Study of IR Light Sensitivity of Graphene/PVDFNanocomposite

Abstract

The synthesis of graphene/polymer composites has been extensively studied due to their potential applications in catalysis, electronics, biology, magnetism, and optoelectronics. This study investigates the photoconductivity response of graphene/poly(vinylidene fluoride) (Gr/PVDF) nanocomposites under near-infrared (IR) light. The nanocomposite films were prepared by dispersing graphene in a PVDF solution, which was subsequently deposited onto glass substrates. The films were exposed to IR light, and resistance variations were recorded over time. Structural and surface morphology analyses of the fabricated films were performed using X-ray diffraction (XRD) and scanning electron microscopy (SEM). Current-voltage (I-V) measurements revealed p-type conduction behavior in the films. Notably, the photoconductivity response demonstrated a significant enhancement under IR light irradiation, particularly at negative applied voltages. These findings highlight the potential of Gr/PVDF nanocomposites for applications in infrared photodetectors, optoelectronic devices, and sensor technologies.

Keywords: graphene, PVDF, nanocomposite, solution-based synthesis, photoconductivity, near-infrared light.

1. Introduction

Graphene, composed of conjugated sp^2 carbon atoms arranged in a two-dimensional (2D) hexagonal lattice, is considered a highly promising building block for electronic and optoelectronic devices. Its unique properties, such as high carrier mobility, zero bandgap, and excellent photon absorption over a broad wavelength range (from ultraviolet to visible and infrared regions), make it an attractive material for these applications [1-5].

The zero-bandgap characteristic distinguishes graphene from conventional semiconductors, enabling the development of nanoscale devices such as field-effect transistors, terahertz sensors, and gas sensors due to its high surface-to-volume ratio [6]. As a result, the photonic response of graphene has been extensively studied, with reports highlighting its ultra-broad bandwidth, high-speed optical communication capabilities, plasmonic resonant enhancement, position-dependent behavior, and hot-carrier-dominated transport mechanisms [7-9].

However, further exploration of graphene is limited by challenges in large-scale production and the synthesis of high-quality graphene. Large-scale manufacturing remains difficult due to the strong interlayer van der Waals forces, and the synthesis of high-quality graphene is hindered by limitations in fabricating the material into arbitrary shapes. These challenges have spurred researchers to explore strategies such as incorporating graphene into nanocomposites (e.g., polymer-based systems) and investigating graphene fibers as alternative approaches [1, 10].

Graphene has been incorporated into hybrid composites with conducting polymers for a wide range of applications. Polymers such as poly(vinylidene fluoride) (PVDF), polypyrrole (PPY), poly(hexylthiophene) (PHTh), and poly(methyl methacrylate) (PMMA) have demonstrated promising results when combined with graphene to form electrode composites for superconductors [11, 12].In a study by Kaur et al., graphene/PVDF nanocomposites were investigated for flexible nanohybrids and supercapacitor applications [13]. Its strong electroactive behavior and simple processability make it an excellent candidate for developing flexible energy harvesting devices [14].

Despite these advancements, challenges persist in processing conducting polymers and nanoparticles within the matrix [12]. For commercial applications, an in-depth understanding is required to address issues such as the strength-to-toughness ratio in bulk nanocomposites and the trade-off between thermal conductance and interfacial thermal resistance in thermal management nanocomposites [15]. Possible application of PVDF/Gr in piezoelectric nanogenerators for energy harvesting has been described by Pusty et al. [16]. Furthermore, more research is needed to explore the effects of nanoscale fillers, including their size, dimensionality, and properties, to develop nanocomposites with significant potential for diverse applications [12,17].

Smart materials are capable of responding to external stimuli, such as temperature, pH, pressure, heat, electric fields, light, magnetic fields, and other environmental changes [18, 19]. The properties and applications of smart polymers have been extensively explored by Aguilar et al. [20]. Among these materials, poly(vinylidene fluoride) (PVDF) emerges as an excellent candidate for developing flexible, multifunctional smart materials and devices. PVDF is a remarkable fluoropolymer with exceptional properties, including thermal stability, chemical resistance to solvents and acids, as well as outstanding piezoelectric, pyroelectric, and ferroelectric characteristics. Consequently, PVDF-based composites and their applications have garnered significant global attention [8, 21–24].

