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Research paper

Bio-waste orange peel and polymer hybrid for efficient energy harvesting

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ABSTRACT

Bio-waste orange peel with poly(vinylidene fluoride) hybrids have been developed as an efficient energy harvester. Bio-wastes in huge amount cause landfills and environmental pollution. An effort in the direction of using bio-waste will be beneficial in many ways. Orange peel, a bio-waste, is mainly composed of cellulose and different proteins that are responsible for its piezoelectric effect. The hybrid exhibits significant piezoelectric properties arising through induced piezoelectricity in the polymer matrix by the smaller dimension orange peel powder as filler causing an electroactive phase of ∼70% in the hybrid. Integrated device has been fabricated for energy harvesting using the hybrid material, without conventional high voltage poling, which displays very high open circuit voltage of ∼90 V and power of 135 μW/cm^2 using finger tapping. The hybrid nanogenerator is proficient in light up the LEDs from the movement of sliding door and from any human body movements like bending, twisting and walking etc. The underlying mechanism of enhanced piezoelectricity in the hybrid is revealed through structure, morphology and thermal studies of the hybrid. Thus, the piezoelectric energy harvester prepared from the bio-waste might be one of the solutions to utilize the bio-waste.

1. Introduction

The consumption of energy sources are constantly increasing with increasing world population that affects our socio-economic conditions (Lucia and Grisolia, 2019). There is a need to work on the alternate renewable energy sources like solar cell, fuel cell, thermoelectric systems for energy generation (Prakash et al., 2019; Kumar et al., 2018; Açıkkalp et al., 2020). In present scenario, a self-powered system is the need of the day, especially for real time biomedical health monitoring. Piezoelectric material based self-powered nanogenerators are of growing interest among researchers due to ease of application in biomedical devices and their suitability as flexible electronics (Hwang et al., 2014; Yan and Jeong, 2016; Kumar et al., 2019). Several attempts also have been done to fabricate the naogenerators using piezoelectric materials such as ZnO (Li et al., 2010), PMN-PT (Hwang et al., 2014), $BaTiO_3$ (Yan and Jeong, 2016), $ZnSnO_3$ (Alam et al., 2015), PZT (Fan et al., 2016) and synthetic polymers such as poly(vinylidene fluoride) (PVDF) and its copolymers (Gaur et al., 2018, 2016; Kumar et al., 2017). The materials should be biocompatible to use these nanogenerators in self-powered biomedical devices like in artificial cardiac pacemaker. A very low level of toxicity is harmful under in-vivo conditions. So, a biomaterial based nanogenerator should be used to overcome this challenge. In this case, the bio-waste based self-powered system is one of the alternatives for power generation.

Bio-wastes are one of the major reasons for pollution because of landfills and the emission of greenhouse gases from domestic waste. Nowadays, the efforts are being done for the use of domestic waste for different applications. By-products of the fruit processing industries are fruit waste that consists of seed, core, and peel, contain a large amount of water and are in a wet and fermentable form. These waste products produce odor, soil pollution and harborage for the insects, which can increase the environmental pollution if these by-products are not processed further (Shalini and Gupta, 2010). The researchers are able to develop high value products such as cosmetics and medicines and the recovery seems to be environment friendly (Ashoush and Gadallah, 2011). The idea of utilizing fruit waste especially peels started gaining popularity after the recent findings of easy processing and better biological activities than that of other parts of the fruits (Moon and Shibamoto, 2009). The fruit wastes are rich in fibers, proteins, oils and flavonoids and orange peel is a good example having its inherent piezoelectric behavior. Bio-waste based hybrid can be developed utilizing the bio-waste and thereby eradicating pollution menace to certain extent utilizing its better processability. Flavoniods, present in

