

7. Photoresponsive properties of PVDF composites

7.1. Optical absorption of PVDF and PVDF/GO composite

Optical absorption spectrum of PVDF and its composite with different concentration (5%, 10%, 15% and 20%) of GO are recorded by UV-Vis spectrometer (Ocean optics) in the wavelength range of 200 – 800 nm and are shown in fig. 7.1(a). PVDF and its GO incorporated composites show a broad band absorption spectrum with highest absorption around ~ 325 nm. There is a sharp absorption edge for all of those films around ~ 310 nm is observed. On the opposite side of maximum absorbance peak, there is gradual decrease in

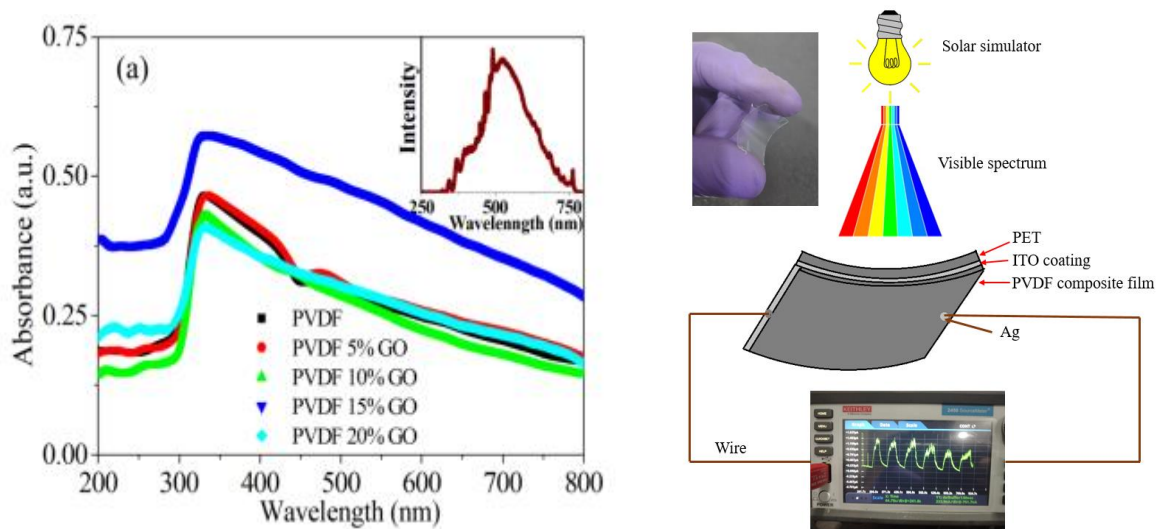


Fig. 7.1(a) optical absorption spectrum of PVDF and PVDF/GO composite film with varying GO concentration with input solar spectrum in the inset, (b) Schematic representation of photoresponse of PVDF/GO composite films with optical image in the inset

absorption up to 800 nm is observed. Gradual increase in absorption with GO incorporation is observed up to 15% GO concentration in the host. Further, GO incorporation reduces the absorption. This absorption of light causes electronic transition of electrons from upper levels of

valance band to lower level of conduction band. Detailed previous report suggests upper levels of valance band contains atomic states of C, H and F atoms, although 2P electron states of atom are contained in larger amount. Lower levels of conduction bands are formed by 2p electron states of those C atoms bonded with F atoms [194].

7.2. Photoresponse of PVDF and PVDF/GO composites

Time dependent rise and fall curves for photoresponse of PVDF and its GO filled composites with different concentrations (5% - 20%) are shown in fig. 7.2(a-e). To measure photoresponse of those composites, they are illuminated by a solar simulator with power density 150 watt while an external voltage of 10 V is applied across them. Incident spectrum is broad in nature with maximum intensity at ~ 525 nm. At an external voltage of 10 V, PVDF shows dark current density of ~ 0.4 $\mu\text{A}/\text{cm}^2$ (fig. 7.2(a)). When external light is turned on, photo induced current rises to ~ 1.0 $\mu\text{A}/\text{cm}^2$. Since it is an organic polymer kind of polycrystalline substance, response and recovery times appears to be very slow compared to conventional photodetectors which possess extreme fast response and recovery time [195-196]. Rise time for pristine PVDF membrane appears to be ~ 44 sec. As GO is introduced as nanofiller in the PVDF membrane, dark as well as photocurrent show a rise. However this gradual increment in photocurrent is observed only up to 15% concentration of GO in PVDF. For PVDF/15% GO composite, photocurrent of ~ 7.5 $\mu\text{A}/\text{cm}^2$ is observed (fig. 7.2(d)) which is a huge rise from 1.0 $\mu\text{A}/\text{cm}^2$ for pristine PVDF. This increment in dark and photocurrent is attributed to easy transportation of charges through GO conducting network which prevents recombination loss to a great extent. But further increment in GO concentration as dopant in PVDF causes agglomeration which reduces conductivity in the composite. Therefore, at a particular concentration of GO inside PVDF, long range connectivity is established also known as percolation threshold [197]. This particular concentration is determined by GO concentration which counters interaction between host – filler [198]. Establishment of long range connectivity also seems to improve response time of the composite. Response time of

