Development of a Self-Charged Photo-Power Cell Based on *In Situ* Synthesized Electroactive and Large Dielectric SrF$_2$/PVDF Nanocomposite Film

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Abstract :

In the modern society, clean energy (mechanical, solar, chemical etc.) investigation and its application to the global development is one of the most intense research topics for overall environmental security. So the present researchers are highly interested to resolve this critical issue for the entire energy demandby establishing new development in the technologies and devices for clean energy conversion, storage and conservation. So our intention is to develop such a self-charging energy storage system capable for both solar energy conversion and its simultaneous storage. A self-charged photo-power cellhas been fabricated in a very simplistic way that can be used as a portable photo-charged power bank and it is named as aself-chargedphoto power bank (SCPPB). To fabricate the device, we have assembled a photoelectrode (FTO) involving an organic dye phenosa-franine-polyvinyl pyrrolidone (PSF-PVP) film, zinc oxide (ZnO) and titanium dioxide (TiO$_2$) NPs solar part, as photo-electrons generator in combination with the electroactive and high dielectric SrF$_2$-PVDFNC film as storage unit. The maximum open circuited voltage 1.48 V is obtained under visible light illumination (~110 mW /cm^2) with a constant discharge current density ~1.64 mA/cm^2 and power density ~ 24.3 W/m^2. The maximum areal specific capacitance is obtained ~ 1600 F/m^2 with 92 %energy storage efficiency. The longevity and efficiency of SCPPB is also demonstrated by lighting up 24 commercially available blue light emitting diodes for 10 days with same intensity.

Keywords: PVDF; SrF$_2$; dielectric; power; storage; stability

1. INTRODUCTION

The major scientific and technical concern for our most feasible development in future is actually renewable energy reserves.[1]The replacement of non-renewable fuel sources like coal, petrol, gas etc. is a very important issue for the overall improvement of global economy

due to the increased ecological impairment and fast devastation of fuel source. [2]So the main attention of the scientists and researchers is to manoeuvre the pure and dexterous mechanism for energy supply and simultaneous storage of fresh and reliable energy from naturally obtainable energy sources like wind, sunlight, water, biomass energies etc. [3]

Transformation of electrical energy from other energy sources like mechanical, solar, chemical etc. is a very well-known phenomenon for piezo-electric nanogenerator, solar cell, metal O_2 batteries etc. [4] Recently, researchers are highly inspired about combined devices capable for both conversion and storage with high stability and low cost.

In the previous work, we demonstrated a two electrode PSESS with Poly (vinylidene fluoride) (PVDF) – Chlorochalcone a dielectric composite could accomplish double activity i.e., energy conversion and storage with a charging voltage of 0.95 volt.SCPPB is a two electrode low cost combined device which is very proficient both for energy conversion and storage like dye sensitized solar cell and battery or capacitor respectively, is able to fulfil the critical deficiency of solar power. The report of conversion of energy with superior storage capacity is very limited till now.

At present, polymer doped with nano-composites have progressively got the attention among the researchers due to their utilization in various purpose like field of piezo-electric nanogenerators , capacitors, thin film transistors, grid levelling, rail runs, non-volatile memories, sensors, actuators and also in biomedical fields. Poly (vinylidene fluoride) (PVDF) ([-CH$_2$-CF$_2$-]$_n$) and its copolymers are most essential electro-active semi-crystalline thermoplastic polymers with advantageous piezo-electric, pyro-electric, ferro-electric co-efficient, excellent thermal stability and chemical resistance, regarded as imminent materials for versatile applications. Five crystalline polymorphic phases $\alpha, \beta, \gamma, \delta$ and ε are detected for PVDF. [5]

In our present work, we have tried to design a low cost, uncomplicated; two electrodes LSESD (light sensitive energy storage device) by using in situ synthesized strontium fluoride (SrF$_2$) nanoparticle incorporated very high dielectric PVDF (PSR) films with the help of organic dye phenosafranine-polyvinyl pyrrolidone (PSF-PVP) film including zinc oxide (ZnO) and titanium dioxide (TiO$_2$) NPs (nano particles) as a solar part. This solar component and the high dielectric PSR films is the main cause of energy conversion and energy storage respectively.