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the orange waste at different stages of the industrial processing, are found to be abundant in peels than that in juice, revealing their great industrial potential (Pereira et al., 2017). Citrus is a major crop with a yearly production of 135.8 million metric tons according to the Food and Agricultural Organization of the United Nations. Citrus fruit waste comprises ∼50% of the total fruit weight (Gonzalez-Molina et al., 2010). The chemical and antioxidant properties (Ahmed Abd El-ghfar et al., 2016) of citrus peel indicate their good source of natural bioactive compounds including blended diesel as alternative fuel (Phate et al., 2015). In the energy sector, the orange peel waste has been used in microbial fuel cell for bioelectricity production, without any chemical pretreatment or the addition of extra media showing output voltage and current density of 0.59 V and 847 mA/m^2, respectively (Miran et al., 2016). Another vegetable waste used for energy harvesting is onion skin, with a meager open circuit voltage of 18 V and power density of 1.7 μW/cm^2 (Maiti et al., 2017). On contrary, filled polymer systems using DNA (Tamang et al., 2015) and activated carbon (Alluri et al., 2017) have been used for energy harvesting with meager power generations like open circuit voltage of 20, 49.6 V and power density of 11.5 and 6.3 μW/cm^2, respectively. The energy harvesting system using PVDF and egg shell membrane (Gaur et al., 2019) has also been studied and the obtained open circuit voltage and power density was found to be 56 V and 55 μW/cm^2, respectively. These devices which use small mechanical stress to generate the electric energy can be used to power small scale electronic devices. Some other bio-wastes have also been used for different energy productions. Nguyen et al. used rice straw (Nguyen et al., 2016) for biogas generation through anaerobic digestion, which produces 3500 MJ energy per ton of straw. Shomal et al. (2019) used oils extracted from micro-algae for the production of bio-diesel with a production yield of 19.3%. In another study, Han et al. (2019) used oleaginous yeast isolated from a traditional Korean fermented fish and used it for bio-diesel production with banana peel as a feedstock.

Here, for the first time, orange peel has been used in the form of polymer hybrid as a potential candidate for energy harvesting novel material. The structural and morphological studies of the hybrid have been done using different characterization techniques and induction of piezoelectric phase has been discussed in detail. A flexible device has been fabricated for energy harvesting from various body movements and lighting the LEDs from common activity like door sliding etc.

2. Experimental

2.1. Materials

Poly(vinylidene fluoride) (PVDF) SOLEF 6008, seasonal orange purchased from local market, dimethyl formamide (DMF) purchased from HiMedia, poly(dimethyl siloxane) (PDMS), and Sylgard 184, were purchased from Ellsworth adhesives, India.

2.2. Hybrid preparation

Orange peels are dried and crushed into fine powder to use as filler for hybrid preparation. The PVDF is dissolved in DMF at 60 °C and the orange peel powder is dispersed separately through sonication in DMF solvent. After completely dissolving the PVDF in DMF, temperature is turned off and mixes the peel powder solution with polymer solution. Both the solutions were mixed together using vigorous stirring. The solution is then poured into petridish and is kept for drying. For complete solvent removal, the polymer/hybrid are kept in vacuum oven for overnight. Pure PVDF, orange peel and nanohybrids are thereby abbreviated as P, OR and P-OR, respectively. The numeric terms after P-OR indicate the percentage of filler in the hybrid.

2.3. Device preparation

Polymer hybrid film is coated with silver paste on both the sides and then copper wires are attached on both the sides for measurements. The assembly is then wrapped with polypropylene tape followed by encapsulation in poly(dimethylsiloxane) to protect it from external damage. The ratio of epoxy to hardener is taken as 10:1 in PDMS.

2.4. Characterization

X-ray diffraction: The structure of pure PVDF and hybrid, was analyzed using X-ray diffraction analysis. XRD patterns of the samples were obtained using a Rigaku Miniflex 600 X-ray diffractometer operating under a voltage of 40 kV and a current of 15 mA using Cu Kα Radiation ($\lambda = 1.54$ Å) at a scan rate of 3°/min at room temperature.

Fourier transform infrared spectroscopy (FTIR): FTIR measurement was performed in the reflectance mode at room temperature from 650 to 4000 cm^{-1} using Nicolet 5700 instrument, with a resolution of 4 cm^{-1}.

Differential scanning calorimetry (DSC): The melting temperature of pure PVDF and hybrid, were determined using DSC (Mettler 832). The samples were heated up to 250 °C at a scan rate of 10°/min.