This paper reports the photoconductivity of graphene (Gr)/PVDF nanocomposites in the near-infrared (NIR) region. The composites were synthesized using a solution-phase method and deposited onto a glass substrate. Infrared light was applied perpendicularly to the film from a distance of 10 cm, and resistance response curves were recorded. Additionally, the current-voltage (I-V) characteristics of the composites were examined and presented. The effect of PVDF binder volume concentration on the composite was also analyzed through scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques.**This manuscript contributes to the fundamental understanding of the properties of graphene/polymer composites, particularly their photoconductivity response under infrared light. By investigating the structural, morphological, and electrical characteristics of Gr/PVDF nanocomposites, the study sheds light on the interaction mechanisms between graphene and the polymer matrix. Such insights are crucial for tailoring the material's properties for specific applications in optoelectronics, infrared photodetectors, and sensor technologies, advancing both scientific knowledge and practical innovations.**

2. Material and Methods

2.1 Preparation of the nanocomposites (Graphene and Gr/PVDF)

The solution-phase technique was used to fabricate Gr/PVDF composites. First, graphite powder was vigorously mixed with 20 ml of acetonitrile. The mixture was ultrasonicated for 3 hours with constant interruptions of 30 min. The ultrasonication was interrupted from time to time to avoid the agglomeration of the graphite particles. The mixture was placed in a still position overnight without interruption to allow all the graphite particles to settle. The upper portion of the solution was carefully separated from the heavy graphite particles. A 2.5 ml of the separated solution was dispersed on a beaker, 0.05 g of PVDF was added, and the solution was mixed thoroughly to form a uniformly dispersed composite. The prepared Gr/PVDFcomposites were coated onto a glass substrate. The films were then set to dry in a clean room for 12 hours. The graphene content of this composite was estimated to be ~ 2.5% by weight.