2. EXPERIMENTAL:

2.1. SCPPB Fabrication:

A well cleaned FTO coated glass with acetone is the most essential part to assemble the device. Firstly, the dye solution (20 mg/ml PSF and 100 mg/ml ZnO and TiO_2 nanoparticle in 10% mass PVP solution) is prepared in distilled water. Now the well stirred dye solution is poured drop wise on the FTO coated glass and desiccated at very low temperature till the solution becomes sticky. Initially *in situ* synthesized $PVDF/SrF_2$ composite (0.2M) thin film is deposited on the sticky layer and dried out. A counter electrode aluminium tape is attached on the top of the film and two wires are connected from each side of the electrode i.e., FTO and Al tape for the photovoltaic measurements.

3. RESULTS AND DISCUSSIONS

The fabrication procedure of the SCPPB and the digital image has been demonstrated schematically in Figure - 1. *In situ* synthesized $SrF_2/PVDF$ NC thin film is used as the active material for storing the photogenerated electrons or charge carriers by the adjacent solar part. This study involves the details characterization of the optical and dielectric properties of the in situ $SrF_2/PVDF$ NC thin films and then fabrication of a self-charged photo-power pack for ensuring best performances in practical utilization.
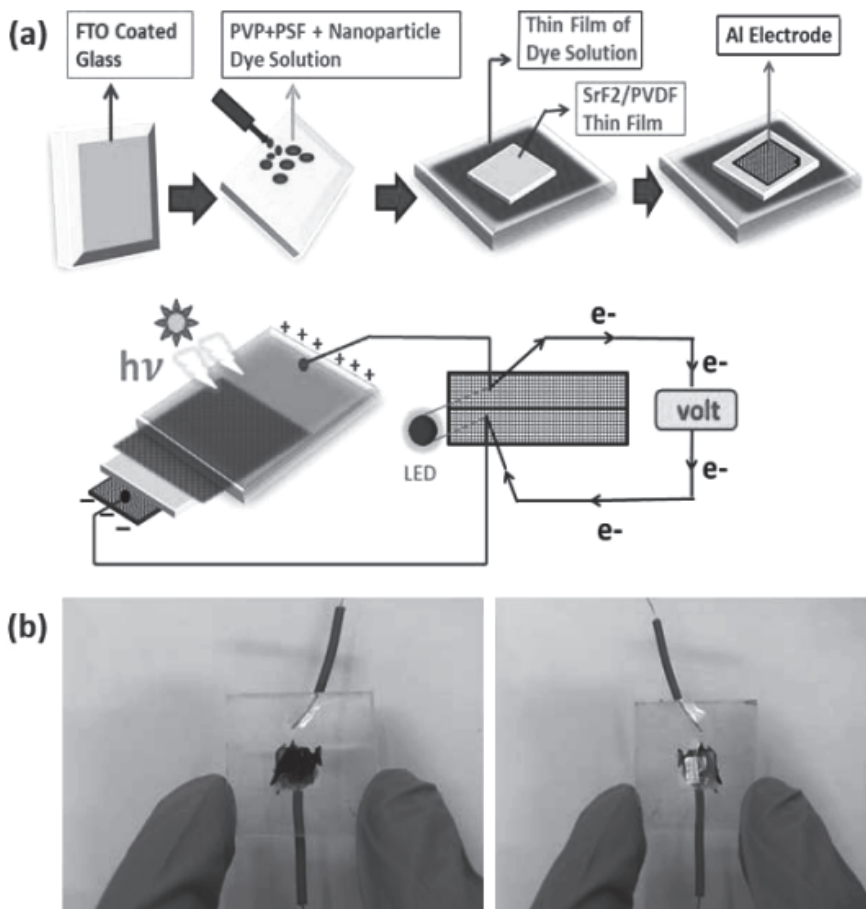
Figure 1: (a) Schematic diagram of the fabrication of the SCPPB. (b) Digital image of the SCPPB

3.1. XRD analysis:

The X-ray diffraction patterns of pure PVDF and SrF_2 incorporated films are depicted in Figure – 2a, to study the crystalline behaviour of the films and also for the investigation of the formation of SrF_2 nanoparticles.

