

Closure Report

File Number : EEQ/2019/000340

Project Title : Development of electroactive polymer nanocomposites based self-charged photo-power cells: A novel and simple approach towards clean energy generation and storage

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Total Sanctioned 19,49,555 (INR)

Total Released Amount 18,82,976 (INR)

Start Date of the 18 Jan, 2020

Date of completion: 17 Jun, 2023 (41 months)

Approved Objectives :

Development of electroactive polymers (like PVDF and its copolymers, Poly-L-lactic acid (PLLA) etc.) based nanocomposites via incorporation of dopants (CTAB, Ag, MoS₂ etc) via solution casting and in situ process. Synthesis of solar active materials like SiO₂, Bi₂S₃, MoS₂ etc.) and also some newest perovskite structures (CH₃NH₃PbI₃, CH₃NH₃PbBr₃ etc.). In-situ integration of the developed polymer nanocomposites and solar active materials in a single cell as self-charged photo-power units. Furthermore, low-cost devices will be designed for the large scale production to facilitate huge demands in energy sectors. Lighting of LEDs and driving of some electronic gadgets using the developed devices will also be demonstrated for practical utility purposes.

Deviation made from original objectives (If Any) :

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Ph.D. Produced/ Likely to be : 2

Technical Personnel Trained : 0

Total Expenditure : 19,49,555 (INR)

Concise Research Accomplishment :

We have developed good number of proposed samples and achieved some very interesting and outstanding results which sounds good for our proposed applications in the field of clean energy fields. 1. First of all, we have developed bio-polymer poly(lactic acid) thin film based K-ion associated photo-rechargeable power cell. After investigation of the charging and discharging phenomenon the maximum open circuit voltage is obtained ~1 V under light intensity ~110 mW /cm². It shows ~ 16 F/m² storage capacity with energy density and power density ~2.22 mWhr/m² and ~5 W/m² respectively. (Published in "Journal of Materials Science: Materials in Electronics"). 2. Electroactive CTAB/PVDF composite based photo-induced hybrid power cell has been developed in a sustainable manner using aqueous electrolyte solution of PVA-MnO₂-Eosin Y has been utilized as solar light absorber and photo-electron generator whereas the high dielectric CTAB/PVDF (~ 400) is used as dielectric separator cum storage part in a very transparent way. The cell shows maximum voltage ~1.1 V with short-circuit current density ~ 7.83 mA/cm² under ~110 mW /cm² normal light illumination. The device reveals almost same performance for a long time (30 days). The high storage impact of the hybrid cell is investigated by its promising conversion efficiency ~ 4.48 % with energy density and power density ~26.9 mWhr/m² and ~5.5 W/m² respectively. (Published in "Scientific Reports") 3. PLA/PVDF Based Photo-rechargeable Mg-ion Cell has been developed successfully. Aqueous electrolyte solution of PVP-MgCl₂-Eosin Y has been utilized as solar light absorber and photo-electron generator whereas the high dielectric PLA/PVDF is used as dielectric separator cum storage part in a very transparent way. The cell shows maximum voltage ~0.8 V with current density ~ 10 mA/cm² under ~110 mW /cm² normal light illumination. The device reveals almost same performance for a long time (30 days). The device able to lighten 20 LEDs for 7 days after single recharge under light. (Communicated) 4. We have fabricated Bi₂S₃/PVDF nanocomposites-based photo-power cell using MnO₂ nanoparticles as solar part. We see some excellent output voltage ~ 1.2 V. (Communicated) 5. WO₃.H₂O doped PVDF film-based photo-rechargeable power unit has been fabricated using perovskite structures (NiMnO₃) as solar part. The cell shows excellent voltage generation ~ 1.0 V under normal light.

The cell is capable to drive commercially available blue LEDs for a long time (7 days) after a single recharge under light. 6. Apart from this we developed Kaolinite/PVDF and ZrO₂/PVDF nanocomposite films and get some outstanding results on piezoelectric performances. And these two works also published in two reputed international journals “Applied Physics Letters” and “Phys. Status Solidi A”. We are also developing photo-power cell using these two developed samples. We believe that we have achieved our proposed goals.

Closure Details

Experimental/ Theoretical Investigation carried out

1. Synthesis of the samples: The samples are synthesized through simplest solution casting method as proposed in the project proposal. The polymer and dopant are mixed in presence of solvents and the dried in a hot air oven to evaporate the solvent. And finally, after drying we get the polymers like poly(vinylidene fluoride) (PVDF) or Poly lactic acid (PLA) based samples.

1.1. PLA film Preparation: Initially, the plain PLA film is prepared by as a dielectric medium to develop the KPPC. To synthesize the PLA film, we have used dimethylformamide (DMF) as a solvent. In the 5 ml solution of DMF, 4% PLA (200 mg) is added and then the mixture is stirred very well for 6 hours. Then this solution is casted in a small petri dish which is placed in a dust-free hot air oven for overnight at 80 to obtain the thin PLA film of thickness ~ 20 m.

1.2. Preparation of CTAB doped PVDF sample Solution casting method is used to synthesize CTAB doped PVDF sample. In this process solution of 200 mg PVDF and 5 ml Dimethyl sulfoxide (DMSO) is initially prepared with 10 mass% CTAB and then it is mixed with a vigorous magnetically stirring for 12 h followed by 30 minutes ultra-sonication. Approximately 20 m thick CTAB doped PVDF films (PCTAB10) are prepared after 6 h drying a dust-free hot air oven at 100 . Simultaneously, pure PVDF films with equal thickness are also prepared. The thickness of the film is measured to be ~20 μm .

1.3. PLA/PVDF film Preparation: PLA/PVDF film synthesis is like the following: Initially, the plain PLA/PVDF film is prepared by as a dielectric medium to develop the photo-power cell. To synthesize the PLA/PVDF film, we have used dimethylformamide (DMF) as a solvent. In the 5 ml solution of DMF, 150 mg PLA and 50 mg PVDF are added and then the mixture is stirred very well for 6 hours. Then this solution is casted in a small petri dish which is placed in a dust-free hot air oven for overnight at 80 to obtain the thin PLA/PVDF film of thickness ~ 20 m.

1.4. Bi₂S₃/PVDF nanocomposites synthesis: Initially, 0.4 g of PVDF was dissolved in 8 ml DMSO at 60 oC to form a clear solution. Then desired amount of Bi₂S₃ (20 mass%) was added to the PVDF solution and magnetically stirred for 12 hours at 60 oC followed by ultrasonication (30 min) under ambient condition. The mixture was then cast on a clean Petri dish to obtain the film and heated at 80 oC in a dust free oven for 12 hours for complete evaporation of the solvent. The thickness of the film was ~ 20 μm .

