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Touch-Interactive Flexible Sustainable Energy Harvester and Self-Powered Smart Card

Easy processable paper based mechano-responsive energy harvester prepared from polyaniline-functionalized raw paper in a cost-effective way. Prototyped “eco-energy” smart card can work as a portable power plant, which is able of powering several light-emitting diodes (LEDs) or portable devices. The vision of the present work is to create a sustainable world through adopting zero e-waste and clean energy.

Touch-Interactive Flexible Sustainable Energy Harvester and Self-Powered Smart Card

Guilherme Ferreira, Sumita Goswami, Suman Nandy,* Luis Pereira, Rodrigo Martins, and Elvira Fortunato*

Sustainable and safe energy sources combined with cost effectiveness are the major goals for the society when considering the current scenario of massification of portable and Internet of Things (IoT) devices along with the huge amount of inevitable e-wastes. The conceptual design of self-powered “eco-energy” smart card based on paper, exacerbates green and clean energy, which will bring zero e-waste challenge one step closer to fruition. Commercial raw filter paper is modified through a fast in situ functionalization method, resulting in a conductive cellulose fibers/polyaniline composite, which is then applied as an energy harvester based on mechano-responsive charge transfer mechanism through metal/conducting polymer interface. Different electrodes are studied to optimize charge transfer based on contact energy level differences. The highest power density and current density obtained from paper-based “eco-energy” smart card device are 1.75 W m^{-2} and 33.5 mA m^{-2} respectively. Also, this self-powered smart energy card is able to light up several commercial light-emitting diodes (LEDs), power on electronic devices and charging capacitors.

1. Introduction

In 21st century, with our growing appetite for new age smart electronic products together with rapid innovation and ever-shorter product lifespans, electron/electrical waste (e-waste)^[1–4] is gradually turning into one of the biggest threats to our planet. On top of all the issues related with pollution, hazard, and negative impacts in sensitive ecosystems, the e-waste is also complex and expensive to treat in a sustainable sound manner. The world produces more than 50 million tons of e-waste each year, worth over \$62.5 billion, among which only 20% of this is formally recycled.^[5,6] However, we cannot stay away from this faster digitalization where tremendous advancement in wearables and portable smart electronics^[5–9] imposes low-cost, wireless, and light energy sources that must include green and sustainable materials/technologies^[10–14] to become

effective in reducing e-waste. When it comes to portability, cost effectiveness and green technology altogether, the contribution of energy harvesters which convert the wasted energy from ambient environment or human body motion into electrical energy for diverse applications is an absolute accomplishment.^[15–18]

The triboelectric or piezoelectric materials are already being explored in the area of mechanical energy harvesters.^[19–22] In this particular, conjugated polymer like polyaniline is a low-cost option in this row. Some recent reports^[16,23,24] have presented the huge potential of this conducting polymer in the energy research topics though it has been immensely investigated and studied in other applications such as electrochemical cells,^[25] supercapacitors,^[26,27] electrochromic windows,^[28] antistatic coatings,^[29] corrosion protection,^[30] electrorheological fluids,^[31] memories.^[32,33] The unique prop-

erty of this renowned member of π -conjugated polymer family is that its physical and chemical properties can be easily modulated through simple doping-dedoping processes and also it can act both as donor-acceptor system through the π - π^* interaction in its backbone.^[34–36] On the other hand, paper which is one of our daily used essential commodities, is also being currently exploited as the substrate in flexible smart electronics and smart packaging^[37–41] due to its low-cost, light weight, superflexible, environmental-friendly, disposable, or easy recyclable qualities. Therefore, to combine both these materials into a single active material to act as mechanical energy harvester will be of great relevance to approach the critical demand for low-cost and green energy, simultaneously dealing with zero e-waste challenge.^[42] Some recent paper-based energy harvesters comprised of conductive active material, e.g., carbon nanotubes, graphene, conducting polymers^[43–45] have shown that the basic structural unit of paper (cellobiose units) can act as a network for ion-transport during the process. Though most of the works have presented the supercapacitor-based application^[46,47] and a very few reports are on the mechanical energy harvesting,^[48,49] leaving an enormous scope of improvement in this field of low-cost technology.