3.2. Fourier transform infrared (FTIR) spectroscopy:

Fourier transform infrared (FTIR) spectra of pure PVDF and NPs doped films are shown in Figure-2c. From the spectrum, for pure PVDF the absorbance bands are observed at 489 cm^{-1}(CF_2 waging), 533 cm^{-1} (CF_2 bending), 615 and 764 cm^{-1} (CF_2 bending and skeletal

bending),795and 975 cm^{-1} (CH_2 rocking) due to the α phase and a small absorbance band at 840 cm^{-1} (CH_2 rocking, CF_2 stretching and skeletal C–C stretching) which is for the β phase. By using, Lambert–Beer law $F(\beta) = \dfrac{A_\beta}{\left(\frac{K_\beta}{K_\alpha}\right)A_\alpha + A_\beta}$, we have calculated the relative fraction of electroactive β phase content ($F(\beta)$) in the NPs doped PVDF films and graphically shown the variation of $F(\beta)$ (%) with dopant concentration (volume %) in the Figure-2d. The maximum $F(\beta)$ value is achieved 80% for the 16.4 (volume %) doping concentration.
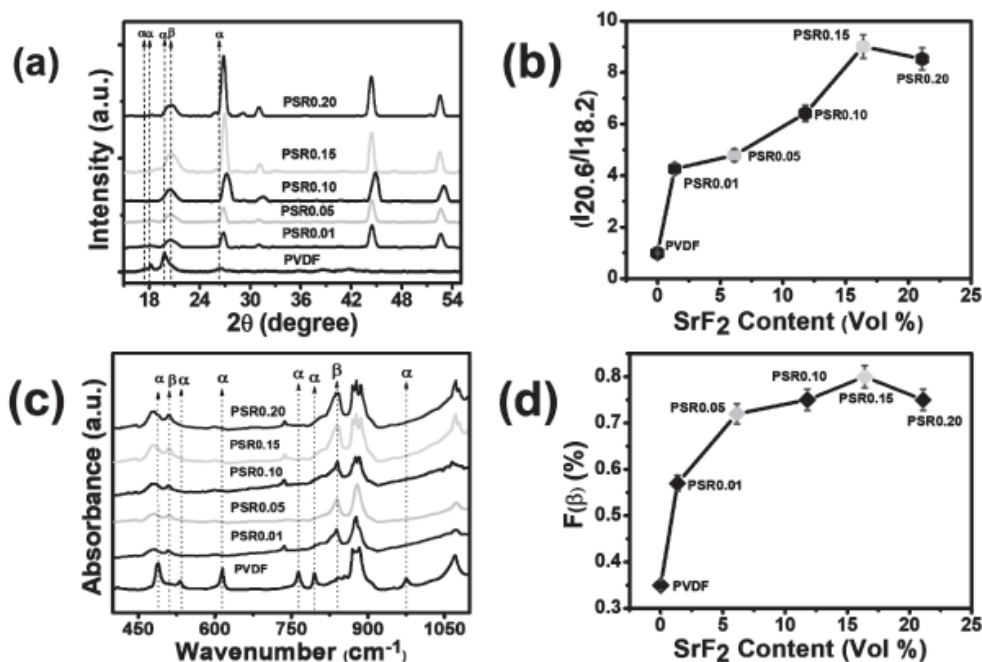

Figure 2: (a) XRD patterns of pure PVDF and SrF_2 – PVDF composite thin films, (b) Ratio of $I_{20.5}$ and $I_{18.3}$ of the thin films, (c) FTIR spectra of pure PVDF and PSR thin films, (d) •phase content with increasing SrF_2 content form IR spectra.

3.3. Dielectric properties (Dependence on NPs content and frequency)

The deviation of the dielectric constant and tangent loss of the SrF_2/PVDF composite films as a function of SrF_2 NPs content at 20Hz and 2MHz is shown in Figure-4a and 4b. According to the graphical studies, the *tan δ* values of the PSR thin films is increased non-linearly with the increasing SrF_2 content and the dielectric constant is slowly increased for the composite

films up to 16.4 volume% NPs content and then decreases for the highest concentration. We have achieved a huge value of the dielectric constant 5141 for PSR0.15M composite sample at 20 Hz and for 2 MHz the dielectric value is 40 for the same composite. This variation of the graphical pattern and the large dielectric value may be justified by Maxwell–Wagner–Sillars (MWS) interfacial polarization.[6]The ac conductivity also increases with increasing SrF_2 molar concentration up to 16.4(volume %) and also with frequency (Figure-4c).