Polarized optical microscopy (POM): Thin films of pure polymer and hybrid were subjected to polarized optical microscope (Leitz, Biomed) for obtaining the morphology.

Scanning electron microscopy (SEM): The surface morphology of pure PVDF and hybrid, were obtained by using SEM (SUPRA 40, Zeiss).

Atomic force microscopy (AFM): Atomic force microscopy was performed using AFM (NTEGRA Prima, NT-MDT).

Power measurement: Open circuit voltage is measured, using Tektronix TBS-1072B digital storage oscilloscope. For power measurement the output voltage is measured against varying resistance and power is calculated by:

$$P = \frac{V^2}{R \times A}$$

where, P is powerdensity, V is output voltage, R is external resistance and A is the area of the device. The active area of the device is kept at 1 × 2 cm^2, while the encapsulated device is 2 × 3 cm^2.

3. Results and discussion

3.1. Structure and morphology

The schematic representation of hybrid preparation is shown in Fig. 1a using orange peel and PVDF indicating the highly flexible and mechanically stable nature of the hybrid. X-ray diffraction patterns of PVDF (P) and hybrid (P-OR) clearly demonstrate the structural change over to electroactive β/γ-phase (2θ ∼20.3° (200/110), 18.6° (020)) in hybrid from the α-phase (2θ ∼17.6° (100), 18.3° (020) and 19.9° (110)) of pure PVDF (Fig. 1b) (Shah et al., 2004; Lopes et al., 2011). Similar electroactive phases in other hybrids and crystalline nature of pure peel are presented in supplementary Figure S1 and S2. The extent of electroactive phases (β and γ) in the hybrids is calculated through the deconvolution of XRD patterns and is found to be ∼70% in the hybrid (supplementary Figure S3). The induced piezoelectricity in PVDF is primarily due to the presence of peel and overall