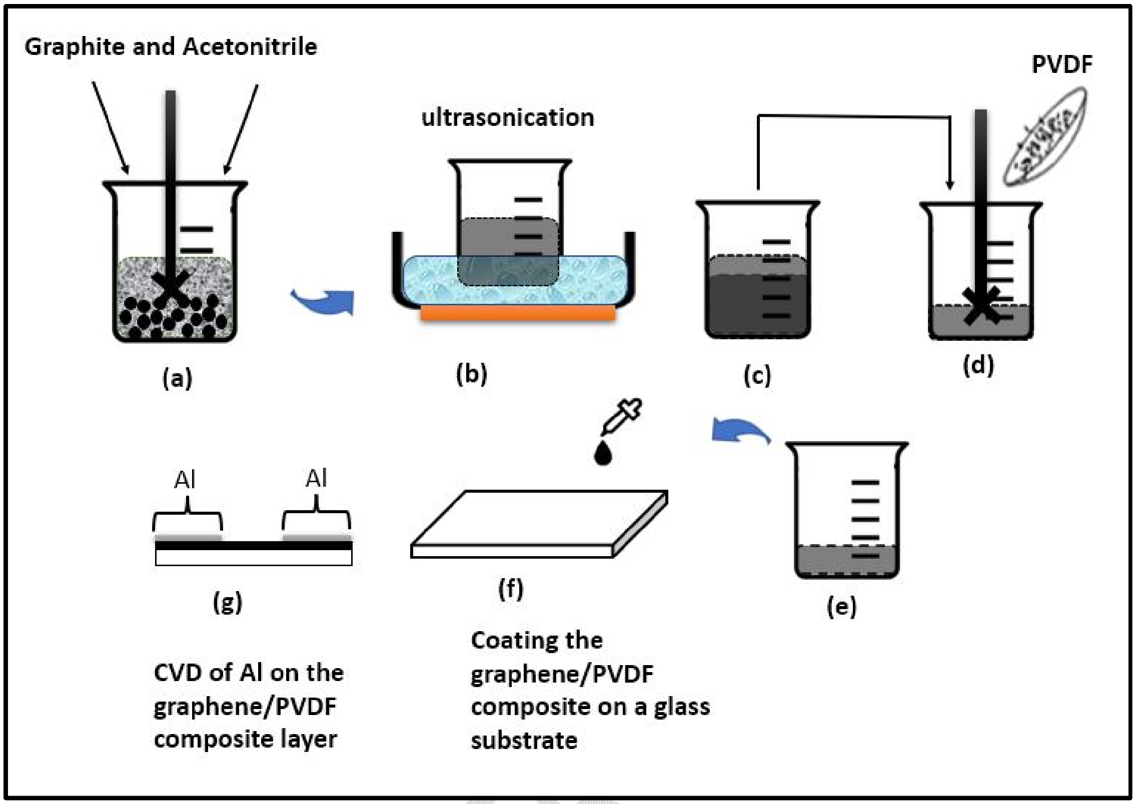

Fig. 1. Gr/PVDF preparation procedure, in (***a)***graphite and acetonitrile were fully mixed to form a homogenous mixture. The mixture is then ultrasonicated with the constant interruption of 30 mins for 3 hrs and then left to settle overnight (***b*** and ***c***).2.5 ml of the top portion of the solution was mixed vigorously with 0.05 g of PVDF (***d***), and the mixture was coated on a glass substrate and airdried for 12 hrs (***e*** and ***f***). CVD technique is then used to coat a thin layer of aluminum to act as electrical contacts (source and drain) which are situated on both ends of the composite film (***g***).Table 1 below gives a summary of the composition of the nanocomposite's solutions. The four films formed were then tested for photoconductivity by using an infrared lamp.

Table 1: The composition of the nanocomposites used to form films.

Nanocomposite Solution	**Composition of the Nanocomposites solutions**
Graphene	2.5 ml of graphene solution
Gr/PVDF	2.5 ml of graphene solution and 50 mg of PVDF

In order to collect photo-resistivity data, gold electrodes were fabricated on samples by thermal evaporation through a shadow mask. The width and spacing of Au finger electrodes were 20 µm and 200 µm, respectively. The photo resistivity sensing property of the thin films was measured by collecting the change of resistance. The sample was installed into a sensing device with tungsten connecting electrodes with inlet and outlet connectors. The infrared light was illuminated on the samples witha lamp placed 10 cm high and perpendicular to the surface of the specimen.

The device was biased with a constant voltage (-2.0 - 2.0 V)during collection of the data. The infrared lamp used had a wavelength of 700-800 nm with a power of 100 watts. Fig. 2 shows the data collection procedure, data acquisition box, and a light source used. The IR lamp was mounted 10 cm above the film. The same procedure was used to collect all the data from all the films, and the data was analyzed using Excel software.

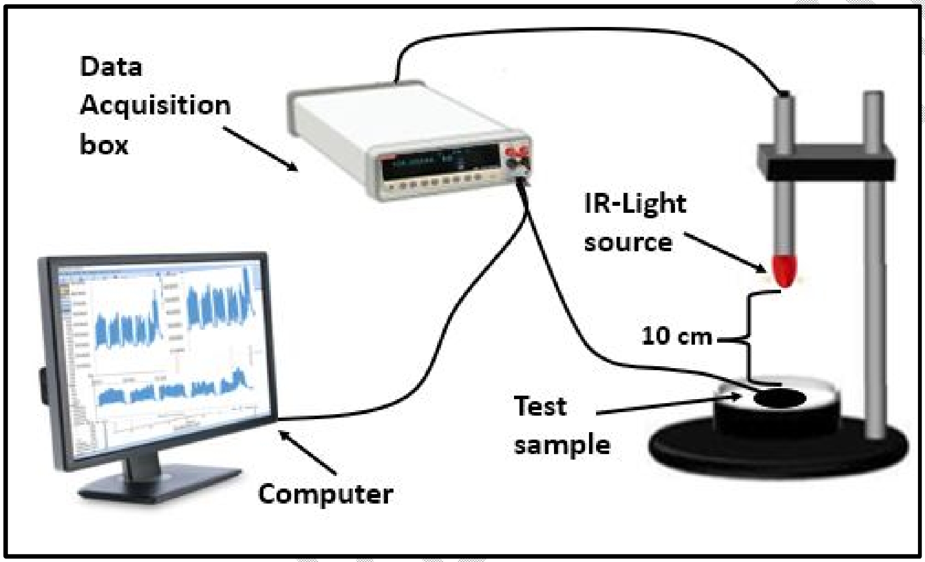

Fig. 2. The schematic representation of the data collection using the IR lamp.

Table 2: The physical properties of the materials used[25].