Variation of the dielectric constant, ac conductivity and tangent loss (*tan δ*) with frequency of the pure and doped film is graphically illustrated in Figure-4**.** From the graph (Figure-4d), a decrease of the dielectric constant at higher frequency and increase of that for lower frequency is observed for the SrF_2/PVDF samples and no such variation is found for pure thin films. The explanation of this variation is actually Maxwell–Wagner–Sillars (MWS) principle.[6] The main cause of the large value of the dielectric constant at lower frequency is large interfacial polarization. The maximum value of the dielectric constant 5.141×10^3 has been obtained for the 0.15M PSR thin films (16.4 volume % NPs doping) at frequency 20 Hz. When the frequency is increased, a restricted movement of the space charge and also low accretion of the charges occur due to the inconsistency of the frequency within the samples, as a result of which MWS effect fails and dielectric constant reduced. The dependence of the tangent loss (*tan δ*) with frequency is shown in Figure-4e**.** Figure-4f is the representation of the frequency dependence of ac conductivity of SrF_2 incorporated PVDF thin films.
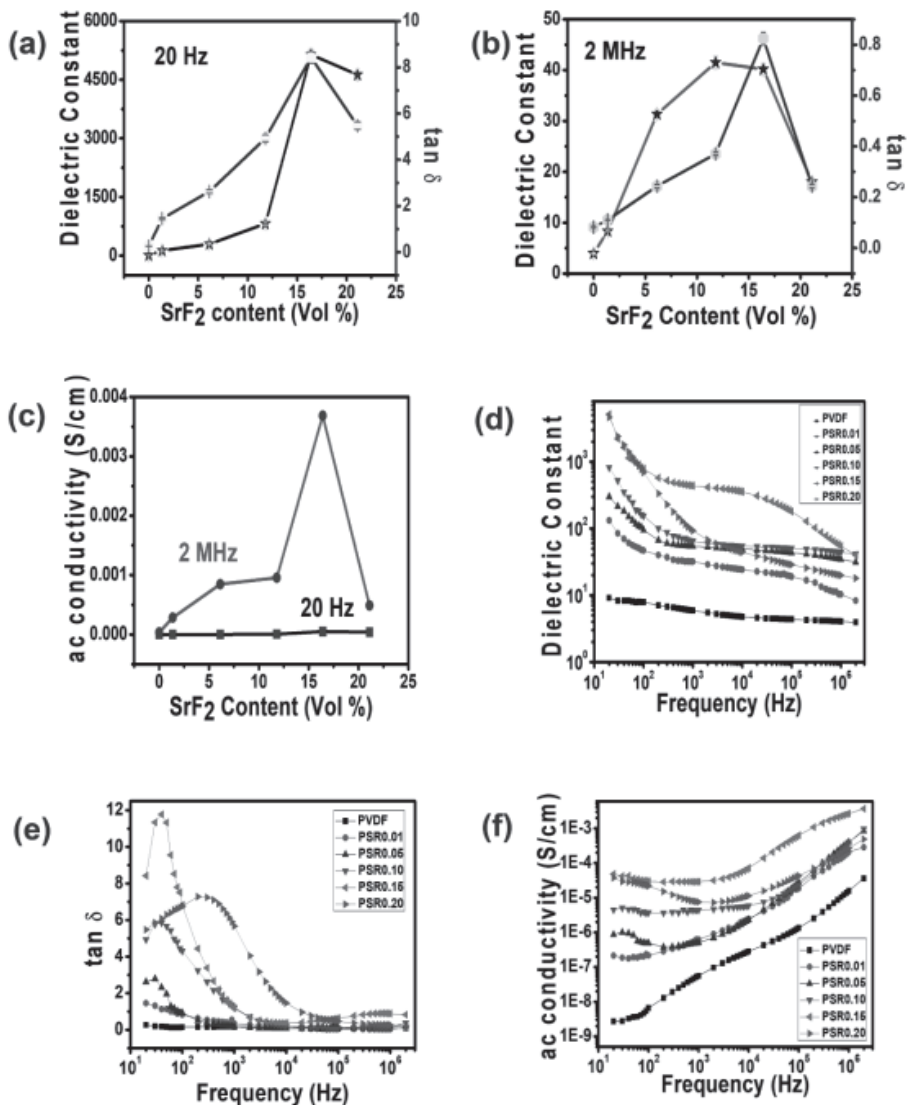
Figure 4: Variation of dielectric properties of pure PVDF and PSR thin films with SrF$_2$ (volume %) (a, b) dielectric constant and tangent loss and (c) ac conductivity. The frequency dependency of (d) dielectric constant, (e) tangent loss (*tan δ*) and (f) ac conductivity of the films.