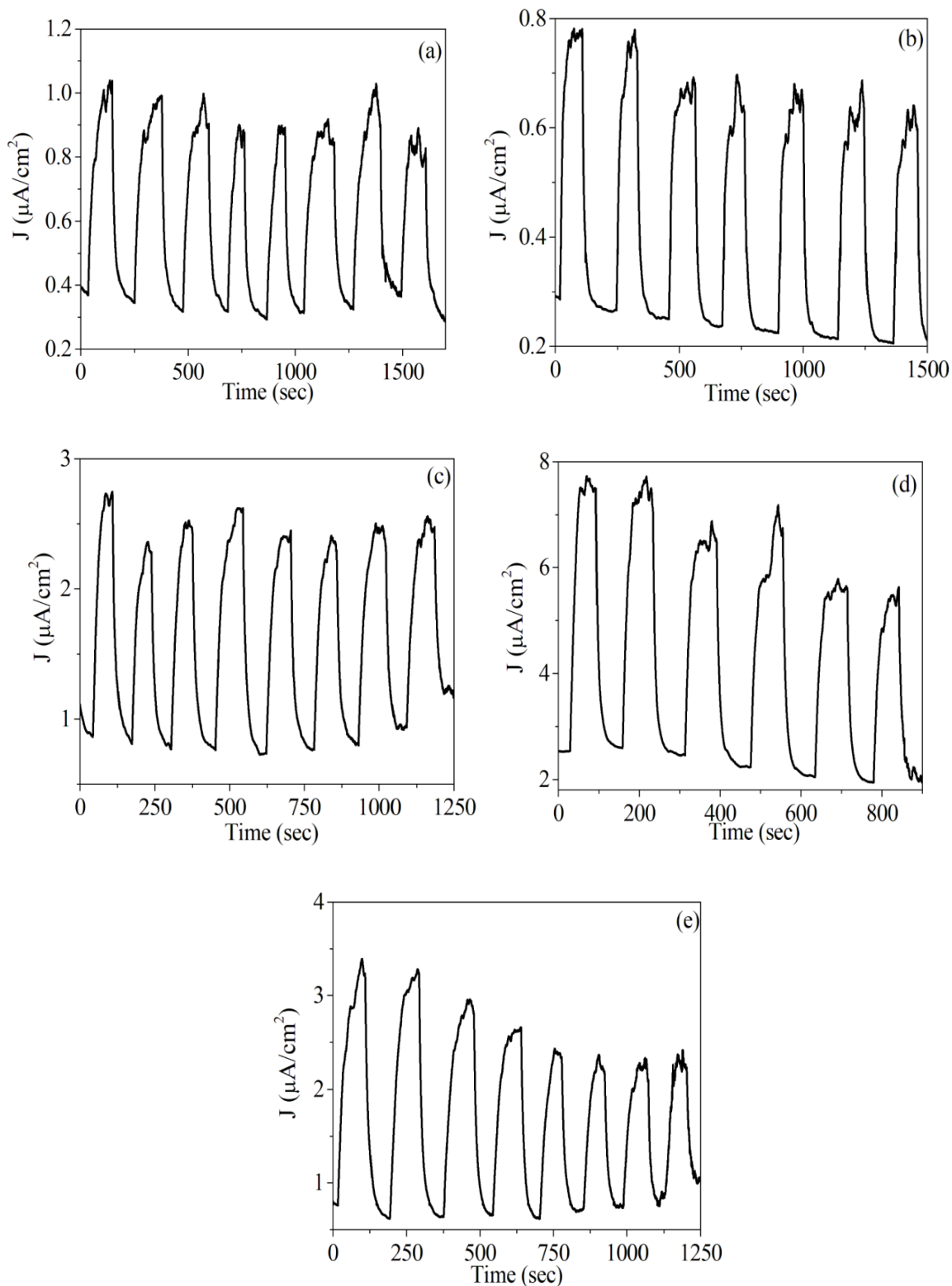


Fig.7.2 Time dependent photoresponse curves of (a) PVDF, (b) PVDF/5 % GO, (c) PVDF/10 % GO, (d) PVDF/15% GO and (e) PVDF/20 % GO composite films

PVDF/GO composite gradually shortens as fraction of GO in PVDF polymer is enhanced up to percolation threshold. Variation of response time with GO concentration is shown in fig. 7.3. This reduction in response time is due to easy transfer of generated charge carriers to electrodes overcoming potential barrier which acts as recombination centers and contribute to photocurrent. The PVDF composite loaded with 15% GO exhibits response time of ~ 21 sec which is shortest among them.