Properties / **Materials**	**Density**	**Melting point**	**Refractive index (n_D)**
Graphene	2.2 g/cm^3	3650 °C	2.68

PVDF	1.78 g/cm^3	155-160 °C	1.42

1. Results and discussion

1.1 Structure and surface morphology (SEM and XRD)

The SEM characterization of the surface morphology of the composites is another crucial factor in demonstrating the film's successful fabrication as already demonstrated in our other studies. Fig. 3 (a) shows the distribution of the particles in the Gr/PVDF film and Fig. 3 (b) is the optical image of the film.The SEM image indicates a uniform mixing of PVDF and graphene during the fabrication of the nanocomposite film. From theoptical image, the solution possessed a uniform particle distribution. The XRD characterization of Gr/PVDF nanocomposite prepared by solution-phase technique was carried out from 10^0-50^0 to examine the phases in the composite Fig. 4. The XRD pattern of Gr/PVDF exhibits a series of peaks corresponding to the 2 θ angles of 18.24^0, 20.48^0, 24.60^0, and 40.32^0 of PVDF, the presence of the dominant peak confirms the presence of the beta-phase in PVDF and the semicrystalline nature of PVDF polymer. The dipole moment of DMF is primarily responsible for producing the beta phase in pure PVDF [26-28].

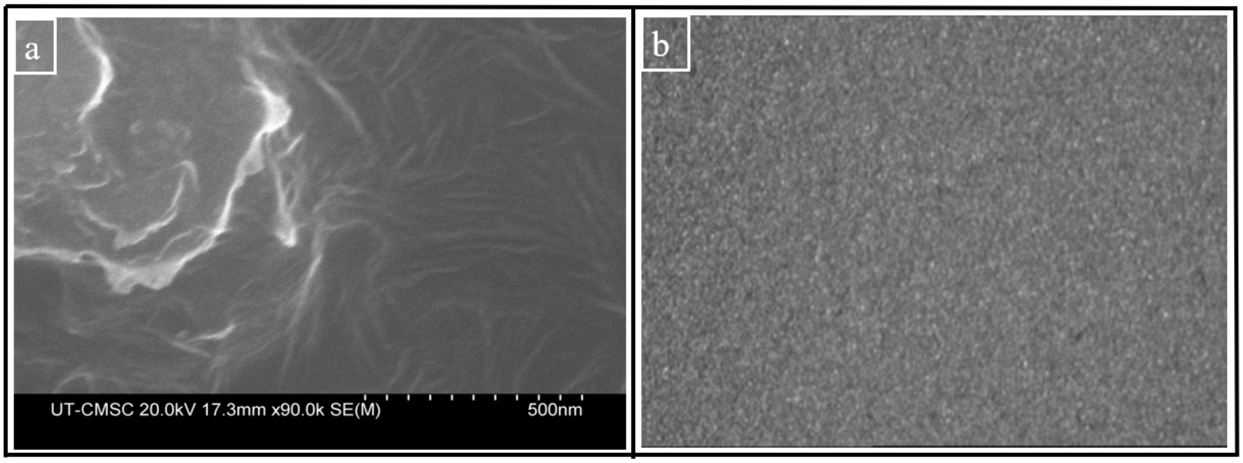

Fig. 3. (a) is the SEM imageand **(b)** optical imageofGr/PVDFat 100Xmagnification.