3.4. Field emission scanning electron microscopy (FESEM):

Surface morphological and microstructural characterisation of the *in situ* synthesized SrF$_2$ NPs in the polymer matrix is elaborately studied by the field emission scanning electron

microscopy (FESEM) in Figure-5. The range of the diameter of the spherulite within 50-70μm is due to the existence of the α polymorph in pure PVDF thin film. But for the PSR thin films, presence of the comparatively smaller size spherulites confirms the nucleation of the piezoelectric polymorphs.[7] The FESEM images show some spherical structure of the NPs that are formed and uniformly distributed within the PSR films. For the higher loading concentration, the augmentation of the *insitu* NPs is seen within PVDF. For the composite PSR thin film, a homogeneous deposition of the SrF_2, NPs in the polymer matrix is the indication of the electroactive β phase formation.
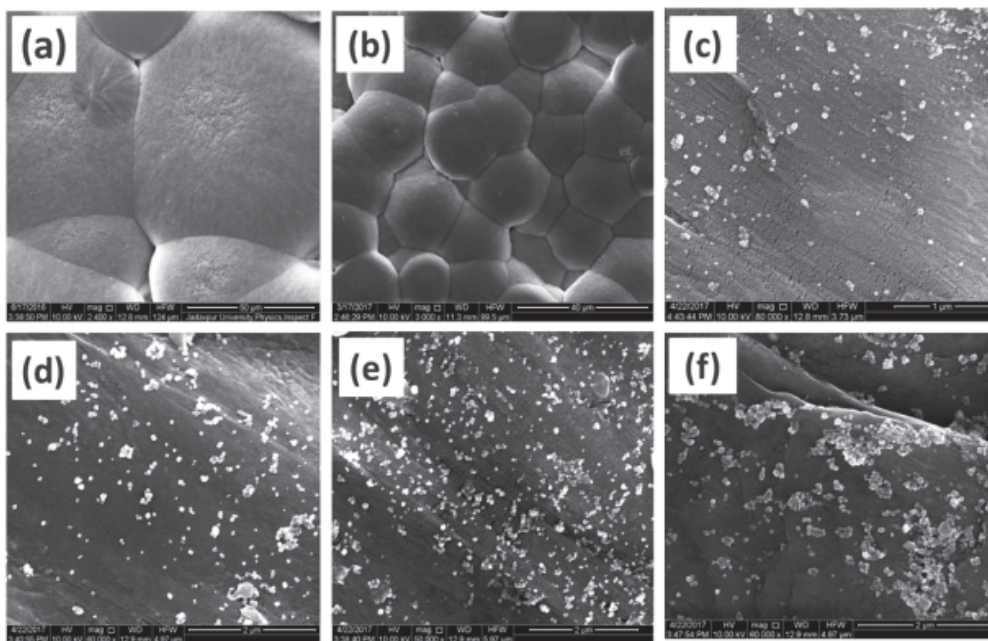

Figure 5: FESEM images of the *in situ* synthesized SrF_2 nanoparticles and surfaces of (a) pure PVDF, (b) PSR0.01, (c) PSR0.05, (d) PSR0.10, (e) PSR0.15 and (f) PSR0.20 thin films.

3.5. Mechanism and photovoltaic studies of the SCPPB:

The schematic representation of the fabrication and the digital image of SCPPB are demonstrated in Figure-1a and 1b. By analysing the internal structure, properties and dielectric studies, the most appropriate choice is PSR 0.15M composite thin film for the

device fabrication due to its giant value of the dielectric constant. A 40 W tungsten bulb covered with ultra-violet and infrared light eliminator filters, is used to charge the device under an illumination of 110 mWcm^{-2}.