1.5. WO₃.H₂O doped PVDF film First, 0.4 g PVDF and desired percentage of WO₃.H₂O NPs was added in 10 ml DMSO. Then the whole mixture was magnetically stirred for overnight at 60 OC followed by 30 min of ultrasonication under ambient condition. WO₃.H₂O doped PVDF film were obtained by casting the solution in clean petri dishes and dried to evaporate the solvent at 80 oC for 24 hours in a dust free oven.

1.6. Kaolinite/PVDF and ZrO₂/PVDF nanocomposite films also developed in similar way discussed in above.

2. Fabrication of photo-rechargeable power cell

2.1. PLA film-based K-ion associated photo-rechargeable power cell: Previously prepared pure PLA films are used to integrate the unique photo-rechargeable system KPPC as an insulating medium. The photo-sensitive part of the device is processed by mixing 40 mg/ml PVA, 10 mg/ml ZnO, 10 mg/ml WO₃, and 20 mg/ml K₂HPO₄ in water with continuous stirring for overnight at 60. After that the texture of the combined photo-active electrolyte solution will be sticky and then a very small amount of this concentrated gel-like solution will be poured on the acting electrode FTO coated glass on which the counter electrode aluminium (Al) attached with insulating PLA thin film is pasted. The effective area of the device is (0.2 cm x 0.2 cm) i.e. 0.04 cm². To characterize the device performance two wires are joined in between the electrodes.

2.2. CTAB/PVDF film-based Photo-power cell: As a high dielectric insulating medium PCTAB10 is used to fabricate power cell. 40 mg/ml PVA, 2 mg/ml eosin Y and 100 mg/ml MnO₂ in water is stirred for 12 h at 60 to prepare the photo – sensitive part in the device. Then a thin layer of the solution is casted on a conducting surface of a FTO coated glass and PCTAB10 high dielectric sample is placed on it with aluminium (0.2 cm X 0.2 cm). Here Al and FTO are acting as two electrodes for the device in which two wires are connected for the further investigation.

2.3. PLA/PVDF film-based Photo-power cell: Now the synthesized PLA/PVDF composite samples are used to fabricate the particular-Mg-ion associated photo-system MPS. Initially, the photo-active part of the system is made by preparing a blend of 150 MgCl₂, 20 mg Eosin Y and 40 mg PVP in water. This mixture is kept under a magnetic stirrer for overnight at 80 . When the mixture turns to a gel – like material, it will be put on a FTO coated glass plate which is an acting electrode. Then alluminium (Al) which is a counter electrode is enclosed with the FTO combined insulating PLDF base medium. The effective area of the device is (0.2 cm x 0.2 cm) i.e. 0.04 cm². Two conducting wires are connected in between the electrodes to study the whole MPS device functions and photo-voltaic performances.

2.4. Bi₂S₃/PVDF nanocomposites-based Photo-power cell: Bi₂S₃/PVDF nanocomposites-based Photo-power cell has been fabricated as similar method described in section 2.2. or

2.3. Here mixture of PVA and MnO₂ nanoparticles in distilled water was used as solar part. Otherwise all methods are same.

2.5. WO₃.H₂O doped PVDF film-based Photo-power cell: High dielectric insulating medium WO₃.H₂O doped PVDF (PW10) has been used to fabricate power cell. 500 mg PVP, 2 mg/ml, 200 ul H₂SO₄ and 40 mg NiMnO₃ was dissolved in water and stirred for 12 h at 60 °C to prepare solar part in the device. Then a thin layer of the solution is casted on a conducting surface of a ITO coated glass and PW10 high dielectric sample is placed on it with aluminium (0.2 cm X 0.2 cm). Here Al and ITO are acting as two electrodes for the device in which two wires are connected for the further investigation. We are showing the fabrication process of our photo-power cell and digital images of developed cells in Figure 1 ((a) and (b) CTAB/PVDF based photo-power cell, (c) & (d) digital image of lightening of LEDs by PLA based photo-rechargeable K-ion cell and PLA/PVDF based photo-power cell respectively).

3.Characterization of the samples and devices: Synthesized polymer based composite samples and the fabricated devices were characterized using the following methods and instruments:

3.1. X-ray diffraction (XRD): The XRD patterns of all the samples were recorded by X-ray diffractometer (Model-D8, Bruker AXS Inc., Madison, WI) at atmospheric pressure and room temperature using nickel filtered Cu target K radiation with scan speed of 0.3 s/step and under an operating voltage of 40 kV with 2 θ varying from 15 to 400.

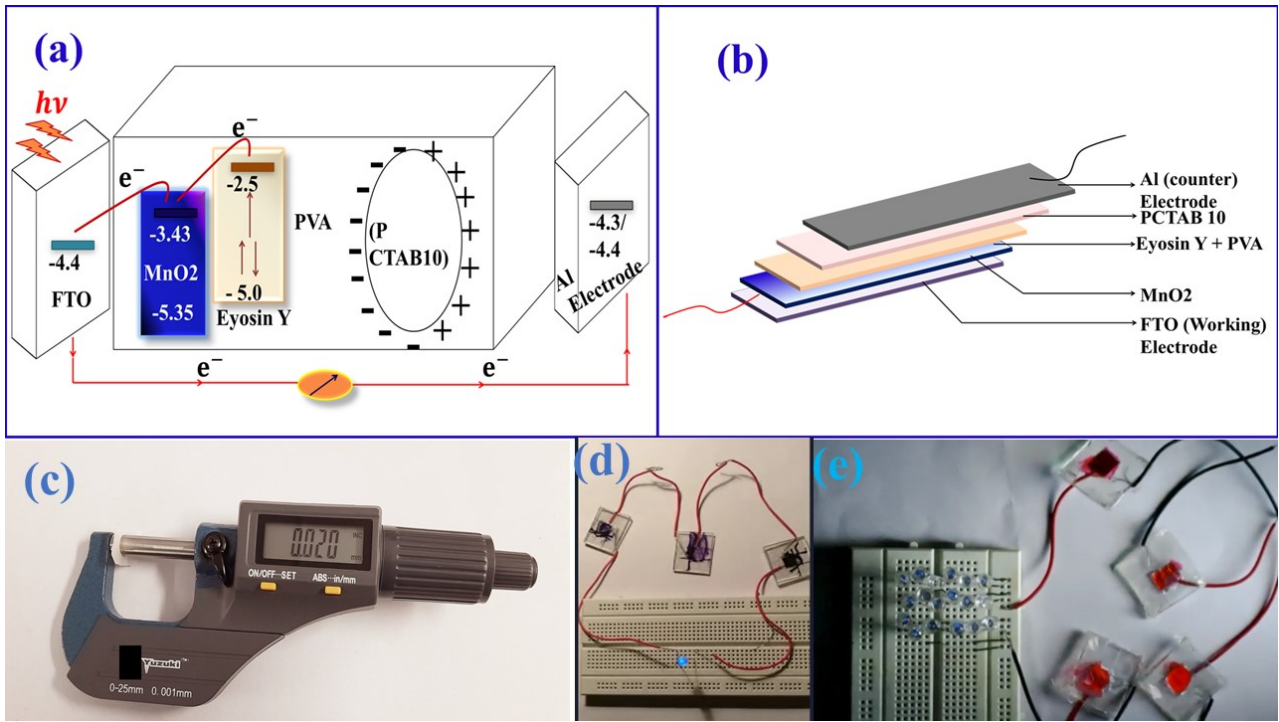
3.2. Fourier transform infrared spectroscopy (FTIR): The effect of fillers on phase crystallization in the samples were further characterized using FTIR (FTIR-8400S, Shimadzu). The absorbance data of the films were investigated performing 100 scans of each sample in the wavenumber range from 400 cm⁻¹ to 1100 cm⁻¹. The fraction of β -phase (F(β)) in the films were evaluated using Lambert-Beer law which is, $F(\beta) = \frac{A_{764}}{(K_{764}/K_{840}) A_{840} + A_{764}}$ (1) where, A = the absorbance at 764 cm⁻¹ and A = the absorbance at 840 cm⁻¹ and K (7.7 x 10⁴ cm² mol⁻¹) and K (6.1 x 10⁴ cm² mol⁻¹) are the absorption coefficients at 840 cm⁻¹ and 764 cm⁻¹ respectively.

