and the peak power density reaches 0.6 W.m$^{-2}$.

Supplementary data related to this article can be found online at [https://doi.org/10.1016/j.nanoen.2019.04.012](https://doi.org/10.1016/j.nanoen.2019.04.012).

For realizing the practical application of MRCTM based power harvester, we have used a rectifier circuit to have a dc output and charged a commercial 10 $\mu$F capacitor, as shown in Fig. 4c. With simple patting by hand, the power delivered from our HITEX can charge the 10 $\mu$F commercial capacitor to 3 V just in 80 s (please see the supporting information in Fig. S2 and Supporting Video SV6). This data confirms the potential applicability of the newcomer d-PANI functionalized HITEX because it is very much comparable to some recent publication by renowned Z.L. Wang group for their hybrid power textile [54] which can charge a 2 mF commercial capacitor up to 2 V in 1 min under ambient sunlight in the presence of mechanical excitation. As a next step, after charging the capacitor up to 3 V, it was discharged through 5 white LEDs in saturated power. Those LEDs have enough power to light up our university logo in a dark room, as shown in Fig. 4d. Ten commercial white LEDs with 2.5 W were also powered (real-time data captured video is shown in the supporting information, Supporting Video SV5) by the instantaneous patting on HITEX, without the need for the rectifier circuit and the commercial capacitor. Moreover, the procured energy from HITEX was used to power commercial portable devices like LCD digital temperature-humidity-time display meter, digital stop-

### Table 1
The output current, voltage and power density are presented in the table below, just to give a scenario of our standpoint with respect to the literature where very few groups have reported on directly textile-based energy harvesting systems (based on the piezoelectric and tribo-electric behaviour of the active materials).

<table>
<thead>
<tr>
<th>No.</th>
<th>Key materials used for textile-based energy harvesters</th>
<th>Human-motion interactive energy harvester</th>
<th>$V_{out}$</th>
<th>$I_{out}$</th>
<th>Maximum power density</th>
<th>Year of Publication</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>ZnO nanowire arrays</td>
<td>Piezoelectric</td>
<td>3 mV</td>
<td>4 mA</td>
<td>16 mW.m$^{-2}$</td>
<td>2008 [19]</td>
</tr>
<tr>
<td>2.</td>
<td>Lead zirconate titanate (PZT) textile composed of aligned parallel nanowires</td>
<td>Piezoelectric</td>
<td>6 V</td>
<td>45 nA</td>
<td>200 $\mu$W/cm$^2$</td>
<td>2012 [47]</td>
</tr>
<tr>
<td>3.</td>
<td>PVDF–NaNbO$_3$ nanofiber nonwoven fabric</td>
<td>Piezoelectric</td>
<td>3.4 V</td>
<td>4.4 $\mu$A</td>
<td>...</td>
<td>2013 [48]</td>
</tr>
<tr>
<td>4.</td>
<td>Polyester–Nylon</td>
<td>Triboelectric</td>
<td>90 V</td>
<td>1 $\mu$A</td>
<td>...</td>
<td>2014 [49]</td>
</tr>
<tr>
<td>5.</td>
<td>Polyethylene–Ni based cloth</td>
<td>Triboelectric</td>
<td>50 V</td>
<td>4 $\mu$A</td>
<td>393.7 mW.m$^{-2}$</td>
<td>2015 [50]</td>
</tr>
<tr>
<td>6.</td>
<td>Al nanoparticles–PDMS</td>
<td>Triboelectric</td>
<td>368 V</td>
<td>78 $\mu$A</td>
<td>33.6 mW.m$^{-2}$</td>
<td>2015 [51]</td>
</tr>
<tr>
<td>7.</td>
<td>ZnO nanorod arrays on a Ag-coated textile template</td>
<td>Triboelectric</td>
<td>170 V</td>
<td>120 $\mu$A</td>
<td>...</td>
<td>2015 [52]</td>
</tr>
<tr>
<td>8.</td>
<td>PDMS-covered Ca-coated ethylene vinyl acetate (EVA) tube</td>
<td>Triboelectric</td>
<td>12.6 V</td>
<td>0.91 $\mu$A</td>
<td>...</td>
<td>2016 [53]</td>
</tr>
<tr>
<td>9.</td>
<td>Polytetrafluoroethylene (PTFE) stripes</td>
<td>Triboelectric</td>
<td>~90 V</td>
<td>~75 $\mu$A</td>
<td>...</td>
<td>2016 [54]</td>
</tr>
<tr>
<td>10.</td>
<td>Silicone rubber</td>
<td>Triboelectric</td>
<td>150 V</td>
<td>2.9 $\mu$A</td>
<td>85 mW.m$^{-2}$</td>
<td>2017 [17]</td>
</tr>
<tr>
<td>11.</td>
<td>Silicone rubber</td>
<td>Triboelectric</td>
<td>540 V</td>
<td>140 $\mu$A</td>
<td>0.892 mW.m$^{-2}$</td>
<td>2017 [55]</td>
</tr>
<tr>
<td>12.</td>
<td>Foam</td>
<td>Triboelectric</td>
<td>70 V</td>
<td>46.6 $\mu$W</td>
<td>...</td>
<td>2017 [56]</td>
</tr>
<tr>
<td>13.</td>
<td>Silicone rubber</td>
<td>Triboelectric</td>
<td>300 V</td>
<td>200 $\mu$A</td>
<td>...</td>
<td>2017 [57]</td>
</tr>
<tr>
<td>14.</td>
<td>PVDF</td>
<td>Triboelectric</td>
<td>3.5 V</td>
<td>...</td>
<td>1.9 $\mu$W/cm$^2$</td>
<td>2018 [58]</td>
</tr>
<tr>
<td>15.</td>
<td>Polyamide coated on carbon mat and PVDF combined system</td>
<td>Triboelectric</td>
<td>95 V</td>
<td>180 $\mu$A</td>
<td>...</td>
<td>2018 [42]</td>
</tr>
<tr>
<td>16.</td>
<td>Polyamide coated torn apron piece and PTFE (layered device)</td>
<td>Triboelectric</td>
<td>350 V</td>
<td>45 $\mu$A</td>
<td>11.25 W.m$^{-2}$</td>
<td>2019 [43]</td>
</tr>
<tr>
<td>17.</td>
<td>Polyamide functionalized free-standing textile fiber</td>
<td>MRCTM</td>
<td>116 V</td>
<td>22.5 mA.m$^{-2}$</td>
<td>0.6 W.m$^{-2}$</td>
<td>2019 (Our present report)</td>
</tr>
</tbody>
</table>