2. Results and Discussions

In the present work, we have reported a low-cost and simple paper based energy harvester responsive to human

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Figure 1. a) Schematic layout of the in situ polymerization of raw filter paper by two-step drop cast method at room temperature. b) Digital image of the polyaniline functionalized conducting paper or pfc-paper. The dark green coloration of both sides of pfc-paper indicates that the paper was fully functionalized with conductive PANi. Corresponding FESEM images of both sides of pfc-paper shown in c,d) with inset high-resolution image of cPANI nanostructures. e) Raman spectra from both sides of pfc-paper and raw filter paper. Identical spectra from both sides of pfc-paper indicate the thorough functionalization of paper with cPANI.

touch-interaction or motion, targeting accumulation of waste energy dissipated by our body movements into the sustainable electrical energy through high performance eco-friendly systems that could be integrated safely into any objects for an improved quality of safest life in future. Our conceptual work promotes zero e-waste challenges toward the step of greener and cleaner world. Filter paper has been functionalized in situ with conductive PANi following an easy and fast wet-chemical route at room temperature. After drying out completely, the functionalized paper (which is operating as a Charge Translocation Layer, CTL) is then clipped with metallic electrodes (acts as a Charge Collector Layer, CCL), which is further connected to the external load. The active CTL made of PANi-Paper combined system is highly conductive, which can start to transmute mobile charge carriers into metallic electrode through the interface during mechanical stimuli. We have designed our paper-based prototype-device in the form of “eco-energy” smart card, applicable for human touch-interactive energy harvester. Also, this harvested energy from smart card has been applied to glow several LEDs or charging capacitors for powering portable device. This kind of harvested energy can be also applied in wireless connectivity.

2.1. In Situ Polymerization of Paper: Surface and Chemical Structure Analyses

Conducting paper through in situ functionalization of raw paper (designed with arrays of typical printed wax-wells) was

developed by a simple two-step drop-casting wet-chemical method using aniline and its cochemicals. The drops of reagent solutions were absorbed by the paper and consequently the constituent cellulose fibers were entirely functionalized with conductive phase polyaniline (cPANI). In-details paper functionalization procedure has been explained in experimental section in the Supporting Information. **Figure 1a** illustrates all the experimental steps toward developing a fully polyaniline-functionalized conducting paper (pfc-paper). Also, in situ polymerization of pixelated paper has been shown in real-time video SV1 in the Supporting Information (drop-casting oxidant based solution: Solution A) and SV2 in the Supporting Information (dropcasting monomer based solution: Solution B). **Figure 1b** shows the digital image of pixelated pfc-paper. The dark green coloration of both sides of pfc-paper indicates that the cPANI does not grow just as a separated nanostructure form on the paper and the raw paper has been functionalized inwardly. The reactant monomer enters into the paper by osmosis process and is converted into polyaniline which helps to make a complete conjoined system between cPANI nanostructure and paper fibrous microstructures. The Field Emission Scanning Electron Microscope (FESEM) images of both sides of pfc-paper have been shown in **Figure 1c,d**. Morphological features of both sides are also quite similar except the back side looking a little bit smoother. It can be ascribed to the fact that as the reagent solutions were directly dropped on the front surface and the back side has the reagents due to absorption, henceforth, the front surface has more polymeric overgrowth than the back one and thus seeming rougher in

its SEM image. Nevertheless, high-resolution images (Insets figures) of both sides depict that the cPANi nanostructures are morphologically quite identical. For further interest, FESEM of unfunctionalized paper (Figure S3, Supporting Information) and EDS elemental mapping (Figure S4, Supporting Information) of pfc-paper are given in the Supporting Information.