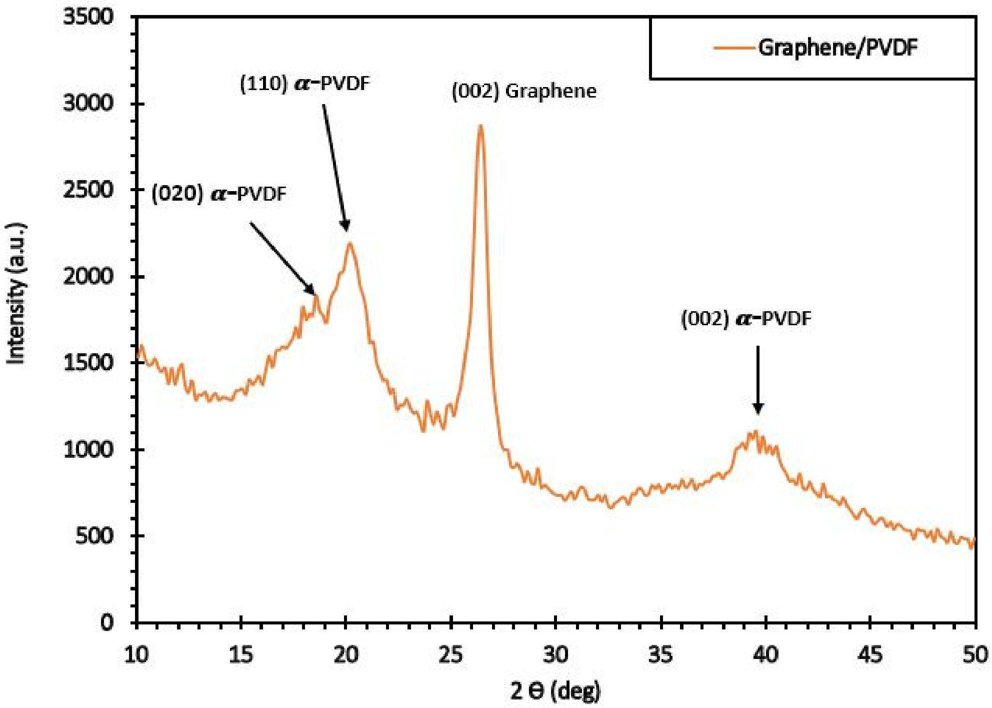

Fig. 4. XRD patterns of Gr/PVDF and Graphene**.**

1.2 Near-Infrared (NIR) lamp properties for the composites

Fig. 5. shows the I-V characteristics of the films were measured for two different conditions. First, the I-V data was collected in a dark room, and then after 2 s, the IR lamp was turned on. As it can be seen from the I-V curves presented in Fig. 5, the composites demonstrate some non-linearity due to weak junction between graphene and gold electrodes. There are different reasons which may contribute to the observed non-ohmic behavior. First is contact resistance, which is dominant in the recombination of carriers compared with thermal generation [29]. Also, the substrate effect provides the general mechanisms for room-temperature limitation of carrier transport and even the formation of a dual barrier diode. The results presented herein allow the use of graphene composites junctions as a sensing platform for simultaneously detecting toxic heavy metals such as cadmium, mercury, and lead. The developed Gr/PVDF films have potential applications in a wide range of fields and particularly for electronic applications. The ability of these films to be used as electronic components in devices was demonstrated by the experiments carried out.

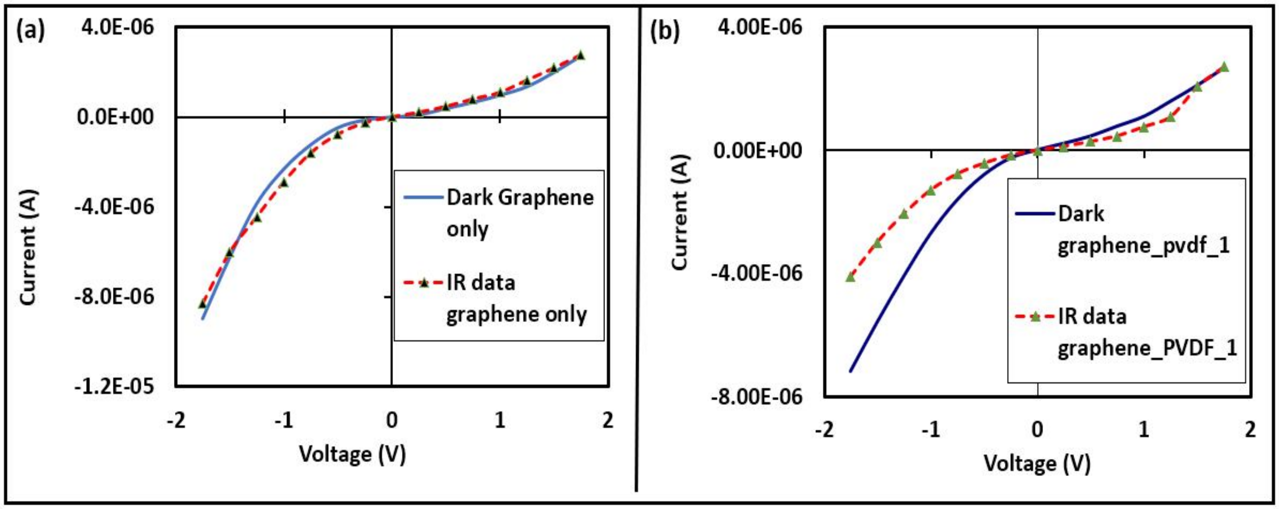

Fig.5. The I-V characteristics of the composites measured for **(a)** graphene film onlyand **(b)** Gr/PVDF film under dark condition and IR light illuminated condition at room temperature.

Fig. 6 shows the photocurrent development curve of Gr/PVDF upon irradiation of IR light at a voltage of -1.5 V. The infrared light was turned on and off in a dark room with the sample placed 10 cm above the IR-light source. The IR-light was made sure that it was placed directly above so that the IR-light rays could project to the sample at a perpendicular point for maximum absorption. All the films were tested in a similar manner for photoconductivity. The average response time and recovery time estimated from 10 samples prepared were 0.67 s and 1.67 s, respectively.