Responsivity is always a crucial parameter to measure performance of photo detecting device. It is defined as the ratio of amount of electrical energy generated to optical energy incident on it. PVDF being a polymer kind of substance its responsivity is nowhere compared to conventional photodetecting materials [199-200]. This is due to high dielectric nature and random orientation dipoles in PVDF which reduces the photocurrent immensely. For pristine PVDF, photoresponsivity of $0.004 \mu\text{A}/\text{cm}^2/\text{W}$ is observed which tends to rise with GO incorporation. Responsivity of PVDF/GO with varying GO concentration are presented in Table – 7.1. Maximum responsivity of $0.026 \mu\text{A}/\text{cm}^2/\text{W}$ is obtained for PVDF/15% GO composite. Beyond this particular concentration of GO inclusion, responsivity falls due to formation of additional grains by GO stacking.

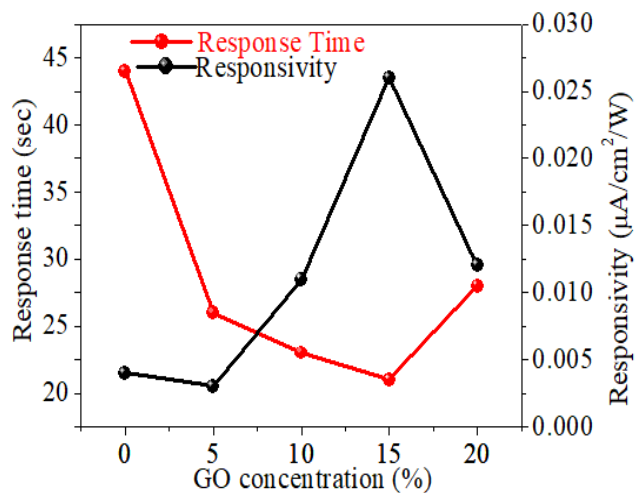


Fig. 7.3 Variation of response time and responsivity of PVDF/GO composite films with varying GO concentration

Table – 7.1 Different parameters of photodetection for PVDF/GO composite films

Film	$J_{\text{light}} - J_{\text{dark}}(\mu\text{A}/\text{cm}^2)$	Saturation time (τ) (sec) during rise	Responsivity ($\mu\text{A}/\text{cm}^2/\text{W}$)	$J_{\text{dark}}(\mu\text{A}/\text{cm}^2)$
PVDF	0.6	44	0.004	0.3
PVDF/5 % GO	0.5	26	0.003	0.2
PVDF/10% GO	1.7	23	0.011	0.7
PVDF/15% GO	4.0	21	0.026	2.2
PVDF/ 20% GO	1.9	28	0.012	0.6

PVDF being a flexible polymer kind of substance its responsivity is extremely low, but still flexibility allows it to operate even on arbitrary surfaces in stressed condition. Photoresponse of PVDF and its varying GO filled composites are measured when they are placed in bend situation and shown in fig. 7.4(a-e). In normal condition, pristine PVDF shows a photocurrent of $0.14 \mu\text{A}/\text{cm}^2$ which shows an increment to $0.24 \mu\text{A}/\text{cm}^2$ when placed in bend situation (fig. 7.4(a)). An increase in GO content in PVDF enhances both dark and photocurrent in the composite. For PVDF/15% GO maximum photocurrent of $0.2 \mu\text{A}/\text{cm}^2$ is which increases to $0.45 \mu\text{A}/\text{cm}^2$ in presence of external stress in form of bending (fig. 74(d)). For all of those composites, photocurrent in bend condition is higher compared to that in relaxed situation. Being a well-known piezoelectric substance, bending dislocates dipoles in PVDF generates an additional field. This formation of piezo-potential helps in separation of generated carriers aiding them to reach electrodes thereby reducing the recombination. Among those prepared films, PVDF/15% GO arises out to be the composite with highest photoresponsive property due to enhanced conductivity.