2.1.1. Raman Spectroscopy

The chemical characteristics of pfc-paper were studied by Raman spectroscopy on both sides and compared with that of the raw paper (Figure 1e). Both sides of the pfc-paper have very similar spectra except few insignificant changes in intensity of some bands. The characterized peaks are typically bearing the identity of doped conductive PANi according to literature.^[50,51] The strong band at 1591 cm⁻¹ is due to the C=C stretching vibrations in the Quinoid (Q) rings. The shoulder peak at 1562 cm⁻¹ can be attributed to C—C stretching in quinoid units whereas the strong peak at 1478 cm⁻¹ is representing the C=N stretching vibration in Q rings. The band at 1336 cm⁻¹ with a shoulder at 1371 cm⁻¹ is associated with the presence of C—N^{•+} vibrations in the delocalized polaronic structures. The weak peak at 1246 cm⁻¹ is ascribed to the C—N stretching vibrations of Benzenoid (B) rings. The very strong intensity band at 1164 cm⁻¹ is due to the C—H bending vibrations of the semiquinoid rings which corresponds to the cation-radical segments. The peaks at 878 and 810 cm⁻¹ arise from C—N—C wagging and or B ring deformations in the polarons or bipolarons of emeraldine salt structure of the polymeric backbone and substituted B ring deformations respectively. The bands at 609 and 575 cm⁻¹ are attributed to the vibrations of B ring deformations and phenoxazine-type units respectively. True identical peaks as observed for both sides of the pfc-paper indicate that the in situ functionalization can fully make a composite of cPANi with paper.

2.1.2. Electrostatic Force Microscopy

Looking at the nanoscale charge-transportation dynamics through nanoengineering, electrostatic force microscopy (EFM) technique^[52] is the most convenient one for getting information with direct visualization of trapped charge distribution in the embedded systems. Figure 2 represents the topographical image with corresponding localized mapping of charge distribution in raw and pfc-paper, based on total electrostatic potential between AFM cantilever and surface of the system. Charge trapping in the embedded systems is explicated from the color mapping in EFM images, where color scale is defined by phase difference, $\Delta\phi$ (in degree) = contact potential difference between AFM probe and sample surface.

$$\Delta\phi \propto 1/\frac{\partial^2 C}{\partial Z^2}$$
 C and Z are probe-sample capacitance and separation respectively.

A clear information of embedded trapped charge distribution effect in pfc-paper has been observed through different color contrast in EFM pictures between raw (Figure 2c) and functionalized (Figure 2d) paper. Corresponding histogram of

EFM analytical images has been shown in Figure 2e. A widening feature of histogram depicts uniform distribution of embedded trapped charge due to in situ functionalization of paper by cPANi. Also, from the topography image it can be calculated that the r.m.s. roughness of the paper decreased after polymeric functionalization.

2.2. Self-Powered “Eco-Energy” Smart Card: Energy from Paper

In general, conjugated polymers (such as polyaniline) exhibit their electrical configuration starting from insulator to semiconductor to conductor depending on the level of doping-de-doping through oxidation or reduction. The electrical conductivity of these polymers arises due to introducing mobile charge carriers into the π -electronic system along the polymeric backbone through molecular doping. Higher doping level causes overlapping of π -orbitals of one monomer unit with those of its neighbors, which eventually raises the high electron mobilities along the intra or inter polymer chain with associated metallic behavior. This kind of doped polymer behaves like a soft-metallic material that can exhibit stimuli responsive functions, thus very useful to achieve an intended output after applying a specific input.

Figure 2. a,b) The topography images of raw paper and pfc-paper. c,d) Localized trapped charge distribution map of raw paper and pfc-paper, simultaneously measured in EFM mode. Phase difference in analytical image with color indications depicts the difference of trapped charge distribution between raw paper and pfc-paper. e) Corresponding histogram of EFM map.

Figure 3. a) Schematic diagram of self-powered “eco-energy” smart card; a prototyped human touch-interactive one electrode mechano-responsive energy harvester. b,c) Lateral and cross-sectional resistance of the pfc-paper. d) Electrical output (V_{oc}) recorded upon periodic mechanical stimuli. The V_{oc} was recorded for different pixelated matrices of pfc-paper as a CTL. It can be observed that V_{oc} increases linearly with increasing CTL area, i.e., number of matrices of pfc-paper. e) Snapshot of our experimental setup with prototyped “eco-energy” smart card.