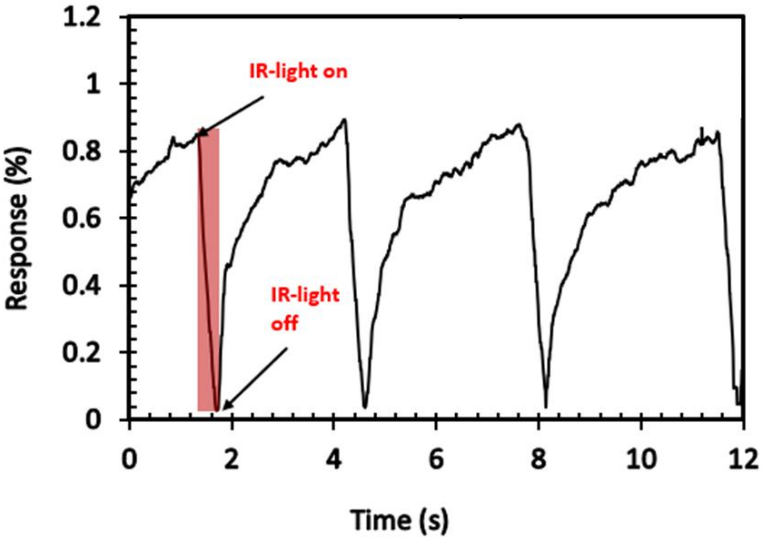

Fig.6. The response curves for the films when IR-light is illuminated on the Gr/PVDF films at a biased voltage of -1.5 V.

Single-layer graphene does not exhibit semiconductor behavior; however, few-layer graphene demonstrates some bandgap features at very low energy levels, primarily due to defect states and interlayer coupling effects [29, 30]. These characteristics have been a subject of extensive research, as they reveal the potential for tailoring the electronic properties of graphene-based materials. In previous work, our group and others observed similar phenomena in CVD graphene with more than two layers, where the presence of defects and stacking interactions contributed to low-energy bandgap features [9].In this study, no detectable photoconductivity was observed for chemically exfoliated graphene, which may be attributed to its structural inconsistencies and lack of interlayer coupling. However, the photoconductivity of graphene/PVDF (Gr/PVDF) composites was evident only under negative bias conditions. This observation suggests that the interface between graphene and PVDF plays a significant role in charge carrier conduction, likely facilitating selective charge transport or enhancing interfacial polarization effects.We hypothesize that this photoconductivity originates from a P-Gr/polymer/P-Gr junction effect, where the interaction between the graphene layers and the polymer matrix induces localized charge transfer mechanisms. Nevertheless, further theoretical and experimental investigations are necessary to fully elucidate the mechanism of photoconductivity in Gr/PVDF composites, including exploring the role of interface engineering, defect states, and external bias conditions in modulating the material's optoelectronic properties.

Photodetection is one of the optoelectronics areas where graphene is actively employed as part of the readout electronics and as the active media. Broadband constant absorption from ultra-violet to near-infrared and absorption peak in the terahertz region make graphene a promising cheap alternative to materials currently used in photodetection[31,32]. The NIR and middle-infrared regions of the electromagnetic spectrum specifically lack low-price and environment-friendly materials that could operate at room temperature. Introducing a new active photodetection material with broadband detection is an exciting task, and graphene appears to be an appropriate choice. Nevertheless, a drop in absorption spectrum in the middle-Infrared spectraldomain introduces a challenge for graphene-based photodetectors in this region.

2. Conclusion

The photoconductivity response of Gr/PVDF nanocomposites was successfully investigated in the near-infrared region of the spectrum. These nanocomposites were synthesized via the solution-phase method and deposited on glass substrates. Morphological and structural characterization using SEM and XRD revealed the microstructural details of the composite films, with XRD further confirming their semicrystalline nature. The I-V measurements demonstrated nonlinear behavior for both graphene and Gr/PVDF, suggesting diode-like properties. Notably, the graphene sample exhibited superior sensitivity, and a stronger photoconductive response compared to the Gr/PVDF composite. However, the Gr/PVDF composite demonstrated significant sensitivity to infrared light under a biased voltage of-1.5 V. The exceptional photoconductivity behavior, coupled with the broadband absorption characteristics of graphene, highlights the potential of these materials for applications in optoelectronics and electronic devices.

Disclaimer (Artificial intelligence)

Authors hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc.) and text-to-image generators have been used during the writing or editing of this manuscript.

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