3.3. Field emission scanning electron microscopy (FESEM): The morphology and shape of the samples and its interaction with the PVDF of PLA matrix in the modified polymer matrix were investigated using Field emission electron microscope (FESEM) (INSPECT F50, Netherland).

3.4. Differential scanning calorimetry (DSC): The phase crystallization and melting behaviour of the films were investigated using a Differential scanning calorimeter (DSC-60, Shimadzu (Asia Pacific) Pte. Ltd., Singapore). The melting enthalpies or enthalpies (H_m) of fusion of samples were calculated from DSC curves. Then, the degree of crystallinity (X_c) of the samples was evaluated using the following equation: $X_c = H_m / H_{100\%}$ (2) Where H_m is the heat of melting or enthalpy of fusion and H_{100%} is the melting enthalpy of 100% crystalline PVDF with value 104.6 J/gm.

3.5. Dielectric properties measurements: The capacitance (C) and tangent loss (tan δ) were collected in the frequency range 20 or 100 Hz to 2 MHz at room temperature using digital LCR meter (Agilent, E4980A). 1 V ac voltage was applied across the two opposite surfaces of the samples. The dielectric constant (ϵ') and the ac conductivity (σ_{ac}) of the samples were evaluated using following equations (3) and (4) respectively, $\epsilon' = C.d / 0A$ (3) $\sigma_{ac} = 2f0 \tan \delta$ (4) where, C, d, A and tan δ are the capacitance, thickness, area and tangent loss of the samples respectively and f is the applied frequency in Hz and 0 is permittivity of free space with value (8.854 x 10⁻¹² F.m⁻¹).

3.6. Device Characterization: The output characteristics of self-charged photo-power cells are measured by an electrometer (Keysight- B2985A) and digital multi-meter (DMM 6500, Keithley) and cyclic voltammetry technique (PGSTAT 10, Auto Lab and PG Lyte-1.0).



Detailed Analysis of result

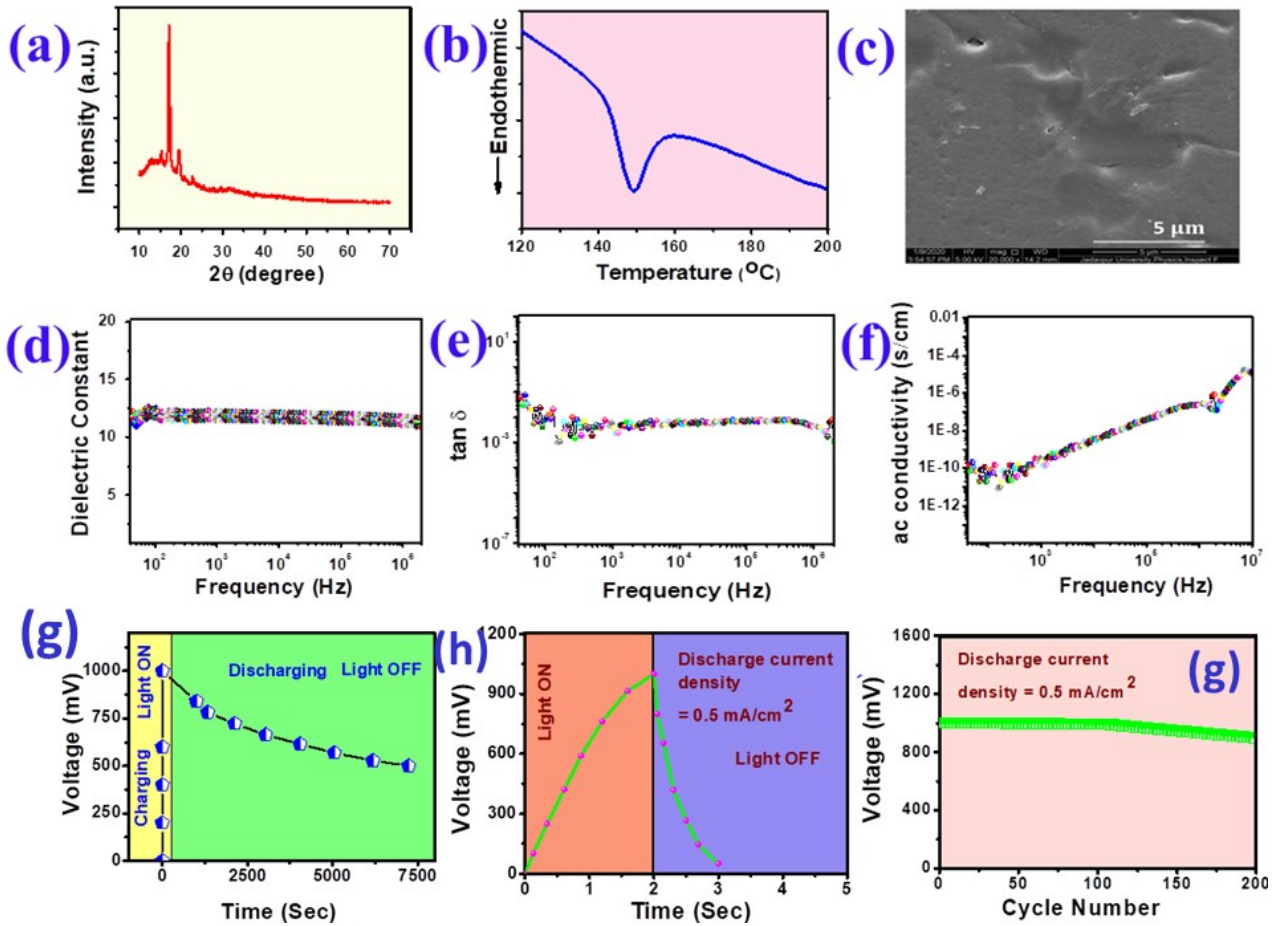
PLA film-based K-ion associated photo-rechargeable power cell: Figure - 2a is representing the X-ray diffraction (XRD) patterns of PLA which has been verified by the X-ray diffractometer. According to the X-ray diffractograms of PLA films a sharp peak at 17.2° (200) has been observed which indicates about the proper preparation of the PLA samples. Some other small peaks around 19.5° (203) and 22.9° (210) are also obtained. Further verification of the PLA thin films, a thermal technique is used by using differential scanning calorimetry. From the DSC thermograph of figure - 2b, a sharp peak at 149°C is observed and it is a clear significance of some endothermic reaction within the PLA samples. The crystallization enthalpy and the degree of crystallinity as well as the melting enthalpy of a PLA crystal can be calculated by using the DSC thermographs. Figure 2c it is observed that a uniform smooth surface of PLA film is formed after the solution casting method. The highest dielectric constant achieved by the PLA sample is nearly equals to 12 at the lower frequency region 40 Hz. From the graphical representation of figure - 2d, a constancy of the dielectric variation is noticed over the full frequency region. The slightly greater value of the dielectric constant may be explained by the proper dipolar alignment of the PLA molecules. Also some interfacial space charge accumulation may be taken place at the junction of the electrode and the PLA film which leads to a good dielectric value of the prepared film. Figure - 2e illustrates the dependency of the tangent loss ($\tan \delta$) with frequency and the graphical nature is almost straight line with the frequency. According to the figure it is seen that the dielectric loss is very small and it is 1. The nature of the ac conductivity is showing in figure - 2f and the curve in this figure is gradually increasing with frequency. At the lower frequency range ac conductivity is low effectively unchanged whereas it has a linear increment at the higher frequency range for the PLA thin films. Here, as an electrolyte composite we have used PVA/WO₃/ZnO/K₂HPO₄ solution which is responsible for the photo - charge