To design our materials particularly for mechano-stimuli current-responsive functions, we in situ functionalized the paper with polyaniline to its best electronic conducting state where cPANi forms a strong 3D-network by making H-bonds with the existing hydroxyl (-OH) groups of the basic cellulose units, resulting in pfc-paper with good conductivity of 0.1 S m^{-1} . Moreover, a hybrid system between paper cellulose and cPANi nanostructure acted as soft-metallic sponge which can be enforced to expand/shrink through localized stress develop/release; consequently, resulting in charge transfer between pfc-paper and nearest metal electrode which further relates to the mechano-responsive energy harvesting. For testing new design toward the application for human-touch interactive paper-based energy harvester device, we have used pfc-paper as an active layer, responding for mechano-responsive charge transfer mechanism.^[16] Schematic of the prototype device named as “eco-energy” smart card has been shown in Figure 3a. Layer 3 and 2 are active as CTL and CCL, respectively. Layers 1 and 4 act as the protecting covers (paper or any flexible desired substrate can be used). Detail of device construction is explained in experimental section in the Supporting Information. Figure 3b,c shows respectively the lateral and cross-sectional resistance of a typical pfc-paper which is quite good for any homogeneous polymeric functionalized conducting paper.

The first measurement was performed by using commercial copper tape as CCL. The mechano-responsive output voltage from “eco-energy” smart card at stress induced/released sequences has been recorded by oscilloscope. Figure 3d shows its output performance which has been determined by measuring repetitively the open-circuit voltage (V_{oc}) generated for each sequential condition of stress developing/releasing state. This spontaneous electrical output is emanated due to the

mechanical stimuli indulged on the electrode/cPANi interface layers. It gives the notion of a charge transfer mechanism through their interface by delocalized electrons charge transfer initiator which is trapped into the cPANi systems. When the mechanical force is imparted upon the pfc-paper (CTL) through the electrodes (CCL), the cPANi molecular structure just beneath the force point, experiences a localized mechanical influence which leads to a localized distortion in molecular chains of the cPANi nanostructure. Also, cPANi exhibited a metallic behavior because of its degenerate medium with delocalized states along with its polymeric softness. Now, when the external mechanical stress is exerted into the cPANi layer, polymeric chain became denser in the localized deformed area, which will create a tiny non-uniform energy state. That non-uniform energy state will further initiate the charge transfer process between the nearest electrode and the cPANi layer through the Fermi energy level pinning at the interface. The mobile charge carriers from the Fermi level in cPANi system transmute into the most preferable energy level (i.e., the nearest energy level of the electrode), that came into contact with the polymeric surface during the time of mechanical stress, causing voltage generation and thus harvesting the electrical power. Afterward with unfettering of indulged stress, the squeezed polymeric chains become expanded causing scarcity of localized charge carriers, which creates non-uniform electrostatic field within the polymeric system again. Further, this shortage of charge in the unfettered portion is compensated through ions transfer from the contiguous energy level within cPANi system by hopping conduction mechanism. Therefore, upon releasing the mechanical stress, the system recovers to its initial position (with uniform charge distribution) before the next force impact could be implied. This recovery time is

very fast. For further convenience, the schematic diagram of the mechano-responsive charge transfer mechanism is illustrated in Figure S5 in the Supporting Information. Figure 3d shows the output voltage from the energy harvesting device using different pixelated area of pfc-paper as CTL. The average recorded output voltage with different matrices of CTL is approximately 25–30 V for 2×1 , 50–60 V for 2×2 and 70–75 V for 2×3 matrices, where each of the pixel functionalized area is 1 cm^2 . With increasing area of CTL, the generated output voltage is observed increasing linearly. Figure 3e shows the real measurement setup with our prototyped “eco-energy” smart card as an energy harvesting device. Throughout the measurements, average mechanical stimuli that has been applied to the devices, was maintained with 16 N force and 6 Hz working frequency. In addition, energy harvesting responses from this self-powered card has been shown in real-time SV3 in the Supporting Information. The force implied by hand patting used for the measurement systems, has been tested through tensile machine and average measured value impact force was around 15 N (Figure S6 in the Supporting Information).