The working mechanism of the SCPPB is schematically shown in Figure-6a. The whole mechanism of the device is mainly divided into two processes, origination of the photoelectrons and storage of the generated charge carriers. A composite mixture of PSF-PVP-ZnO-TiO$_2$ dye solution in aqueous acidic medium (H$_3$PO$_4$) is used as a solar part for photoelectron generation by absorbing photons from light illumination and the storage mechanism is mainly controlled by the PSR0.15M thin film of dimension 0.3cm x 0.3cm and thickness 15 μm. We have used FTO coated glass and Aluminium tape as the working and counter electrodes respectively. The HOMO/LUMO energy configuration of the photon absorbing PSF, nanoparticles ZnO, TiO$_2$ and UV-Visible absorption spectroscopy of the entire dye solution is shown in Figure-6b and 6c. Superior amount of electron injection by absorbing light determines the efficacy of the organic and metal−organic dyes in case of the photovoltaic performance of the energy storage device. The combination of nanoparticles with PSF-PVP is used due to its excellent opto-electronic, sensing, and catalytic characteristics which is very essential to enhance the light to-electricity conversion efficiencies of SCPPB.[8,9] The use of H$_3$PO$_4$ is just as an electrolyte within the dye solution.[10]
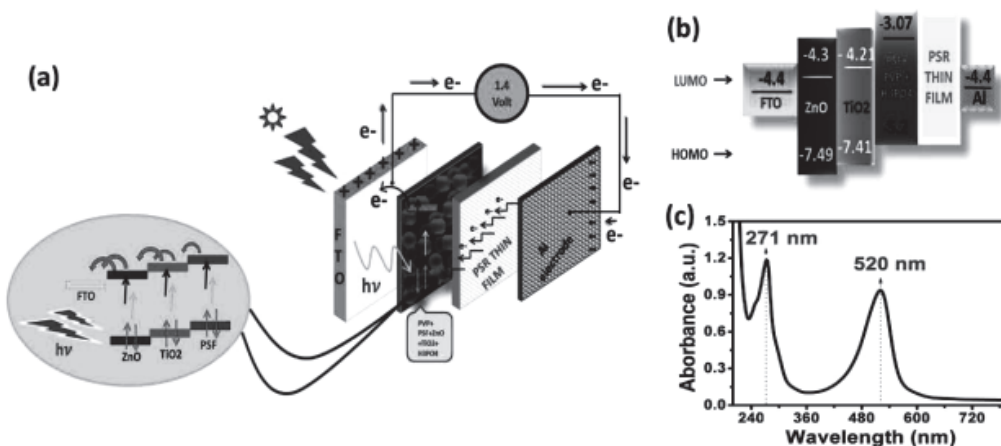

Figure 6: (a) Schematic representation of the working mechanism of the SCPPB. (b) HOMO and LUMO state of dye solution, (c) UV-Visible absorption spectrum of the dye solution.

Self-charging and discharging phenomenon (V-t and J-V curves) of the composed SCPPB is graphically shown in Figure-7. During the charging process under the light illumination, maximum attained voltage is 1.48 Volt within 2 min for the SCPPB involving PSR0.15M composite high dielectric thin film. From a close observation of the curve, a very slow decrease of the voltage i.e., apparently, a time-independent voltage variation is seen, signifies the superior storage stability of the device. A quite large value of the initial current density 3.9 mA/cm^2 is found from J-V curve (Figure-7a) with a decreasing pattern and finally becomes zero after reaching the highest voltage. The discharging action is totally performed in a dark room.
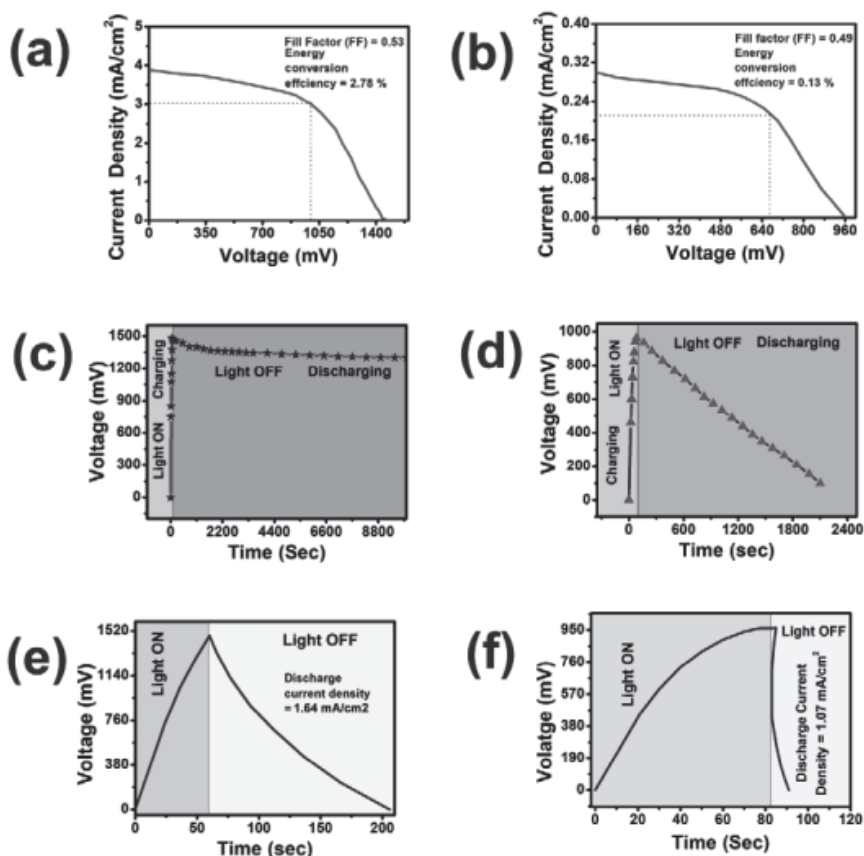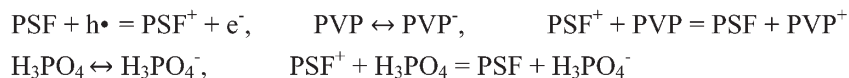