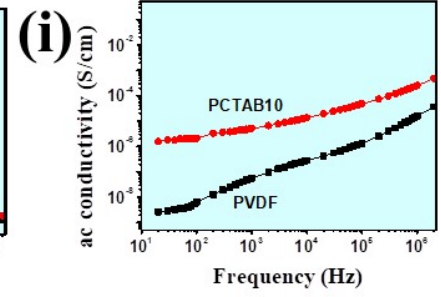
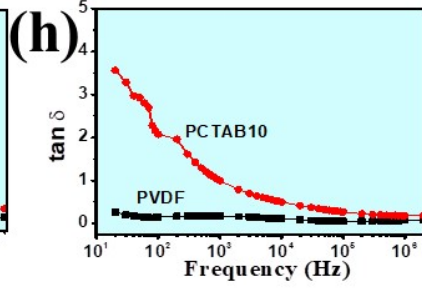
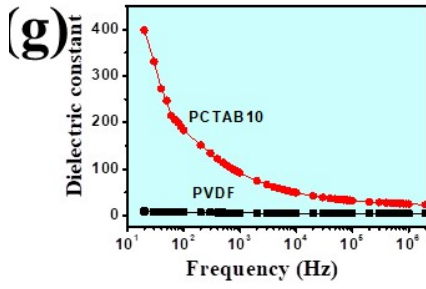
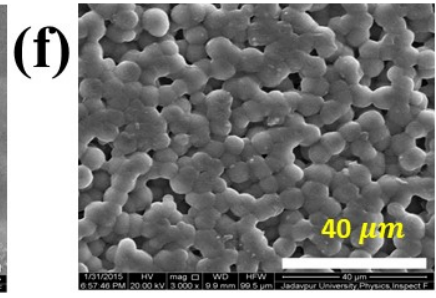
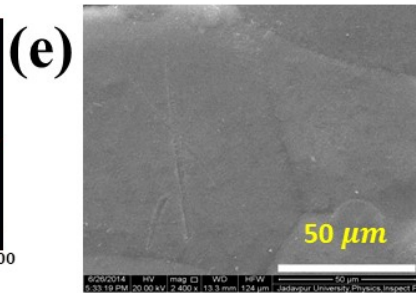
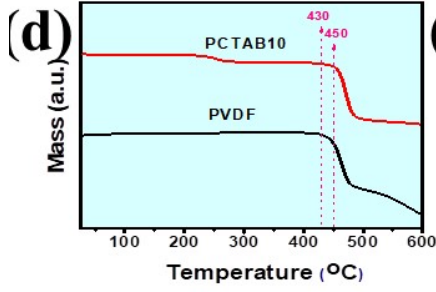
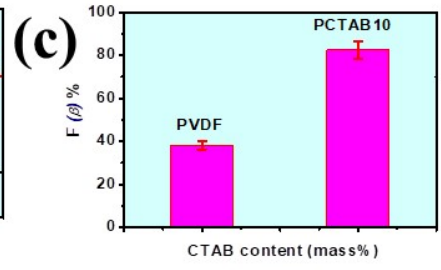
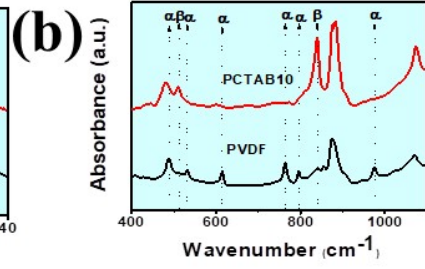
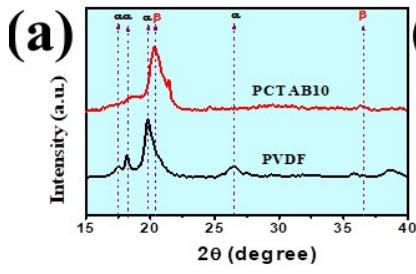
carriers formation. As electrolyte potassium salt K_2HPO_4 is used in the photo-sensitive solution including with PVA. The sticky texture of the electrolyte solution is just due to the use of PVA. Then the assembled device is kept in front of a 40 W tungsten bulb of intensity 110 mWcm^{-2} with covering ultra-violet and infrared light eliminating filters. Figure – 2g is illustrating the self-charging and discharging behaviour of the KPPC and this is plotted graphically as a function of time. When the tungsten bulb is switched on, there is an effect of the photon particles (h) on the lower energy electrons of the ZnO and WO_3 molecules and as a result of which the electrons will be realized an excitation to reach the higher energy level. After that the charge carriers will rapidly shifted to the FTO glass electrode. As we connect the acting and counter electrodes by two conducting wires, there will be a conduction of the photo charge-carriers to the Al electrode. Since we have used a dielectric insulating material (PLA), these photo-carriers will be accumulated across the PLA thin film. Consequently, Al electrode will become a negatively charged electrode due to the excess charge accumulation and the FTO will become a positively charged electrode due to the charge deficiency. When a certain amount of photo-charge carriers will be generated by WO_3 and ZnO, there will be a shortage which is fulfilled by the electrolyte solution combined with K – ion. Recently, different types of metal – ion batteries are developed with different electrolytes like $NaPF_6$, KPF_6 , $KMnO_2$, $NaCO_3$, $NaClO_4$ etc. To fabricate the prototype K – ion based KPPC, K_2HPO_4 mixed PLA solution is used. Here, the possible working principle of KPPC can be explained by the energy level structure of the composite solution including electrodes under the illuminating circumstances. Since we have used a water base solution of the photo sensitive part and W+6 has a great oxidising power in WO_3 , it may be reduced to W+5 state. PVA/ K_2HPO_4 compound in the solution will be acted as an electron donor for the solar medium and it will fulfil the deficit of the photo-generated electrons which may be considered as photo-generated holes. Method can be regarded as the charging process which gives the maximum open circuit voltage 1V within 2 seconds (figure – 2g). KPPC is charged rapidly which is mainly because of the huge and steady transmission of the photo-charge carriers. After that, the light is switched off to study the discharging