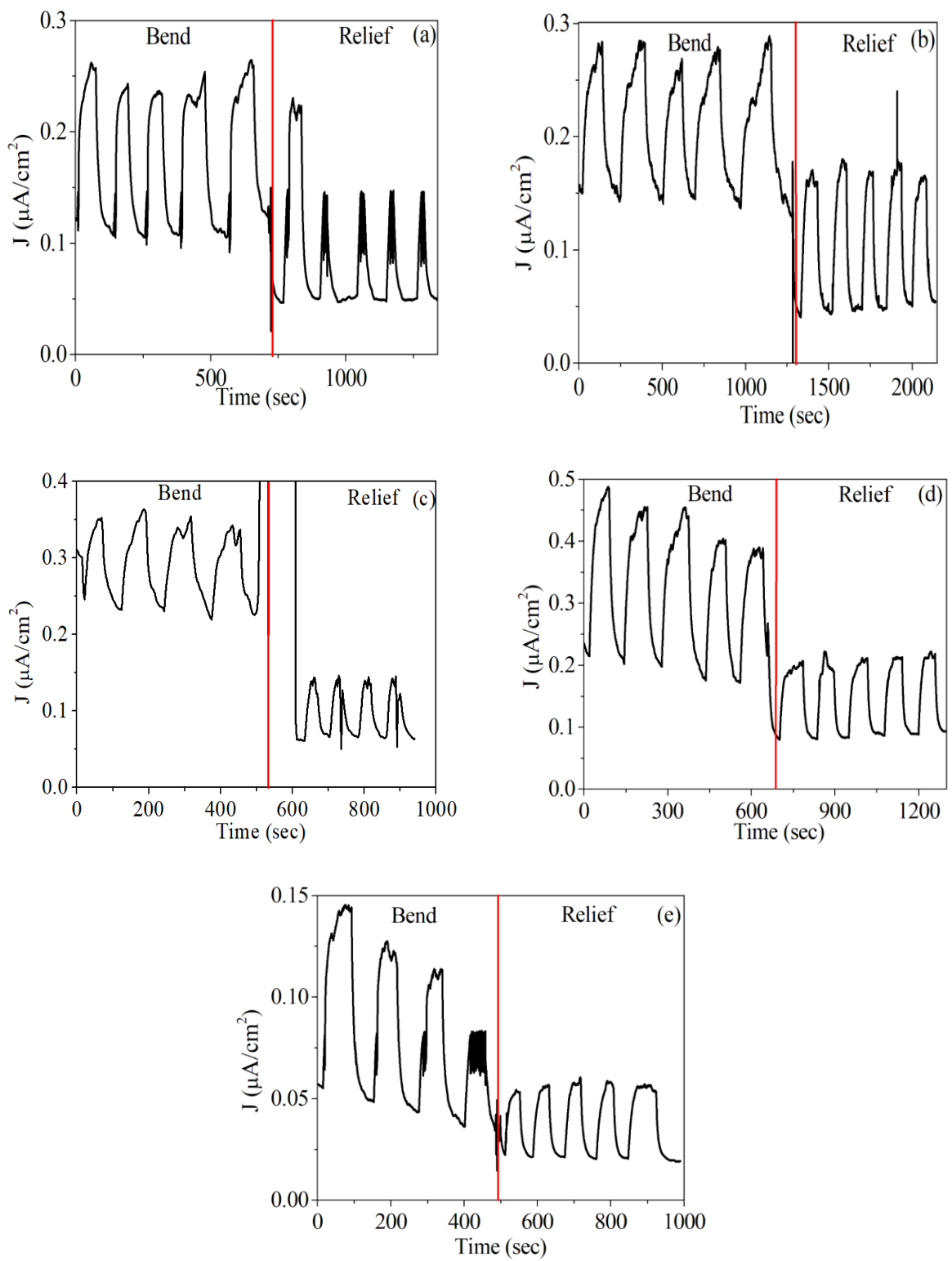
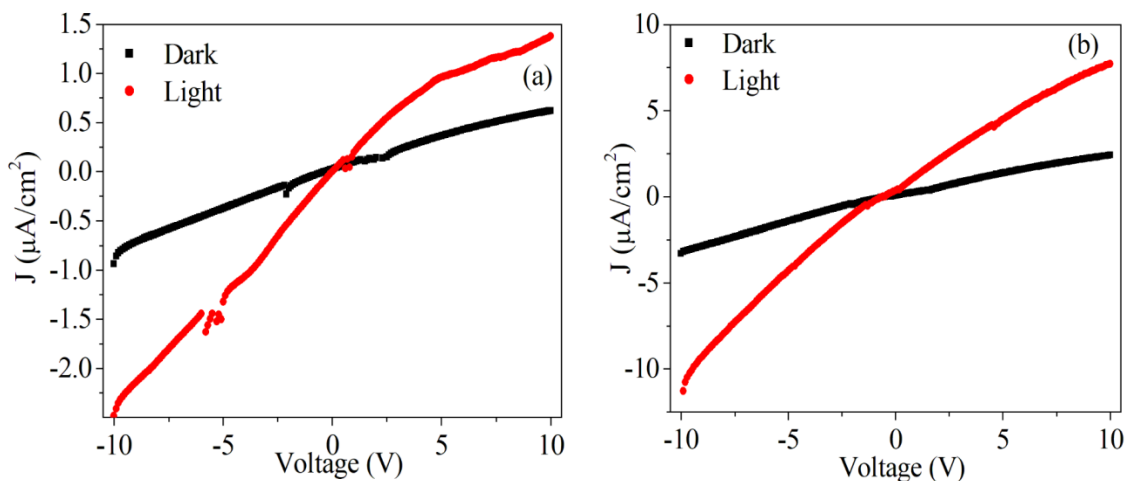


Fig.7.4 Photoresponse of (a) PVDF, (b) PVDF/5% GO, (c) PVDF/10% GO, (d) PVDF/15% GO and (e) PVDF/20% GO composite films in bend and released situation