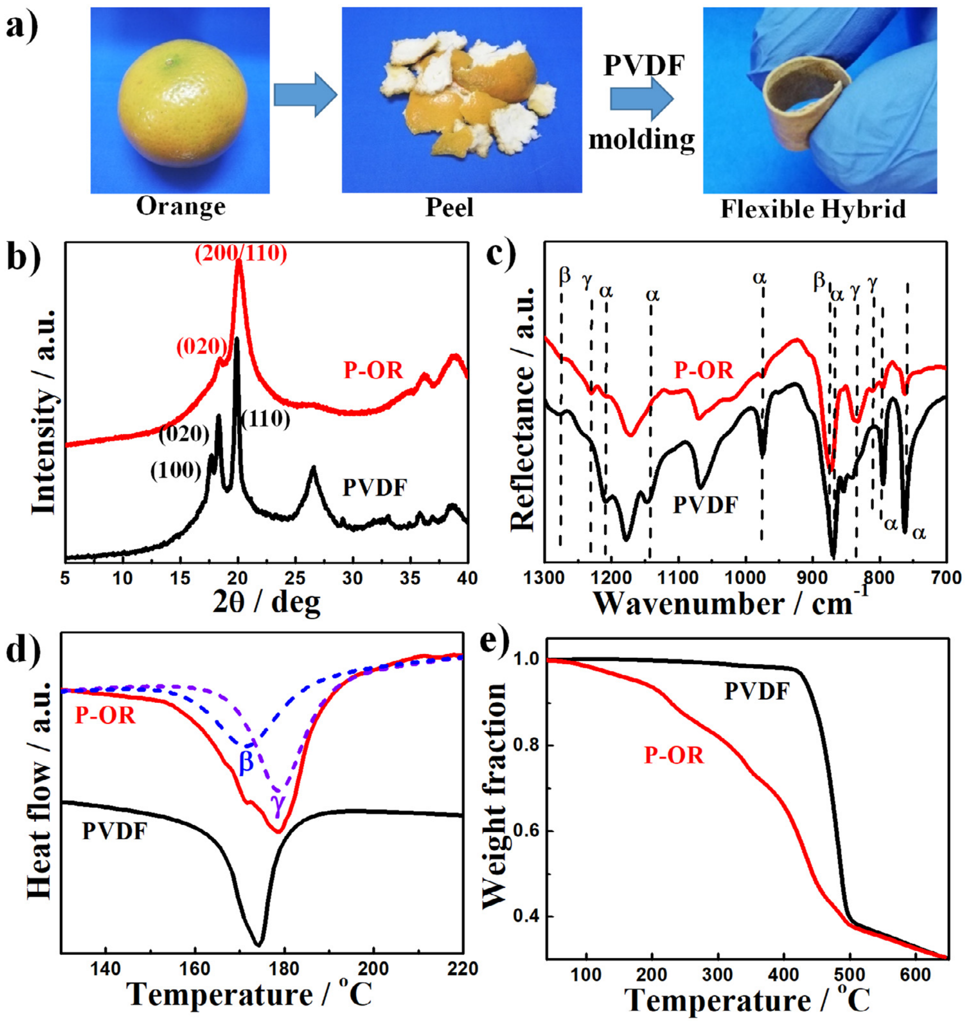

Fig. 1. (a) Photographic images of orange peel and synthesized hybrid showing its high flexibility and mechanical stability; (b) XRD patterns of PVDF and hybrid showing different crystalline planes; (c) FTIR spectra of PVDF and hybrid indicating peaks corresponding to different phases; (d) melting thermograms of PVDF and hybrid. Dashed lines indicate the deconvoluted patterns of β- and γ-phase of hybrid; and (e) thermal stability of hybrid as measured through thermogravimetric studies.

piezoelectricity of the hybrid is much higher considering the piezo-phase of orange peel filler.

The presence of orange peel in the hybrid is also confirmed through FTIR studies (supplementary Table S1 and Figure S4) (Rivas et al., 2008; Van den Bruinhorst et al., 2016). The α-phase peaks at 760, 796, 866, 975, and 1210 cm^{-1} are evident in pure PVDF (Lopes et al., 2011; Lanceros-Mendez et al., 2001) while the characteristic β-phase peak at 1275 cm^{-1} and γ-phase peak at 1232 cm^{-1} are prominent in hybrid in addition to combined β- and γ-phase peaks at 810, 840 and 878 cm^{-1} (Fig. 1c) (Kumar et al., 2019; Martins et al., 2014; Tiwari et al., 2019). The phase alteration is also reflected in melting behavior as evident from single melting temperature of 173.5 °C in pure PVDF against double melting at 171 °C (due to lower melting β-phase) and 179 °C (arises from high melting γ-phase) (Fig. 1d) following order of melting as $\gamma > \alpha > \beta$ (Manna and Nandi, 2007). The structural change in hybrid is due to the crystallization of PVDF on the surface of orange peel which leads to the induction of β and γ-phase (supplementary Figure S5). The thermal stability of hybrid has been shown to be up to 150 °C and the reduction of degradation temperature appears due to excess water molecules, cellulose and lignin present in orange peel (Fig. 1e) (Rivas et al., 2008). The thermal stability behavior of pure orange peel is explained in supplementary Figure S7.

Solution cast thin film of PVDF shows α-phase spherulitic pattern as observed through a polarized optical microscope while γ-phase is evident in hybrid (P-OR) as further confirmed from its higher melting (180 °C) under slow scan (Fig. 2a) (Shalini and Gupta, 2010; Gaur et al., 2017). The complete change in morphological patterns with temperature both for PVDF and P-OR are presented in supplementary Figure S7 showing the respective phase melting at two different temperatures. Surface morphology as observed through scanning electron microscope indicates the presence of α-spherulites in pure PVDF as opposed to fibrous morphology due to orange peel along with smaller and bright γ-spherulites in P-OR (Fig. 2b). The appearance of fiber in the hybrid is due to the presence of peel as the surface morphology of orange peel clearly exhibits the fibrous pattern. Now, the induced crystallization of electroactive β/γ-phase is revealed and polymer chains can crystallize at the periphery of orange peel fiber both in all-trans needle-like β-phase, mostly at the side wall of the fiber, and tiny bright γ-spherulite, mostly at the edge of fiber, leading to thicker and dumble-like fiber in the hybrid. This induced piezoelectric crystallization has been shown in the form of a cartoon where thicker and dumble-like fiber is shown in the hybrid which directly corresponds to the thin fiber structure of pure orange peel and thick dumble-shape morphology of the hybrid (Fig. 2c).