process of KPPC. According to the figure – 2g, it is seen that discharging process is quiet slow and it is discharged for a long time~ 2 hours. Since the surroundings of KPPC is completely dark, the photo-sensitive material cannot be able to regenerate more photo-carriers and the dielectric insulating medium will restrict the immediate movement of the stored carriers across the insulating PLA films. But after a certain point, a few amounts of carriers will be discharged and therefore, a slow discharging process is obtained. To investigate the discharging phenomenon, KPPC is also discharged through a constant current density ($\sim 0.5 \text{ mA/cm}^2$) under no light condition (figure – 2h). The use of dielectric PLA medium improved the charge storing capacity so that KPPC is showing a better storage potential $\sim 16 \text{ F/m}^2$. The maximum stored charge density of KPPC is found to be 1.5 mC/cm^2 with a higher energy density $\sim 2.22 \text{ mWhr/m}^2$. The performance of our power cell is very promising and a comparison of performances with other devices previously reported by different research groups. It is observed that the maximum power density attained by the device is 5 W/cm^2 . The following equations are used to calculate the parameters mentioned above. The long lastingness and durability is also checked for the K – ion based system and graphically shown in figure – 2i. This investigation is done taking by the charging – discharging recyclable activity for 200 cycles for 25 days and it is observed that the drop of photo-voltage is only 10.2 % for the KPPC after 25 days. CTAB/PVDF composite film-based Photo-rechargeable Hybrid Power Cell: Fig-3a is the representation of the X-ray diffraction (XRD) patterns of the CTAB incorporated PVDF films and a clear indication of the electroactive phase nucleation. The diffraction peaks around 17.6° (100), 18.3° (020), 19.9° (021) and 26.6° ((201), (310)) are prominent for the existence of the non-polar phase in pure PVDF. Crystalline phase of PCTAB10 is nucleated and confirmed due to the existence of peaks at 20.8° ((110), (200)). FTIR-8400S, Shimadzu instrument is used for the Fourier transform infrared spectroscopy pure PVDF and PCTAB10 films shown in Fig - 3b. -phase in pure PVDF ensured for the absorbance bands at 489 cm^{-1} (CF₂ wagging), 533 cm^{-1} (CF₂ bending), 615 and 764 cm^{-1} (CF₂ bending and skeletal bending), 795 and 975 cm^{-1} (CH₂ rocking), whereas, 475 cm^{-1} (CF₂ deformation), 510 cm^{-1} (CF₂ stretching), 600 cm^{-1} (CF₂ wag) and 840 cm^{-1} (CH₂ rocking, CF₂ stretching and skeletal C–C stretching) are responsible for the crystalline phase creation in PCTAB10 sample. Lambert–Beer law is used for electroactive phase is calculated and it is almost $\sim 81 \%$ for PCTAB composite sample. The relative fraction of electroactive phase percentage in the concentration of CTAB10 doped PVDF films is