7.3. Current – voltage (I – V) relationship of PVDF and PVDF/GOcomposites

Current – voltage relationship for all of those prepared composite membranes are recorded by a sourcemeter (Kiethley 2450 - Tektronix) at room temperature in the range of - 10 V to + 10 V in dark and illuminated condition. These measurements are presented in fig. 7.5(a-e). For PVDF dark current density is $\sim 0.6 \mu\text{A}/\text{cm}^2$ at 10 V which rises to $\sim 1.4 \mu\text{A}/\text{cm}^2$ when light is incident upon them (fig. 7.5(a)). This rise in current must be the effect of generation of additional charge carriers in presence of light. Introduction of GO sheets into the host polymer increases dark as well as photocurrent. For PVDF/15% GO maximum dark as well as photocurrent is observed to be $\sim 5.1 \mu\text{A}/\text{cm}^2$ and $\sim 15.0 \mu\text{A}/\text{cm}^2$ respectively (fig. 75(d)). Further increment in GO concentration in host polymer causes reduction in dark and photocurrent due agglomeration. All of those I - V curves show some kind of non – linearity due to having difference in conductivity in host and filler materials. Although, in pristine PVDF, non-linearity is also observed may be due to difference in conductivity between grains and the boundaries separating them [201].



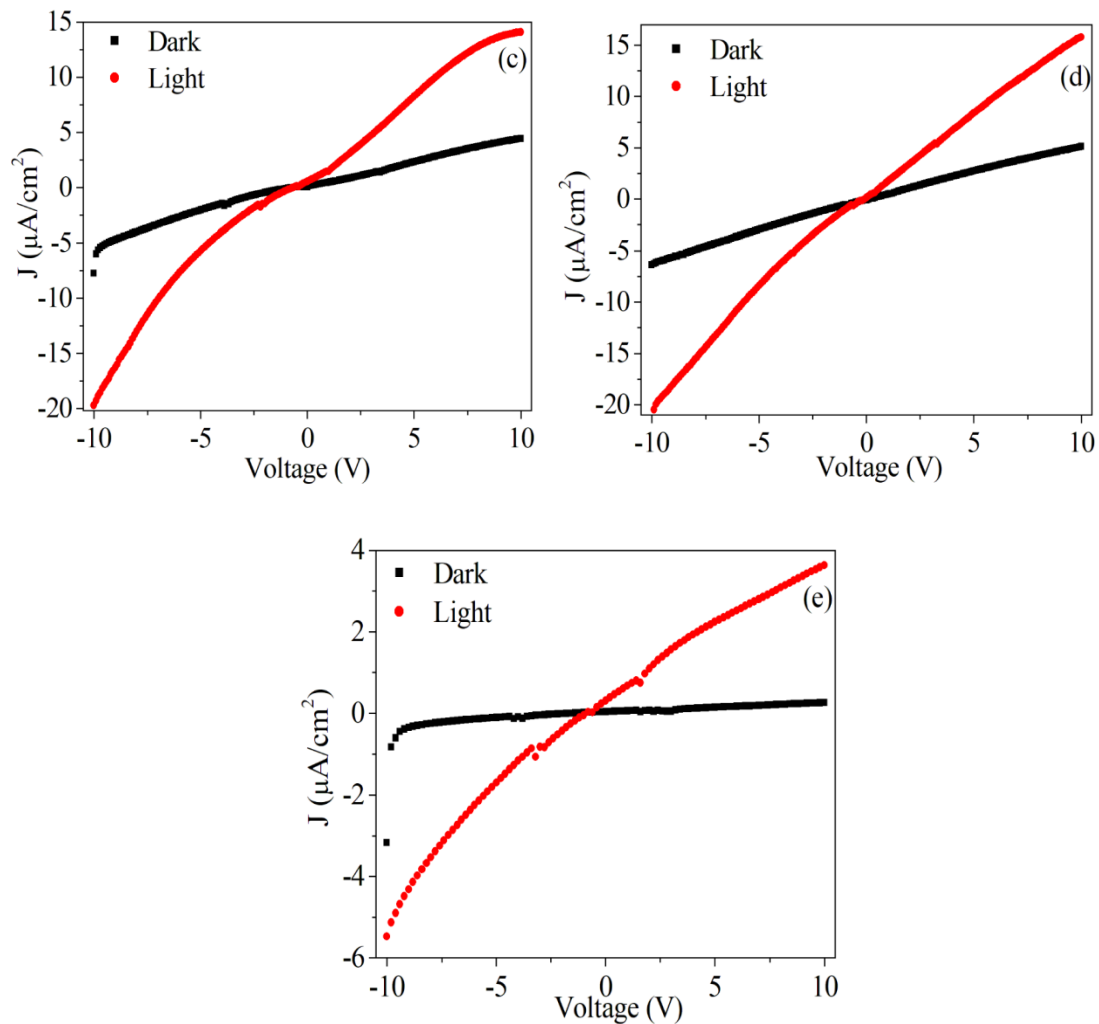
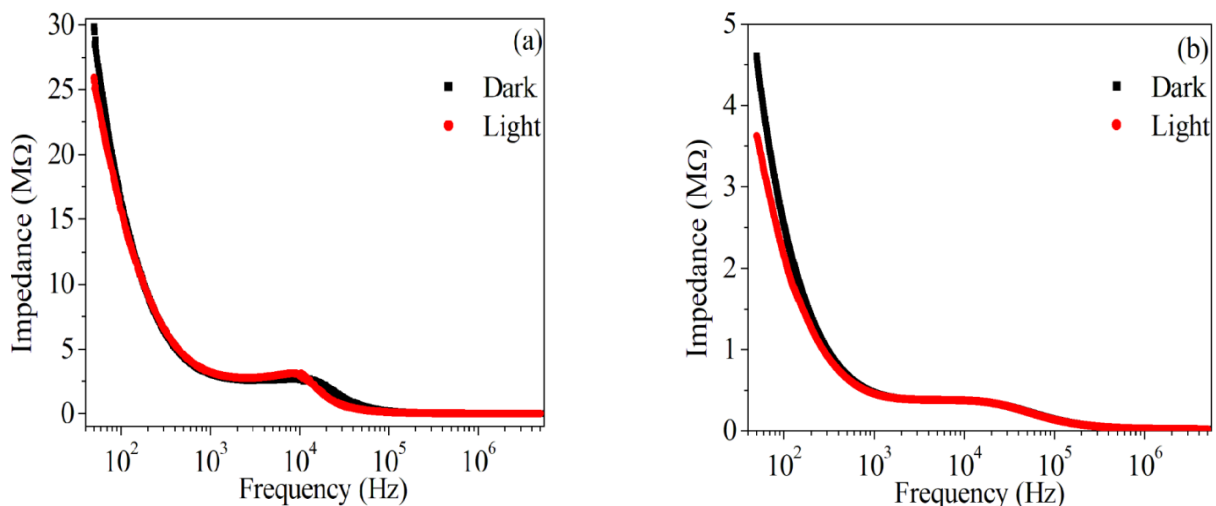