*We have also included here the results of Z.L. Wang group published in 2016 regarding hybrid power textiles, but only mentioned the human motion induced contribution from them (as they have also solar cell and supercapacitor devices in these fibers). # They have used 20 substrates (carbon mat or cotton piece) to coat polyamide, also for device structure another triboelectric counterpart like PVDF or PTFE have been used.
watch etc (please see Fig. 4d; corresponding real time video is shown in Supporting Video SV7). We have also tested the robustness and durability of the functionalized fibers through different kind of bending tests and huge number of patting over six months. Its energy harvesting properties remain essentially unchanged, as exemplified in Fig. 4 for a representative sample. Fig. 4e and f shows the average output voltage and current after completing 5000 numbers of patting as each interval. As the patting on the devices is not applied through a machine, we have counted it for several months. Each time after completing 5000 times of patting we took an average of 10 consecutive output current and voltage data and noted it. The data as shown in the figure is an approximate average value. Even after patting more than 100 thousand times, HiTEX has shown negligible changes in its electrical performances. Hence, our newly designed HiTEX based on polyaniline as a conjugated polymer is sustainable enough for practical applications.

Supplementary data related to this article can be found online at https://doi.org/10.1016/j.nanoen.2019.04.012.

3. Conclusion

We have shown for the first time human-motion interactive power harvesting from single textile fiber, where d-PANI as a conjugate polymer has been used as the active layer. A simple metal/polymer (semiconductor in nature)/metal structure has been deployed to the way of motion induced power harvester device through MRCMT. Direct visualization of emerging current and electrostatic field distribution pattern over the d-PANI functionalized fibers have been demonstrated by AFM, which suggests that the charge transfer mechanism has been incited at the metal/polymer interface layer due to applied stress induction. By introducing the MRCTM model for conjugated polymer, this report has exhibited super-flexible, robust, light weight, low-cost sustainable energy wearable modules, which is strong enough to take a challenge of next-generation wearable energy plant. As a very initial candidate in the field of reported textile oriented energy harvester platform, we have reported 0.6 W m⁻² impulsive power density. Each single functionalized fiber is a generatrix of sustainable energy. Our prototype textile based energy harvester device responds stably over 100 thousand times of patting, bending for six months without any degradation. Energy harvesting based on mechano-responsive platform, our recent scientific outturn have opened up a new route using π-conjugated polymeric materials.