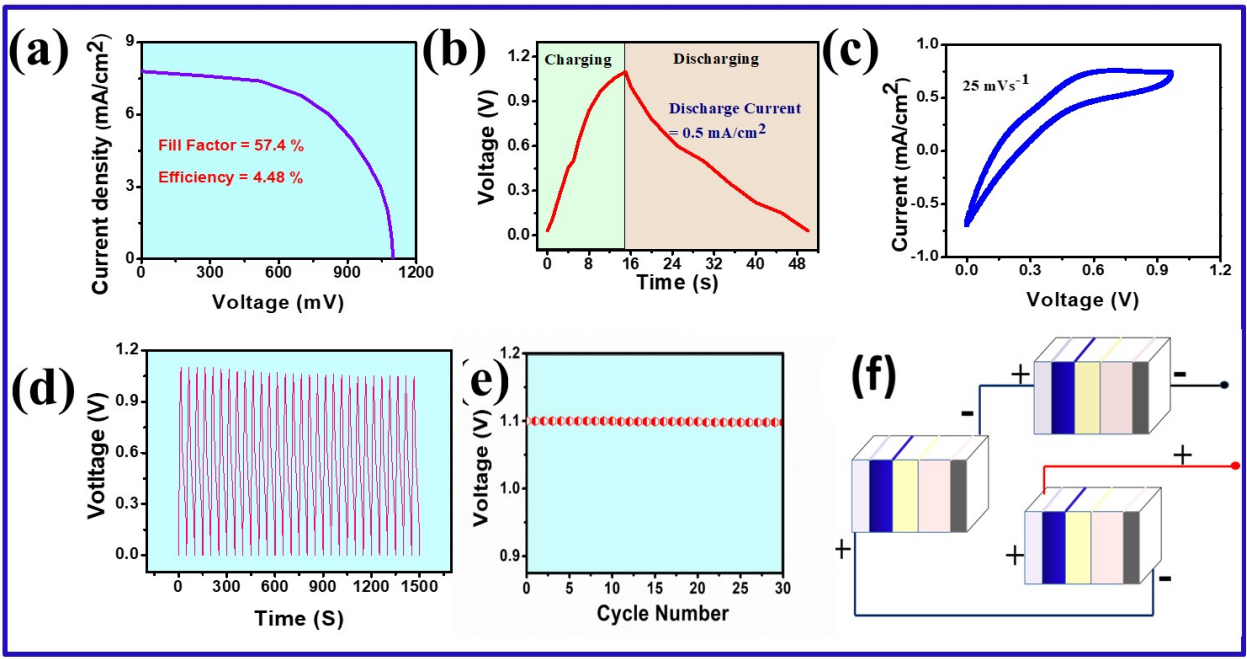
estimated by using . The $F(\%)$ of the both samples are graphically shown in fig – 3c. It is observed that the maximum $F(\%)$ is obtained ~ 83% for the doped PVDF film whereas the β -phase in pure one is just ~ 38 %. TGA thermographs are shown in fig - 3d to study the thermal stability of pure PVDF and CTAB modified PVDF thin films. There is an only single mass loss is observed at 430oC for pure PVDF film. However, two stage mass loss is occurred in PCTAB10 composite samples, one is ~ 220oC and the second is 450oC due to the decomposition of some CTAB and the PVDF respectively. The 20 oC increase in the thermo-degradation temperature in PCTAB10 samples is the confirmation of the interaction between the CTAB and the PVDF polymer matrix. The field emission electron microscope (FESEM) is used to obtain the microstructures of the pure PVDF and CTAB incorporated PVDF films which are shown in fig – 3e and 3f. According to the previous study ~ 50-70 nm is approximate diameter size of the spherulite of the pure PVDF but after CTAB doping the spherulite size become smaller which is the evidence of the β phase formation. Micrographs are also showing the uniform distribution of the CTAB particles within the PVDF polymer matrix (fig – 3f). Dielectric constant, tangent loss, ac conductivity – these three dielectric parameters of the pure PVDF and CTAB modified PVDF composite samples are recorded within the frequency range 20Hz to 2MHz by using a digital LCR meter PCTAB10 composite samples have the maximum dielectric value ~ 400 where it is ~ 9 for the pure PVDF films at the lower frequency region 20 Hz (Fig 3g). Dielectric value is consistently decreasing with increasing frequency for the PCTAB10 sample and almost constant for pure PVDF. MWS interfacial polarization can be used to explain the high value of the dielectric constant and the main reason is the proper arrangement of the large number of dipoles. Fig – 3h is showing the tangent loss ($\tan \delta$) variation pure PVDF and PCTAB10 composite samples with frequency. From the graphical representation, the $\tan \delta$ value is primarily decreasing and then it becomes constant with frequency. From fig – 3i, no prominent change is observed in the ac conductivity value for PCTAB10 at the low frequency region but a quite linear increment is observed at the higher frequency region. So, the large dielectric (~ 400) and electroactive (~ 81 %) PCTAB10 composite film is finally synthesized which is the appropriate choice to integrate the PESD as the photo charge carrier storage medium. A FTO coated glass is taken to design the PESD which contains the photo-electrons generating combined aqueous electrolyte mixture of eosin Y/MnO₂/PVA in association with the high dielectric storage material CTAB improved PVDF film (PCTAB10) of average thickness ~ 20 nm and dimension 0.20 cm x 0.20 cm. As a main charge carriers suppliers eosin Y is used including with MnO₂ and PVA which is responsible for the formation of sticky type electrolyte medium. The developed PESD is charged by a normal 40 W tungsten bulb of intensity 110 mWcm⁻² which is covered by a ultra-violet and infrared light eliminating filters. Fig - 1a is the schematical representation the working mechanism of the PESD including HOMO/LUMO energy structures of the solar electrolyte with electrodes. In Fig – 1b the full structure of the PESD is shown schematically. The whole device is working with two fundamental processes i.e., photoelectrons are generated by the light sensitive part PVA/MnO₂/eosin Y and that generated electrons are stored across the high dielectric PCTAB10 thin composite film. We have studied the photovoltaic characteristics of the PESD elaborately during both charging and discharging conditions. Graphically, current-voltage (J-V curve) and the photovoltaic behaviour of PESD are shown in Fig – 4a – 4c. From the variation of current density with voltage (fig – 4a), it is observed that a very good short circuit current density (I_{sc}) ~ 7.8 mA/cm² is obtained for the PESD fabricated by PCTAB10. When the device is placed in front of the light illumination, at very first a large amount of charge carriers will start flowing which results the high value of short circuit current density. Fig – 4b explains the self-charging and discharging phenomenon of the device. A tungsten bulb filament is used to illuminate the device so that photo-electrons of the dye eosin y can be excited to the LUMO energy state (~2.5 eV) from the HOMO level (~ -5.0 eV) by absorbing the photon particles (h). After that, since the photo charge carriers are already reached to higher state it will be transmitted to lower energy state of FTO by using the LUMO level (~-3.43 eV) of MnO₂ due to tunnelling effect. Here MnO₂ is added to the dye for making a smooth and easy tunnelling of the photo-electrons. Now, Al electrode is connected to the FTO through a conducting wire, so that the photo-electrons are rapidly start flowing to the counter electrode side. Due to the use of high insulating medium i.e. PCTAB10, photo-electrons will be reserved at the side of PCTAB10 sample and that will be acted like a negatively charged electrode. In comparison with this electrode, the conducting side of the FTO glass will be positively charged. After a while, eosin y will be unable to produce more charge carriers and then the deficit of charge carriers will