Moreover, to investigate the mechano-responsive charge transfer mechanism based on the applied mechanical stimulus character, another series of electrical outputs were systematically recorded under different frequencies and impact forces. Figure 4a shows the open-circuit output voltage under various impact forces from 1 to 16 N with the fixed operation force frequency at 6 Hz. It is observed that with increasing impact forces, the output voltages increase. It can be noticed that below the implied force of 4 N, the output voltage increment is quite low (below 10 V) and it is rapidly enhancing in between 4 to 12 N. The phenomenon indicates that there is a threshold force impact after which the amount of charge transmutation increases rapidly. The peak voltages increase 6 times until the impact force reaches from 4 to 12 N. After that, raising forces even more up to 16 N, the V_{oc} increases a little. It is obvious that the charge transfer mechanism, which completely depends on the mechanical-stimulus effect on polymeric chains, will be prominently depended on the implied forces. The average maximum value of V_{oc} is recorded to be 75 V under the maximum impact force of 16 N. On the other side, no remarkable changes in the output voltage could be found under working frequencies from 1 to 6 Hz (in comparison to the changes observed for different applied forces) which is shown in Figure 4b. The output voltages are found marginally low at 1 to 2 Hz and with raising frequencies, a bit higher V_{oc} has been recorded which is quite stable in the operation frequency region of 3–6 Hz. Herein, the higher frequency that could make faster the duration of the charge transfer process, presumably enhances the output voltage value. This became saturated after a certain frequency. To exhibit the stability of

the device for continuous operation under a fixed consecutive implied force, the electrical outputs were tested for more than 1000 cycles which is shown in Figure 4c.

2.3. Self-Powered “Eco-Energy” Smart Card: Measurements with Different Electrodes (CCL)

To know more about the mechano-responsive charge transfer at metal/cPANi layer, we have performed further electrical output for different electrode materials keeping same size of CTL, i.e., pfc-paper. Each of the “eco-energy” smart card has been built with 3×2 matrices of pfc-paper with different electrode materials (Figure S7, Supporting Information) like gold (Au), carbon (C), copper (Cu), silver (Ag), and aluminum (Al), namely as D_{Au} , D_C , D_{Cu} , D_{Ag} , and D_{Al} respectively. Details of fabrication method is discussed in experimental part in the Supporting Information. Figure 5a,b shows the open-circuit output voltage (V_{oc}) and short-circuit output current (I_{sc}) for each of the corresponding devices starting from D_{Au} , D_C , D_{Cu} , D_{Ag} , to D_{Al} respectively. Average approximate values of V_{oc} and I_{sc} recorded are different, depending on the electrode material that has been used for CCL. This is quite interesting that the mechano-responsive charge transfer mechanism depends on the Fermi energy level difference at the interface between electrode and active layer. For estimating the work function difference ($\Delta\Phi$) between the electrode and the active layer, we have performed Kelvin force microscopy

Figure 4. The output electrical performance of the mechano-responsive energy harvesting based on a) various impact forces with 6 Hz working frequency and b) various working frequencies with 16 N implied force. It is noticeable that the change of electrical performance is quite remarkable at lower frequency and forces rather than higher values. c) The stability test of the device for more than continuous 1200 cycles under the same experimental conditions.