Fig. 7.5 Current – Voltage (I – V) curves of (a) PVDF, (b) PVDF/5% GO, (c) PVDF/10% GO, (d) PVDF/15% GO and (e) PVDF/20% GO composite films in dark and solar light illuminated condition

7.4. AC impedance spectroscopic analysis of PVDF and PVDF/GO composites in dark and illuminated condition

In order to gain insight of conduction mechanism and role of GO inside PVDF, ac impedance spectroscopic measurement has been performed in the frequency range of 50 Hz – 5 MHz when a voltage of 1 V is applied across them by HIOKI IM 3570 impedance analyzer. Figure 7.6(a-e) depicts variation of complex impedance with frequency in dark and illuminated condition. For pristine PVDF, at 50 Hz frequency impedance is ~ 50 Hz in dark condition. Then there is gradual fall in impedance is observed with increase in frequency due to inability of dipoles to follow such high frequency alteration. Impedance shows a slight fall in low frequency region when solar light is incident upon it. Before complete fall of impedance at high frequency there is a small peak in impedance at ~ 13 kHz is observed implying existence multiple relaxations associated with it. This double relaxation is due to crystalline motion at low frequency and non-crystalline motion at high frequency. Inclusion of GO into host PVDF polymer gradually decreases the impedance due to formation conducting network. Among different synthesized composites, PVDF/15% GO exhibits lowest impedance of ~ 3 M Ω at 40 Hz. In presence of light, impedance further reduces to ~ 1.3 M Ω due formation of additional carriers.