4. Experimental methods

4.1. Materials

Commercially available silver coated conductive textile fibers, CTF (Diameter 400 μm, Statex, Germany), were used as the core fiber material for further coating process with doped polyaniline (d-PANI). Aniline from Sigma-Aldrich has been used as the monomer to form PANi through a simple and cost-effective wet chemical oxidation polymerization route. Each time it was distilled under vacuum, prior to use in the polymerization process. Ammonium persulfate (APS; 99.99%, Aldrich) was the oxidant used during the reaction. Besides, hydrochloric acid (HCl) and D-10-camporosulfonic acid (CSA, Aldrich) were used as dopant and surface functionalization element, respectively, for the current fibers coating procedure. All of these chemicals were used as received without any prior purification process. Deionized water (DI wa-
4.2. Coating with d-PANI

The commercial fibers were at first cleaned with dip immersion in ethanol for 15min, followed by washing with DI water several times. After that they were set inside the reaction vessel having one end covered with kapton (to avoid polymer coating on that end and also to have access to the metal core contact). Initially, the fibers used were of 9 cm in length; but the process is now adapted for longer fiber as well. Meanwhile, the solutions for the reaction were in making. Aniline and CSA were added in 4:1 M ratio to 20 mLDI water to make a colourless aqueous solution of Aniline-CSA complex and left for cooling in an ice bath (0 °C). In a separate container, the oxidant APS was dissolved in 10 mL DI water, followed by mixing of 100 μL of HCl into it. This was also set for pre-cooling process in the ice bath, before starting the main polymerization process. Aniline and APS were used in a 1:1 M ratio for the optimized test. This mixture was then added dropwise to the Aniline-CSA complex solution, while vigorously shaking the latter. The final mixture was immediately transferred to the reaction vessel (already set with fibers at 0 °C in an ice bath) to continue the polymerization process without any further agitation for the next 1 h. After 1 h, the fibers were taken out from the solution and thoroughly washed with DI water for several times to remove residuals. Also, with the final rinsing of fibers with methanol for three times, the removal of any excess monomer or oligomers was ensured. After this chemical deposition, a uniform dark green coating of d-PANI was obtained throughout the surface of the fibers. Finally, compressed air was passed smoothly over the surface of coated fibers for few minutes and then these functionalized conducting textile fiber (f-CTF) were stored in ambient environment for a few days before making the energy harvesting system.

4.3. Fabrication of HITEM

Each f-CTF was wrapped up with different number of windings with another commercial silver-coated conductive textile fiber (150 μm diameter) in a manner so that, the uncoated metallic end of the thicker fiber (the one end of the f-CTF which was left covered with kapton during polymer coating to further access its conductive core) was used as one electrode to reach the polymeric part, and the other electrode was obtained from taking contact to the thinner metal coated fiber on the other side. The as-woven system was protected from usual mishandling with a thin polydimethylsiloxane (PDMS, purchased from Syllgard 184) covering (elastomer to curing agent ratio of 10:1, curing at 65 °C). The contacts were taken outside this PDMS cover and connected through copper tape (3M) to the electrical measurement systems. Different number of windings and fibers have been systematically covered by the PDMS system according to the measurement requirements.

4.4. AFM analyses

AFM measurements in electrical mode were done by Asylum Research MFP-3D Stand-alone system using commercial Pr→Ir tip coated probes. The electrical data recorded under the different applied forces was measured with standard calibration. Measured data was analysed with the Asylum Research tools developed within the IGOR Pro 6.22A data analysis software.

Author contributions

S.G and S.N designed the experiments and wrote the manuscript. S.G developed the materials and functionalized the textile fibers. A.S, S.N and S.G performed the electrical experiments. S.N performed the AFM experiments. All the authors discussed the results, commented and reviewed the manuscript thoroughly.

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Appendix A. Supplementary data

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References