Figure 5. Mechanical-stimuli spontaneous output power for different devices. a, b) Touch-interactive effect from “eco-energy” smart card to harvest electrical energy (V_{oc} and I_{sc}) with different charge collector layer (CCL) using different electrode materials; gold (Au), carbon (C), copper (Cu), silver (Ag), and aluminum (Al) keeping the same size of charge translocation layer (CTL, i.e., pfc-paper). A systematic trend in V_{oc} and I_{sc} is observed for different devices, namely D_{Au} , D_C , D_{Cu} , D_{Ag} , and D_{Al} (depending on different CCL), respectively. It can be noticed that the foremost value of electrical output is achieved from device D_{Ag} , where the Fermi energy difference ($\Delta\Phi$) at the interface between CCL (Ag)/CTL (cPANi) is minimum. And the values of electrical output decrease according to the values of $\Delta\Phi$ increases between CCL-CTL. c) Shows surface potential mapping for different CCL (with different electrode materials) including CTL (pfc-paper). d) The corresponding histogram distribution shows the mean of contact potential difference (CPD) for each material. Inset shows the calculated $\Delta\Phi$ between CCL-CTL. e) A schematic (not in scale) energy diagram based on mechano-stimuli charge transfer mechanism between CCL-CTL is illustrated.

(KPFM) measurement^[32,52] for all the materials with their substrate which has been used for the device. KPFM technique acts as a tool to measure the local contact potential difference (CPD) between a conductive AFM tip and the sample surface, through applying external DC voltage between them, which finally yields the work function or surface potential of the sample with high spatial resolution. Figure 5c shows the

CPD mapping images, starting from cPANi (pfc-paper), Au (deposited on paper), C (screen printed on paper), Cu (copper tape), Ag (screen printed on paper), Al (Tetrapak) respectively. Corresponding histogram is displayed in Figure 5d. As $CPD(V) = (\Phi_p \approx \Phi_s)/e$; where Φ_p , Φ_s is the work function of AFM probe and sample respectively, therefore, difference between two average values of CPD for two samples (CPD_{S1} , CPD_{S2}) will be the work function difference ($\Delta\Phi = \Phi_{S1} \approx \Phi_{S2} = \Delta CPD_{S1-S2}$) between them. From the histogram profile, the approximate $\Delta\Phi$ between cPANi (WF; Φ_{CP}) and the different electrodes (WF; Φ_{Ag} , Φ_C , Φ_{Cu} , Φ_{Ag} , Φ_{Al}) are shown in inset. It can be calculated that the two lowermost values are for Ag ($\Delta\Phi_{Ag-CP} = 90$ mV) and Cu ($\Delta\Phi_{Cu-CP} = 190$ mV) and two higher most values are for Al ($\Delta\Phi_{Al-CP} = 900$ mV) and Au ($\Delta\Phi_{Au-CP} = 700$ mV). For carbon, $\Delta\Phi_{C-CP} = 300$ mV. The notion behind the discrimination in V_{oc} and I_{sc} for different devices (D_{Au} , D_C , D_{Cu} , D_{Ag} , and D_{Al}) can be portrayed by WF difference between cPANi and electrode material, the interface of which two has been implanted for charge transfer during mechanical stress. It is obvious that as the energy barrier height (i.e., Fermi level difference or $\Delta\Phi$) between cPANi and electrodes, be low or high respectively, requires less or more mechanical stress to stimulate the mobile carriers through the interface layer. In other way, applying the same mechanical force amount of mobile charge stimulated and transferred through the interface will be increasing or decreasing according to decrease or increase in the barrier height between the systems, respectively. Schematic of the difference of Fermi energy level at interface between electrode-cPANi is shown in Figure 5e. Experimentally, that conceptual mechanism based on Fermi level difference is explained by electrical output in Figure 5a,b. Notably, V_{oc} and I_{sc} are maximum (91 V, 12 μA) for D_{Ag} (all paper-based device). Close to that, D_{Cu} shows the second highest value for V_{oc} and I_{sc} (80 V, 8.5 μA).

A standard rectifier circuit is employed to output connector of “eco-energy” smart card devices for converting dc pulse which is further used to charge up commercial capacitor or lightning LEDs. The instantaneous power outputs ($W = I^2 \cdot R$) are recorded after rectification. Figure 6a shows the current and power density against the load from 55 kΩ to 150 MΩ for five different devices. As we have experienced before, the maximum current density and power density vary for different devices, i.e., for D_{Au} , D_C , D_{Cu} , D_{Ag} , and D_{Al} . As expected, the highest value of power density has been recorded for D_{Ag} , which is 1.75 W m⁻².