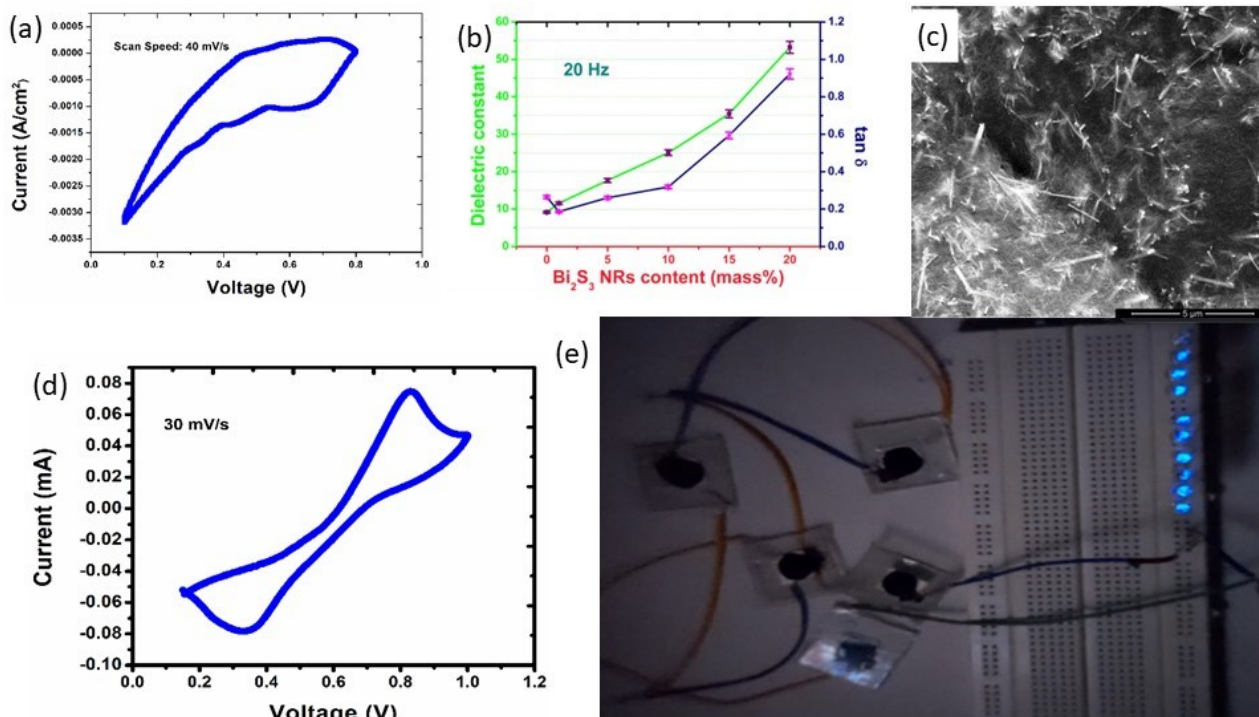
be filled by the electrolyte material PVA in the aqueous solar solution. In this project, a very simple possible mechanism is expressed to explain our device performance including the help of HOMO-LUMO energy state under solar light illumination. PVA in PVA/MnO₂ is also acting as electron donating agent along with the dye. Here our actual aim is to describe all probable electron refilling agents including the dye materials in the solar electrolyte solution. When visible light energy is fall on the device, the EY molecules and MnO₂ nanoparticles in the photoelectrode i.e. EY/MnO₂/PVA composite, start absorbing the photons (~ 494 nm and 532 nm). The photon induced electrons of EY jump out from its HOMO (-5.0 eV) to its LUMO (-2.5 eV) energy state. Also MnO₂ NPs are excited from its corresponding HOMO (-5.35 eV) to its LUMO (-3.43 eV) state and generate photo-electrons. Then photo-generated electrons are moved towards to the photo-electrode FTO with energy state of -4.4 eV. During photo-charging, photo-generated electrons at FTO move along the external circuit through the Cu-wire and reach the counter (Al) electrode and store in the adjoined high dielectric CTAB/PVDF (~ 400) film. Basically, the process can be said as the charging process of the PESD under light on condition. Since there is a potential difference between two oppositely charged electrodes as a result of which, approximately 1.1 V is obtained within 15 seconds (DMM 6500, Keighley). The device is charged very fast because of the rapid and smooth transportation of the electrons. From the graphical plot (fig-4b) the device discharged quiet slowly under light off situation within 35 seconds with constant current density 0.15 mA/cm². Calculate the storage capability of PESD and that is ~ 164 F/m² due to the superior electrochemical features of solar electrolyte regarding to charging-discharging action. The maximum output energy for PESD is attained to ~ 26.9 mWhr/m² with power density 5.5 W/m². The potentiality of the device is checked by calculating the photo-electric conversion efficiency. After the device performance study, all the output parameters are provided in a tabulated form in Table-1. Table – 1: Tabulated presentation of device performances: Parameters PESD Energy Density 26.9 mWh/m² Power Density 5.5 W/m² Storage Ability 164 F/m² Energy Conversion Efficiency 4.48 % Energy Storage Efficiency 13 %, Overall Efficiency 0.59 % All the essential equations and comparison for the device performance are supplied in the supporting information with the previously reported different types of photo-power cells. We have done the cyclic voltammetry (CV) (PG Lyte 1.0, Kanopy Techno Solutions Pvt Ltd) action of the PESD and are shown graphically in Fig 4c. This voltametric performance within 0–1.2 V potential range at a scan rate 25 mV/s ensures us about the good strength of electrochemical activity of the photo power cell (PESD). The data for self-charging and discharging variation is taken for 30 days daily (1 cycle (50 seconds) per day) to test the constancy and staying power of the composite PCATB10 based device and there is no such notable maximum voltage drop is observed (Fig-4d). In Fig-4d, we have presented the 30 cycles of data in a combined frame of common X-axis so, the range of x-axis is 0-1500 seconds (1 cycle ~ 50 s, so 30 cycles (observed one cycle per day for 30 days span) means 30 x 50s = 1500 s). And maximum output voltage achieved by the devices over 30 days i.e. 30 cycles versus cycle number has also been illustrated in Fig. 4e. In Fig- 4f, a schematic representation of a series connection with three PESDs is shown and that arrangement produces almost 3 V. So it is cleared that we can use our fabricated device for illuminating the commercially available different LEDs by making a series connection as a photo power bank. We have demonstrated lighting of LEDs by our fabricated cells which show its practical utilization. PLA/PVDF Based Photo-rechargeable Mg-ion Cell: Herein We have electroactive polymer-based photo-induced hybrid power cell has been developed using Poly-lactic acid (PLA)/ poly(vinylidene fluoride) (PVDF) composite film in a sustainable manner. First high dielectric polymer film has been prepared by PLA/PVDF (75/25 wt.%) matrix via solution casting method. In the basic configuration of this cell, aqueous electrolyte solution of PVP-MgCl₂-Eosin Y has been utilized as solar light absorber and photo-electron generator whereas the high dielectric PLA/PVDF is used as dielectric separator cum storage part in a very transparent way. The cell shows maximum voltage ~0.8 V with short-circuit current density ~ 10 mA/cm² under ~110 mW /cm² normal light illumination (Figure 5a). The device reveal almost same performance for a long time (30 days). The device able to lighten 20 LEDs for 7 days after single recharge under light (Figure 1e). Bi₂S₃/PVDF nanocomposites-based photo-power cell: We have synthesized Bi₂S₃ nanowires and doped into the PVDF matrix. The Bi₂S₃/PVDF nanocomposites also shows outstanding crystal formation and dielectric value. Highest dielectric value is measured ~ 54 (Figure 5b.). FESEM images shows uniform distribution of the nanowires in polymer matrix (Figure c). Further we have prepared photo-power cell with this sample using MnO₂ nanoparticles as solar part. We