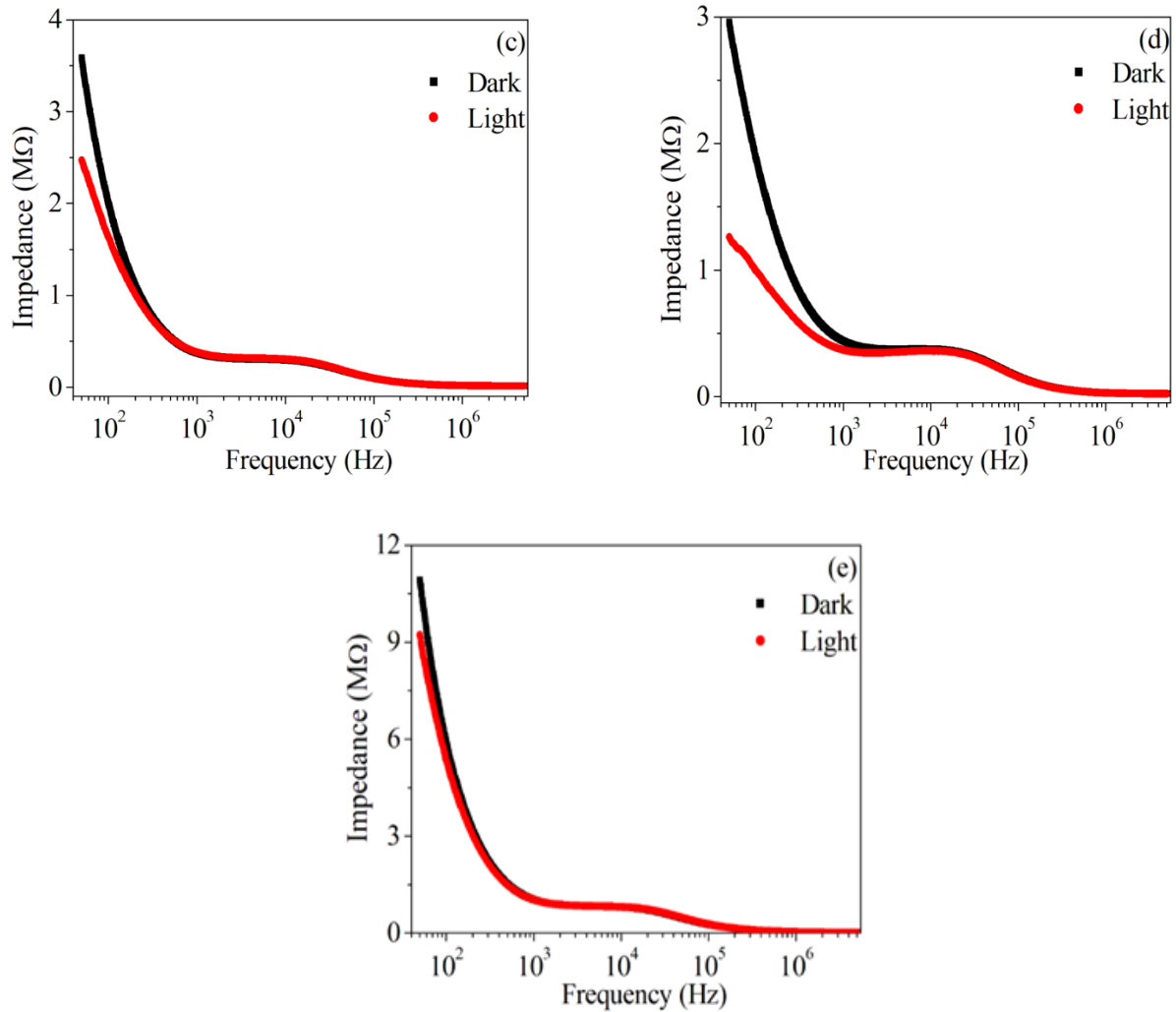
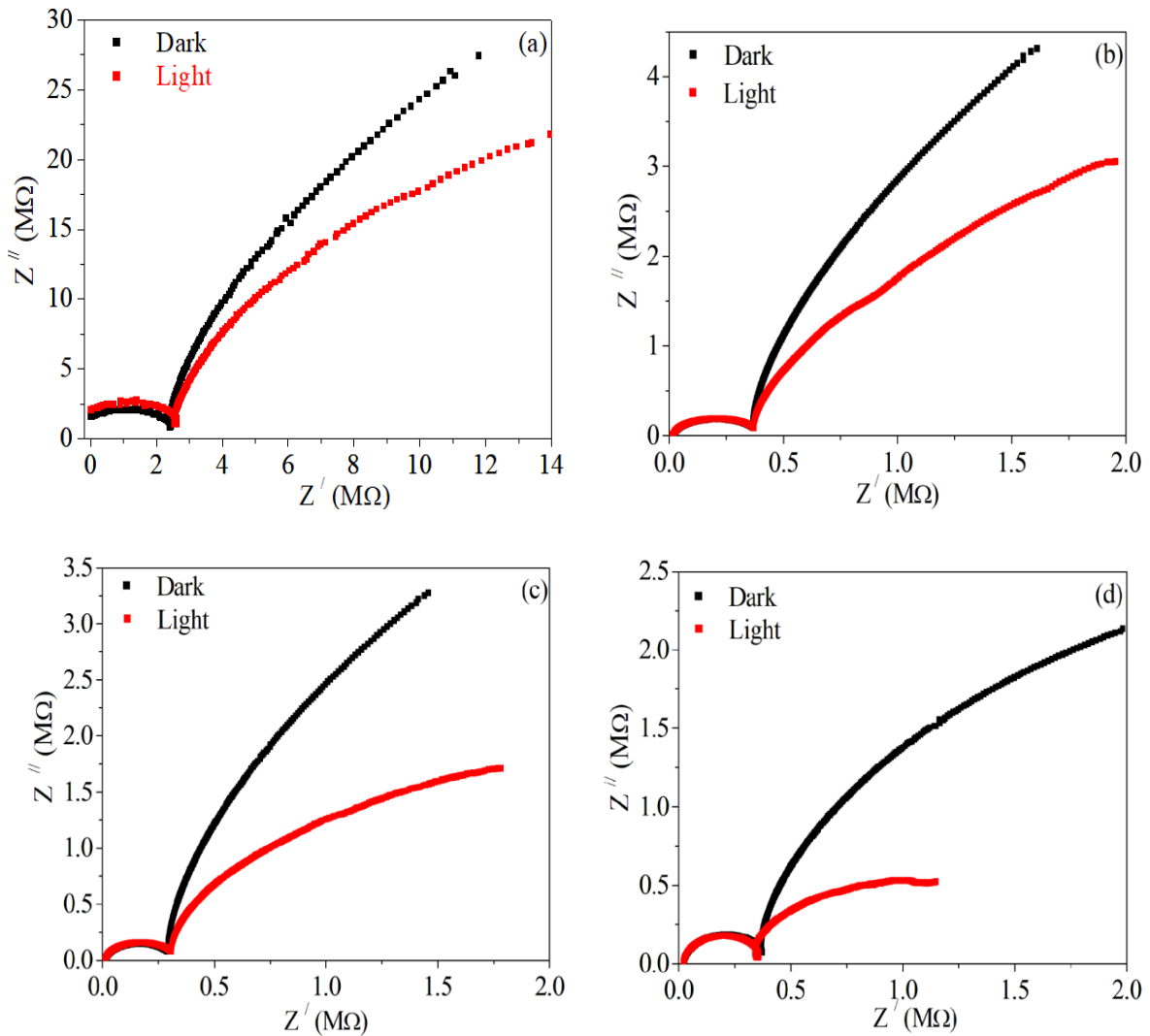