Figure 6. DC output characteristics from “eco-energy” card after rectification. a) Shows the current density and power density curve against different loads for different devices, i.e., D_{Au} , D_C , D_{Cu} , D_{Ag} , and D_{Al} respectively. Following the same trend, the maximum power density is achieved for lowest $\Delta\Phi$ between CCL-CTL and decreases with increasing value of $\Delta\Phi$. b) The charging of commercial capacitor (10 μ F) through different devices (D_{Au} , D_C , D_{Cu} , D_{Ag} , and D_{Al}). Capacitor can be charged up to 1.5 V (a typical value) in less than 10 min for devices, D_{Cu} and D_{Ag} . c) Portable device has been powered up through charging a 47 μ F commercial capacitor. Inset shows the measuring setup and schematic of rectifier circuits. d, e, f) Snapshots of the LEDs powered by “eco-energy” card.

Table 1 shows the comparative data of electrical output for different devices. A commercial capacitor with 10 μ F capacitance has been used for charging under the rectifier circuit, as shown in Figure 6b. For D_{Ag} and D_{Cu} , the capacitor can be charged up to 1.5 V, approximately within 10 min. It is noticed to take longer time for the rest of the devices. Moreover, the electrical energy harvested from the “eco-energy” card was utilized to power up the portable devices, e.g., digital display, LEDs etc. A

47 μ F commercial capacitor has been used for charging through “eco-energy” card and after that powered to the portable electronic meter which was shown in Figure 6c (real-time video has been shown in video SV4 in the Supporting Information). Furthermore, by simple touch interaction, this smart card has been used to instantaneously powering several LEDs (20 mA rating, 5 mm diameter, and 8.6 height). Figure 6e shows that almost 40 LEDs can be powered instantaneously, where 20 LEDs were

Table 1. Mechanical-stimuli output power for different devices based on different CCL layers.

No.	Device Name	CCL (used electrode)	Work function difference between CCL and CTL ($\Delta\Phi$ in mV)	Avg. V_{oc} [V]	Avg. I_{sc} [μ A]	Max. power density [$W m^{-2}$]	Max. current density [$mA m^{-2}$]
1.	D_{Au}	Gold	500	35.5	2	0.26	15
2.	D_C	Carbon	303	54	6.5	0.7	22
3.	D_{Cu}	Copper	191	80	8.5	1.35	32.5
4.	D_{Ag}	Silver	90	91	12	1.75	33.5
5.	D_{Al}	Aluminum	695	22	1	0.24	12

in series and each of 20 LED set were in parallel. Moreover, as a proof for enough current generation, 5 LEDs have been powered where, each of them were in parallel connection. Also, we can light up much more powerful white LEDs of power 1.5 W (Shown in Figure S10, Supporting Information). All real-time videos of instantaneous lighting LEDs including FCT logo are shown in videos SV5 and SV6 in the Supporting Information. Robustness and durability of the “eco-energy” cards have been rigorously tested over six months, keeping all the devices in ambient atmospheres.

3. Conclusions

In the present context of new-age smart technology being on the verge of the biggest challenge to provide enormous energy which will be portable, green and simultaneously with zero e-waste, our projected vision accepts both these challenges. In this work, we have presented our prototyped human touch-interactive self-powered “eco-energy” card which is completely paper-based and presents zero e-waste with 100% clean and green energy. The maximum power density and current density obtained from our best device are 1.75 W m^{-2} and 33.5 mA m^{-2} respectively. Also, the devices are able to light up several commercial LEDs. All these results from “eco-energy” smart card can have a huge impact not only in the paper-based industries but also as a cheap and green source of energy harvesting for uprising smart electronics. Moreover, the presented work vision also supports the UN sustainable goals including zero e-waste challenge.

4. Experimental Section

Aniline monomer (Aldrich), ammonium persulfate (APS; 99.99%, Aldrich), camphorsulfonic acid (CSA), and hydrochloric acid (HCl; $\approx 37\%$, Alfa Aesar) were the main reagents used in the synthesis. Throughout all the experiments and washing procedures only deionized (DI) water (Millipore Elix Advantage 3 purification system) was used.