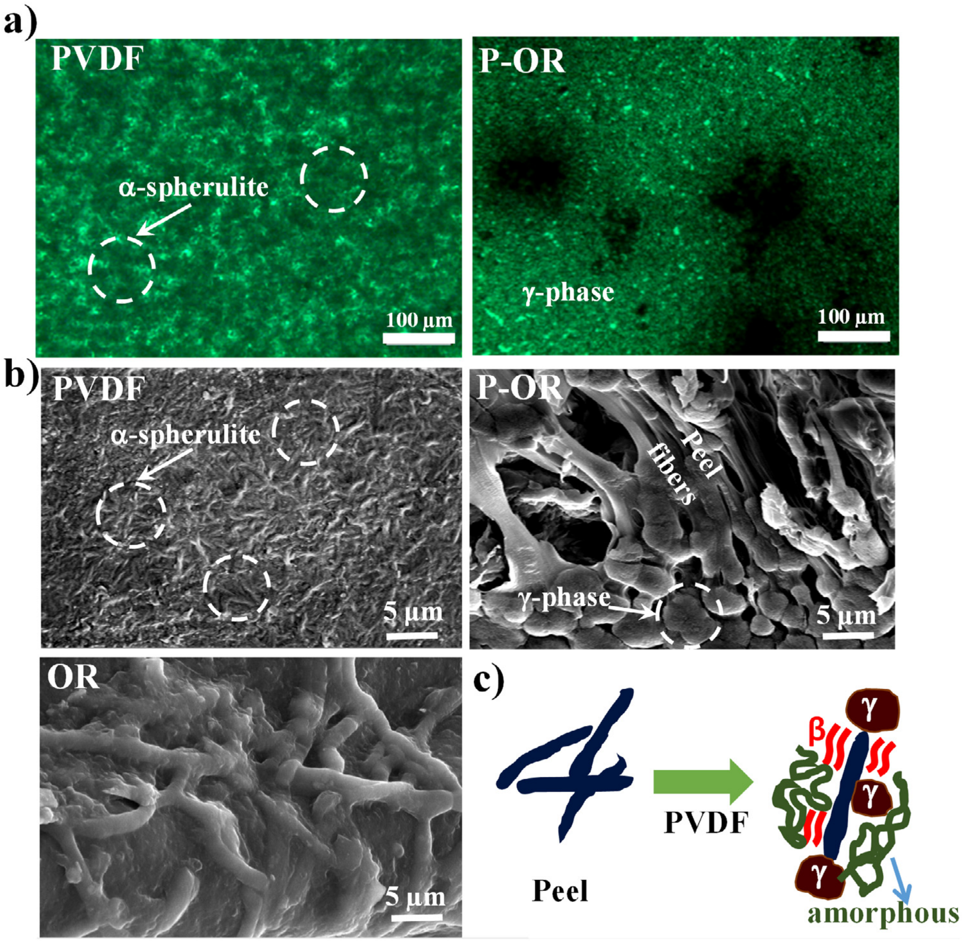

Fig. 2. (a) Polarized optical microscopic images of as cast PVDF and hybrid thin films indicating various phase of crystallites (details are in supplementary information); (b) Surface morphology of PVDF, hybrid and orange peel showing different crystallites and fiber as observed through SEM; and (c) schematic of PVDF crystallization at the edge of peel fibers demonstrating the appearance of electroactive induced phases in polymer matrix.