Figure 7: (a-f) Self-charging and discharging behaviour (V-t and J-V curves) of the fabricated SCPPBs as a function of time and different dielectric films (pure PVDF and PSR films) under light illumination and dark conditions.

When the device is kept below the tungsten bulb filament under switch on condition, initially PSF molecules will be excited by absorbing photons (hν) and it will generate electrons which are excited to the LUMO state of the PSF (~ -3.07eV). The charge creation process is mainly enhanced by the mixing of TiO_2 and ZnO NPs with PSF and according to the electronic configuration of TiO_2 and ZnO NPs (Figure-6b), photons (hν) will also excite the valance band electrons which will move to the conduction band of the nanoparticles. The photoelectrons generated by PSF will transfer to the comparably lower energy state of TiO_2 (~ -4.21eV) and also ZnO NPs (~ -4.3eV). Similarly, the carriers initiated in the TiO_2 and ZnO NPs will also move to the corresponding lower LUMO states. Since the LUMO state of FTO (~ -4.4eV) is the lowest energy level with respect to the others, electrons will finally come to the FTO glass from all other higher energy levels. After reaching on the FTO, enormous flow of electrons will occur through the wire connected with FTO and emigrates towards the Al counter electrode and collected at the adjacent surface between the Al and high dielectric PSR thin film. When saturation condition is reached, PSF and the NPs dye will not be able to generate further electrons, and this electron shortage is fulfilled by PVP and H_3PO_4. The excitation phenomenon of PSF and reaction process is explained as,

$$PSF + h\bullet = PSF^+ + e^-, \qquad PVP \leftrightarrow PVP^-, \qquad PSF^+ + PVP = PSF + PVP^+$$
$$H_3PO_4 \leftrightarrow H_3PO_4^-, \qquad PSF^+ + H_3PO_4 = PSF + H_3PO_4^-$$

The heavy electrons flow results the large initial current density (3.98 mA/cm^2) of the device. Due to the large collection of the electrons, Al electrode will act as a negatively charged and huge inadequacy of electrons at FTO, it will behave as a positively charged electrode. The electron-hole recombination will be lagged by the high dielectric SrF_2 containing PSR0.15 thin film acting as a separator between the two electrodes. So a potential difference will appear between the two electrodes. After that, no further movement of charge carrier will take place and current will be decreased to the zero value (Figure-6a) i.e. the photovoltaic phenomenon will stop and the photovoltage (1.48V) is obtained

The discharging characterization is observed under switched off condition. In the dark atmosphere, there is no photon to excite the PSF molecules, will cease the photo-electrons generation process. However, high dielectric PSR thin film behaves as an insulating medium, small ac conducting nature will allow very few amount of electrons to pass through the insulating medium and recombine with the positively charged particles. Due to very slow

recombination, a very small voltage drop and a constant discharge current 160 μm has been found.

A SCPPB is also constructed with pure PVDF thin films in same procedure and the photovoltaic performance is shown in Figure-7. The initial current density and maximum voltage have been found for pure PVDF based SCPPB is 0.3 mA/cm^2(Figure-7b) and 962mV which are much lower than that of the PSR composite thin film based SCPPB. From Figure-7d it is noticed that the discharge time is decreased for the pure device which is the clear significance of the lesser storage capacity of the pure device than that of the composite device due to the very small value of dielectric constant of the pure PVDF thin films.

To study the storage performance of the devices, after completion of the charging process, both the devices are discharged across a 10 kΩ resistance connected in parallel under the dark ambient and the discharge time is 146 seconds and 12 seconds (Figure-7e and 7f) for the PSR and pure PVDF based SCPPB respectively. During the discharging phenomenon the discharging current is also measured by connecting the resistance in series and the constant discharge current density for the composite and pure devices is found to be 1.64mA/cm^{2}and 1.07mA/cm^2 respectively (Figure-7e and 7f).