Active Energy Generating Layer Fabrication—Printing Pixelated Well on Paper: First of all, the commercial raw paper (Whatman, Chromatography Paper, Grade: 1 CHR) was cut into different required sizes and then different number of square-shaped wells ($12.5 \times 12.5 \text{ mm}^2$) were wax-printed in an array form (e.g., 7×4) by using solid wax (Ref: 108R00935, Black) in a normal office printer (Xerox ColorQube 8580). The paper was dried at 100°C for 2 min while the wax got melted and absorbed within the paper making a solid periphery for the wells. This was done to control the drop-casting process in a precisely known area ($10 \times 10 \text{ mm}^2$) where the functionalization was actively done.

Active Energy Generating Layer Fabrication—Functionalization of Paper with Polyaniline: Each of the pixelated area, which was printed on the paper, was used for in situ functionalization. The polymerization process was done directly on the paper by two-step drop casting method at room temperature. The reaction was really fast and simple as described follows: Firstly, 10 mL aqueous solution of APS (0.14 M) was made and 100 μL of HCl was added to it with mechanical agitation for preparing solution A (as shown in the schematic of Figure 1a). Then, 20 mL aqueous CSA solution was made and 365 μL of aniline monomer was added to it for making the required aniline-CSA complex solution (namely, solution B). The molar ratio of CSA:APS was 1:2. Afterward, the two solutions A and B were sequentially drop-casted in each pixelate in 1:2 volume ratio and left unagitated for about 5 min until the dark green

color was seen visually. After that the functionalized paper was rinsed with DI water and methanol to remove the excess unreacted reagents or oligomers. Then they were left for drying at room temperature until the next step of device fabrication started. The reactant monomer and coreagents were entirely penetrated through the elemental cellulose fibers of raw paper. This enacts a complete functionalization to form a conjoined system between cPANi nanostructures and cellulose fibers by in situ polymerization technique. Final form of polyaniline functionalized paper was well conductive in both sides to use it as a soft metallic active layer for energy harvesting device. More steps of the reaction with real-time video of polymerization has been added in the Supporting Information. Also, in situ polymerization of pixelated paper has been shown in real-time video SV1 in the Supporting Information (dropcasting Solution A) and video S2 in the Supporting Information (dropcasting solution B).

Device Fabrication for Harvesting the Wasted Energy from Human Body Movements: Meanwhile, to make human-interactive energy-harvesting device using pfc-paper as an active layer, different kind of metallic films were adopted as flexible electrodes. This was done indeed to further explore the difference of using different materials (gold, carbon, copper, silver, aluminum) for electrodes having the same active layer. Carbon (CRSN2644 C INK, Sun Chemical) and silver (CRSN2442 AG INK, Coated Screen Inks) electrodes were screen-printed using a mesh (120t, I.C.M.) and later dried on a hotplate at 80°C (for 40 and 15 min for silver and carbon respectively) on paper. For gold, conductive layer was deposited on paper as electrodes by e-beam deposition technique. Aluminum coated commercial cardboard paper (Tetrapak) was also used as another type of electrode for the device. And for copper electrode, commercial copper tape was used. The pfc-paper (1st layer, with variable pixelated area) which has acted as a CTL, was clipped with electrode materials (2nd layer) acted as CCL. Both the layers have been cased with protective covers (3rd and 4th layers) to build human touch-interactive energy harvesting device. The single electrodes, i.e., CCL was connected to the oscilloscope for measuring output signals.

Prototype Self-Powered “Eco-Energy” Smart Card: Also, for prototype device, “eco-energy” smart card was designed with different types of electrodes. Protected cover (standard size of $85.60 \times 53.98 \text{ mm}^2$), either photo paper or flexo (shown in Figure 3e) was used for encapsulation of the devices. Inside each “eco-energy” smart card, 3×2 pixelated area of pfc-paper has been used.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

clean energy, functionalized cellulose, paper electronics, polyaniline, triboelectricity

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