3.2. Energy harvesting and useful applications

Device has been fabricated using the electroactive hybrid assembly and is wrapped with PDMS for its mechanical stability, a schematic design is shown in the inset of Fig. 3a. The energy harvesting performances have been studied using the devices which exhibit open circuit voltages (OCV) of 3, 58, 70 and 90 V from P, P-OR-10, P-OR-20 and P-OR-40, respectively, indicating higher voltage output from greater peel content hybrid against meager voltage output from pure PVDF being non-piezoelectric (Fig. 3a). The power density, calculated from the equation $P = \frac{V^2}{RA}$, is found to be as high as 135 $\mu W/cm^2$ under varying applied resistance (Fig. 3b), which is much higher than the reported values using other biomaterials (supplementary Table S2). Device made of pure orange peel generates meager 30 V (OCV) and 25 $\mu W/cm^2$ power density (supplementary Figure S8), very low as compared to hybrid, raising a synergistic effect in hybrid as revealed through induced piezoelectric phase in polymer matrix (*cf.* Fig. 1) in presence of tiny peel powder as filler. The bio-waste (orange peel composed of many bio-polymers like cellulose, lignins, proteins and different flavonoids) demonstrates the piezoelectricity due to the rotation of the polar atomic groups or the formation of new dipoles upon the application of stress (Kumar et al., 2017; Fukada, 2000). The hydroxyl (–OH) groups in cellulose can interconnect the molecules through inter- and intra-molecular hydrogen bonding which develops the electric dipoles inside the crystal and, thereby, favors the induced crystallization of PVDF matrix to electroactive phase at the edges of the peel fiber as shown in the scheme of Fig. 2c (Alam and Mandal, 2016). The piezoelectric effect is due to the displacement or reorientation of the dipoles in the crystal upon the application of stress (Kim et al., 2006; Fukada, 1968). The long-range ordered polymer crystals undergo stress induced polarization causing the piezoelectricity under the mechanical stress. Although, the origin of piezoelectricity in the biomaterial is not yet clear, as they do not follow the classical model of piezoelectricity, based on ideal crystalline structure (Fukada, 1995). However, the better piezoelectricity in the hybrid is due to electromechanical coupling arising from better interaction between the two phases under the application of pressure (Persano et al., 2014). The working principle of the device under compressed and release mode is explained in supplementary Figure S9.

The harvesting ability of the device is also verified with different human activities like bending (Fig. 3c) and twisting (Fig. 3d) and walking (Fig. 3e), which show output voltages of 5, 4 and 9 V, respectively, demonstrating the capacity of the device to generate power from normal body movements which otherwise go waste. A capacitor has been deployed to store the electricity generated by the hybrid generator and is able to be charged up to 1.2 V in 40 s using the finger tapping method and release the stored charge in another 40 s time (Fig. 3f). Another demonstration of LED lightening has been performed from the household door sliding using the hybrid generator to understand the efficacy of the