Fig. 7.6 Frequency vs. impedance for (a) PVDF, (b) PVDF/5% GO, (c) PVDF/10% GO, (d) PVDF/15% GO and (e) PVDF/20% GO composite films in dark and illuminated condition

From the experimentally obtained impedance spectroscopic result, imaginary part of complex impedance (Z'') is plotted against real part of it (Z') known as Nyquist plot in dark and light induced condition and are shown in fig. 7.7(a-e). Each plot consist of two semi circular segments identified as capacitive effects of grains and boundaries separating them. The incomplete semi circle at low frequency region is assigned to grain boundary or interfaces since interfacial polarization responds in this frequency region. At high frequency region, orientational polarization corresponding dipoles forming grains becomes effective. Incorporation of GO into host PVDF tends to reduce arc of those semi-circles implying reduction in overall impedance. Moreover, when

light is incident upon them, one of those semi circular arcs assigned to boundaries show significant change in presence of light. This effect of light becomes more prominent with increase in GO content inside PVDF upto 15% of concentration. The other part of Nyquist plot corresponding to core grains remains unaltered hints that core grains are unaffected by presence of GO there. These results verify presence of GO in the composite ensures better transport of photo – generated carriers by helping them to overcome the barriers at those boundaries.



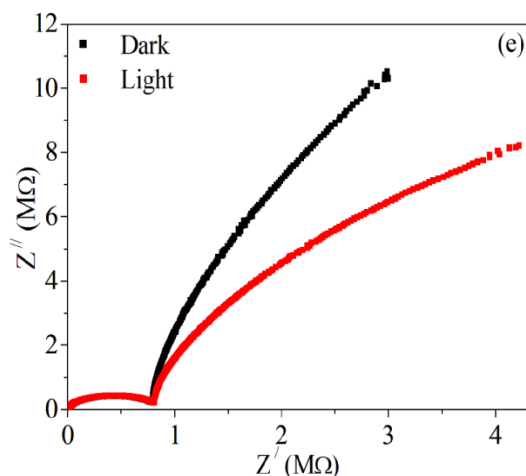


Fig. 7.7 Nyquist plots for (a) PVDF, (b) PVDF/5% GO, (c) PVDF/10% GO, (d) PVDF/15% GO and (e) PVDF/20% GO composite films in dark and illuminated condition

Nyquist plots for PVDF/15 %GO composite membrane have also drawn in bend and relaxed situation to reveal the effect of bending on those prepared samples. From fig. 7.8 it is apparent that bending distorts both core and its boundary. At bent condition, imaginary part of complex impedance in low frequency region is slightly decreased due to apperance of fixed charges on the surface. In high frequency region where effect of grain is dominant, semi – circular arc is enlarged. In bend situation dominance of grain is observed to start at lower frequency mostly due to additional dipole formation because of distorted condition.

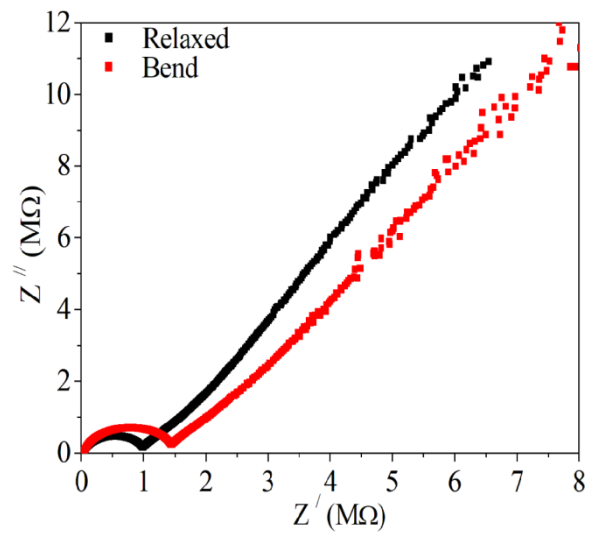


Fig. 7.8 Nyquist plot for PVDF/15% GO composite film in bend and relaxed situation