see some excellent output voltage ~ 1.2 V. Cyclic voltammetry data shows very capacitive nature of the device. WO₃:HO doped PVDF film-based Photo-power cell: Herein, a prototype device, photo-rechargeable photo-power cell (PPC) has been fabricated using electroactive and high dielectric WO₃:H₂O/PVDF composite film. Perovskite NiMnO₃ is used as the main solar part in our fabricated device for photo-electron generation by absorbing the photons from solar light. The PPC shows output voltage (V_{oc}) ~ 1.0 V and the maximum areal specific capacitance ~ 1200 F/m² with 90 % energy storage efficiency. The charging-discharging data of the PCC was almost same by 12 weeks. The cyclic voltammetry data also shows the super capacitive nature of the fabricated device (Figure 5d). The realistic applications of our devices have been demonstrated by driving electronic gadgets. The PPC able to drive 20-25 LEDs for 7 days (Figure e). Thus, our study provides two powerful and cost-effective prototype devices for the next generation superior renewable/clean energy harvest from nature and storage in same unit for daily life utilizations.









Conclusions

In summary, we have fabricated several numbers of polymer film based proposed prototype energy harvesting unit able to harvest electrical energy from mostly available clean resources of our living system that is solar energy and able to store the energy in same unit with superior performances. Two secondary metal ion (K^+ and Mg^{2+}) based photo-rechargeable power cell fabricated successfully using bio-polymer PLA and PLA/PVDF composite films respectively. The K^+ -ion and Mg^{2+} -ion based photo-rechargeable cells shows interesting output voltage ~ 1 V and 0.8 V respectively. K^+ -ion based photo-rechargeable cell shows ~ 16 F/m² storage capacity with energy density and power density ~ 2.22 mWhr/m² and ~ 5 W/m² respectively. Further, we have prepared large dielectric (~ 400) and phase nucleated CTAB doped PVDF via simple solution casting method. Then eosin Y/ MnO_2 /PVA composite aqueous electrolyte solution is used to fabricate the exclusive and accessible photo-induced power cell PESD in association with the PCTAB10 composite sample as an insulating separator. Highest ~ 1.1 V is attained with very good storage efficiency $\sim 13\%$ including ~ 5.5 mW/m² power density. Bi_2S_3 /PVDF based photo-power cell also some excellent output voltage ~ 1.2 V. Further, we also prepared some perovskite structure based photo-power cell as proposed in the project. Perovskite NiMnO_3 is used as the main solar part in $\text{WO}_3 \cdot \text{H}_2\text{O}$ /PVDF composite film-based device for photo-electron generation by absorbing the photons from solar light. The cell shows output voltage (V_{oc}) ~ 1.0 V and the maximum areal specific capacitance ~ 1200 F/m² with 90 % energy storage efficiency. All fabricated photo-power cells able to lightening the blue LEDs using the cells as power supplier after charged under solar light. Thus, our study provides some powerful and cost-effective prototype polymer (PLA or PVDF) based devices for the development of next generation superior renewable energy harvester and self-charged photon induced self-charged power bank for daily life utilizations.

Scope of future work

The materials and devices will be eco-friendly, biocompatible and cost-effective. Totally clean and green approach have been suggested. There are no such environmental risk issues. These developed photo-power cell may have the long-term application in large-scale of energy demands of the society. The developed photo-power cell may be used as portable power bank which is able to charge under natural light. We have also fabricated two potential piezoelectric nanogenerators using kaolinite/PVDF and ZrO₂/PVDF based film which are able to generate electrical energy under mechanical impulse of our nature. As. Our developed polymer samples are able to store energy also can generate electrical energy capturing mechanical impulse. In future we can develop a hybrid device by proper designing and integration which is able to generate electrical energy under both light and environmental mechanical stress and store the energy in single unit behaving as capacitor/battery. As we developed two secondary metal ion (K, Mg) based photo-power cells which may be used as alternative of Li-ion battery due to its simple processing method and low cost. It may be a very vital future scope of our recent project studies.

List of Publications (only from SCI indexed journals) :

Title of the Paper	List of Authors	Journal Details	Month & Year	Volume	Status	DOI No	Impact Factor
Sustainable and superior polymeric piezoelectric nanogenerator for sensing human body vibration, air flow, and water wave	Ujjwal Rajak, Farha Khatun, Prosenjit Biswas, and Pradip Thakur* (PI)	APPLIED PHYSICS LETTERS (International)	Feb-2021	118 (053502-4)	Published	10.1063/5.0034879	3.791
Bio-polymer poly (lactic acid) thin film-based K-ion associated photo-rechargeable power cell	Sanoar Molla, Farha Khatun, and Pradip Thakur* (PI)	Journal of Materials Science: Materials in Electronics (International)	Feb-2024	(1-7)	Published	10.1007/s10854-021-07385-1	2.478
Self-Polarized ZrO ₂ /Poly(vinylidene fluoride-cohexafluoropropylene) Nanocomposite-Based Piezoelectric Nanogenerator and Single-Electrode Triboelectric Nanogenerator for Sustainable Energy Harvesting from Human Movements	Md. Minarul Saikh, Nur Amin Hoque,* Prosenjit Biswas, Wahida Rahman, Namrata Das, Sukhen Das,* and Pradip Thakur* (PI)	PHYSICA STATUS SOLIDI A-APPLICATIONS AND MATERIALS SCIENCE (International)	May-2021	218 (2000695)	Published	10.1002/pssa.202000695	1.981
Electroactive CTAB/PVDF composite film based photorechargeable hybrid power cell for clean energy generation and storage	Sanoar Molla, Farha Khatun, Ujjwal Rajak, Biswajoy Bagchi, Sukhen Das and Pradip Thakur* (PI)	Scientific Reports (International)	Feb-2024	12 (22350)	Published	https://doi.org/10.1038/s41598-022-26865-w	4.996

List of Papers Published in Conference Proceedings, Popular

Title of the Paper	List of Authors	Journal Details	Month & Year	Volume	Status	DOI No	Impact Factor
Not Available							

List of Patents filed/ to be filed :

Patent Title	Authors	Patent Type	Country/Agency Name	Patent Status	Application/Grant No.
Not Available					

Equipment Details :

Equipment Name	Cost (INR)	Procured	Make & Model	Utilization %	Amount Spent	Date of Procurement
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Equipment Name	Cost (INR)	Procured	Make & Model	Utilization %	Amount Spent	Date of Procurement
Handheld Digital Multimeter	82,600	Yes		50	0	
Cyclic Voltammetry	4,99,376	Yes		70	0	
Laptop	1,18,000	Yes		0	0	

Plans for utilizing the equipment facilities in

All equipment will be utilized in my research laboratory by my Ph.D. students. I also have another approved project of SERB (EEQ/2023/000316) this equipment will be very helpful for future data collection and analysis.

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