An estimated value of the stored charge density, capacitance, energy density and power density of SCPPB has been calculated from the discharge V-t graph (Figure-7e and 7f).

The values of energy conversion, storage, overall efficiencies and some of the afore mentioned parameters (energy density, power density and storage ability) of the devices constructed with PSR0.15 thin film are shown graphically in Figure-8a, 8b.
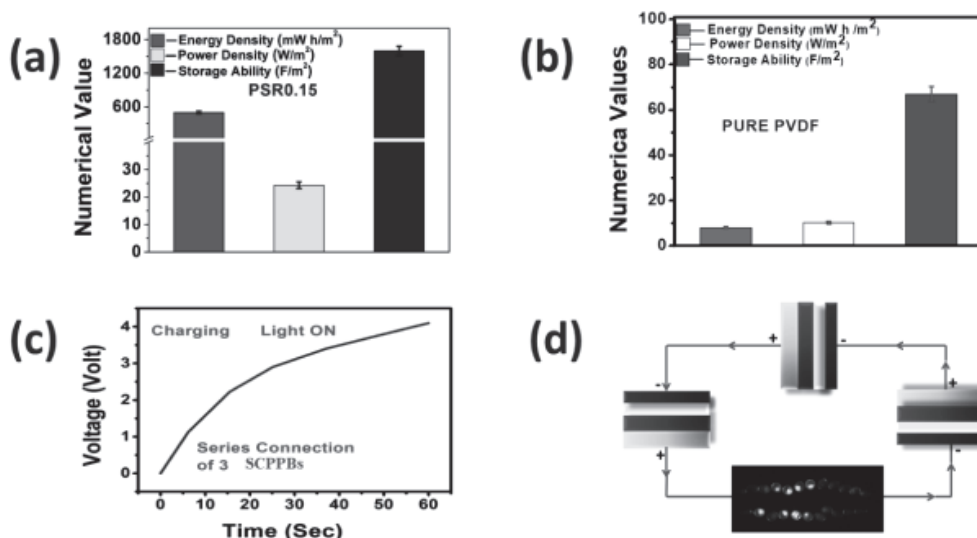
Figure-8: (a, b) Variation of the some parameters of the LSESDs for pure PVDF and PSR thin films and (c) Self-charging (V-t) curve of three serially connected SCPPBs with PSR0.15 thin film as storage part under light illumination. (d) Schematic diagram of the glowing of the blue LED by serially connected three SCPPBs as a power bank

Here, we have used a fundamental and low cost technique to construct the two electrode self-charging energy storage device with very high storage capability which may have promising acceptance in these renewable energy developing areas. Our attempt is just to design a simple and single system of solar energy conversion and storage in the form of electrical energy. We have achieved 92% energy storage efficiency and 2.78% energy conversion efficiency which is quite large and rarely reported in previous, whereas these values are much lower for pure PVDF based SCPPB. To analyse the self-charging ability (V-t curve) and also storage capability under light and dark atmosphere, we have developed a series connection of three SCPPBs made of PSR0.15 sample which is schematically shown in Figure- 8c and d.This combo connection is charged within 1min and 4.1 volt is obtained and this connection light up 24 blue light emitting diodes (LED) continuously up to 10 days with same intensity.

4. CONCLUSIONS

In summary, we have formed SrF_2 by *in situ* synthesis within PVDF matrix and characterize the composites thin films to develop an energy storage photo-charging system by using a simple and low-cost technique, proficient in the energy harvesting fields. According to the study it is confirmed about the enhancement of the phase of PVDF ($\sim$80 %) and also the dielectric constant from 9 to 5000 at lower frequency region. The maximum open circuit voltage 1.48 volt and short circuited current density 3.9 mA/cm^2 is obtained from SCPPB made of PSR0.15 under the photo illumination with superior storage capability due the use ofPSR0.15 thin films as a storage part. The maximum energy conversion and energy storage efficiency of the self-charged device is found to be $\sim$ 2.78 % and 92% respectively. The storage potentiality of the SCPPB is much higher than that of the earlier stated photoinduced devices. We have also demonstrates the practical utilization of the SCPPB by lighting up commercially available 24 blue LEDs with same intensity. High storage efficiency and also the stable reusing capacity of our self-charging device under light are highly applicable in the field of renewable energy bank of our future modern society.

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