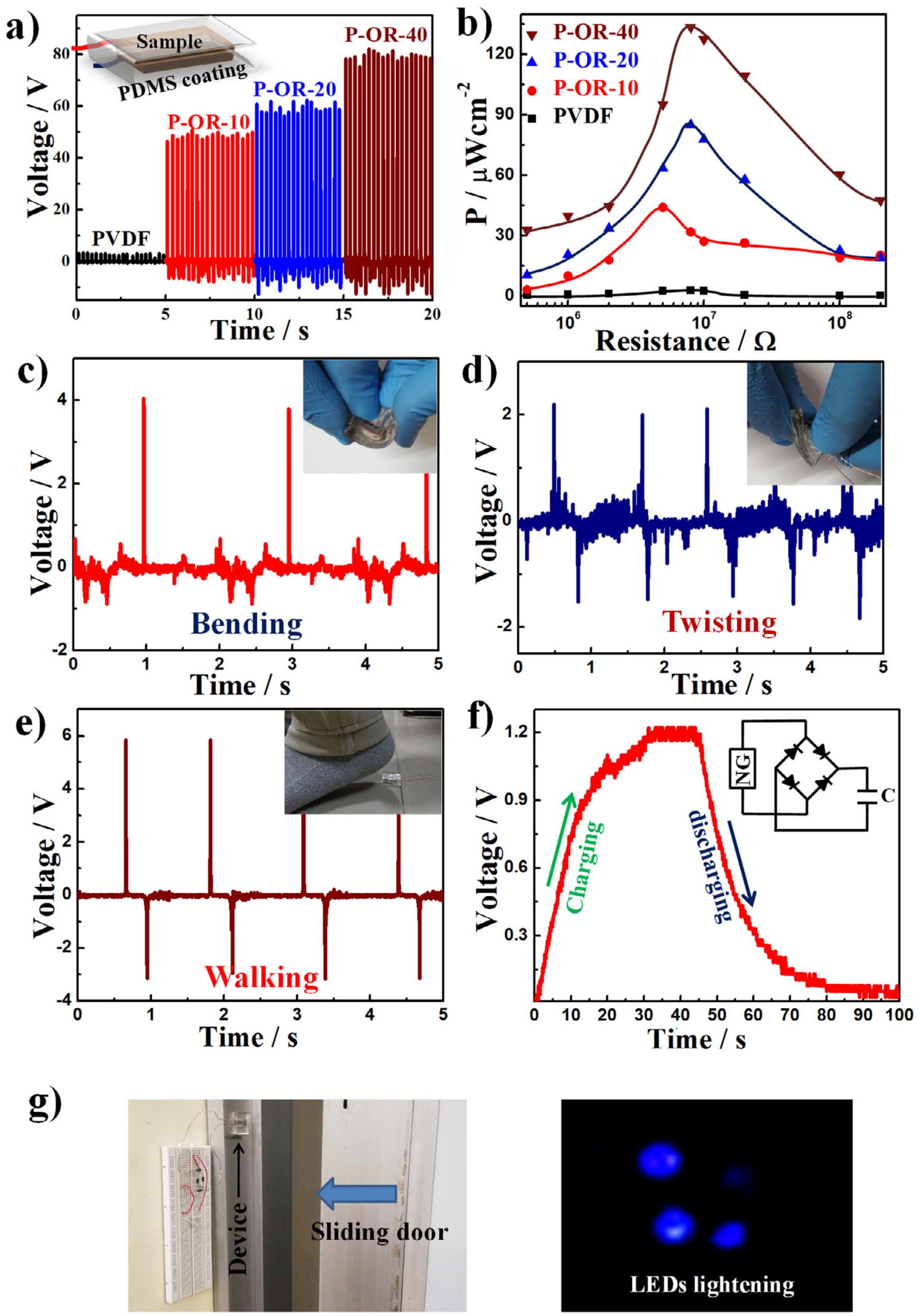

Fig. 3. (a) Open circuit voltage obtained from devices made of indicated hybrids or pure PVDF (inset shows the schematic of the prepared device). The numbers after P-OR represent the amount of orange peel (w/w); (b) output power density from the devices under varying applied resistance; Voltage generation from the device under different body movements; (c) bending; (d) twisting; and (e) walking on the device. Inset figures show the type of loading on the device; (f) charging and discharging nature of a capacitor from the energy produced by the device under finger tapping; (g) lightening of LEDs from energy produced by the device from household door sliding.

hybrid device using bio-waste (Fig. 3g and supplementary video VS1). In gist, common bio-waste has been utilized to prepare hybrid material for energy generation by fabricating suitable devices focusing on the underlying mechanism of piezoelectricity arising from the synergistic effect. Body movements and other waste mechanical energy like door sliding can efficiently be harvested through this hybrid device.

4. Conclusion

Bio-waste orange peel has been used to synthesize piezoelectric hybrid to harvest energy from body movements and common household activity. PVDF-orange peel hybrid is found to be flexible, mechanically and thermally stable. Orange peel induces the electroactive phases (β and γ) in matrix PVDF which eventually enhances the extent of piezo-phase (∼70%) in the hybrid. The mechanism of induced piezoelectricity has been revealed through the synergistic effect of peel fiber and polar PVDF molecules. Devices have been fabricated using hybrid assembly which exhibits open circuit voltage of ∼90 V and power density of 135 μW/cm^2 without conventional high voltage poling. The deployment of human body movements also shows significant energy generation along with lightening of LEDs from the door sliding performance, usual household activity. This new generation hybrid materials, composed of bio-waste orange peel, shed light of new technology of energy harvesting from waste mechanical energy (human body movements) and common household/office activities in order to solve the future energy mission. The device is able to charge a capacitor, thus, the bio-waste based hybrid is a promising material for the energy harvesting and as an alternative green energy source for powering small electronic devices.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.egyr.2020.02.020.

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