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Green-Synthesized Bi-Doped PEI N-GQDs Enabling Long-Term Stable Silicon Heterojunction Photodetectors

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ABSTRACT

In this study, BiNPs&PEI N-GQDs nanocomposites were synthesized via a green approach by incorporating bismuth nanoparticles (BiNPs) into polyethyleneimine-functionalized nitrogen-doped graphene quantum dots (PEI N-GQDs). The nanocomposites were characterized using Transmission Electron Microscopy, Ultraviolet–Visible Spectroscopy, Fourier-Transform Infrared Spectroscopy, x-ray Photoelectron Spectroscopy, Ultraviolet Photoelectron Spectroscopy, and Photoluminescence Spectroscopy. The photoluminescence spectra exhibited dual emission bands at ~ 2.95 eV (420 nm) and ~ 2.42 eV (512 nm). When deposited onto a p-type silicon substrate, the nanocomposites formed a heterojunction with rectifying behavior and pronounced photoresponse under illumination. Current–voltage measurements revealed an illumination-induced shift of the photocurrent onset toward negative bias, suggesting photovoltaic activity. The photocurrent increased significantly with increasing illumination intensity, confirming the photoactive nature of the device. At a bias of 5 V and an illumination intensity of 240 mW cm^{-2} , the photodetector exhibited a responsivity of 0.16 A W^{-1} and a specific detectivity of $\sim 7.84 \times 10^{10}$ Jones. A comparative analysis with an undoped PEI N-GQDs/p-Si device fabricated under identical conditions was conducted to assess the effect of Bi incorporation. Furthermore, measurements conducted after 24 months showed that the heterojunction retained its electrical and photodetection characteristics, confirming its long-term stability, highlighting its potential for sustainable and low-complexity optoelectronic applications.

1 | Introduction

The ever-increasing demand for efficient and cost-effective optoelectronic devices, such as high-performance photodetectors and solar energy harvesters, has spurred extensive research into novel nanomaterials and their integration into functional device architectures. Among these emerging materials, graphene quantum dots (GQDs) have recently attracted significant attention owing

to their tunable band gaps, strong quantum confinement, and superior charge transport properties, making them promising candidates for both photovoltaic and photodetection applications [1, 2].

Recent research on GQDs-based heterojunctions has demonstrated their effectiveness in enhancing photoresponse and carrier dynamics through favorable band alignment and surface

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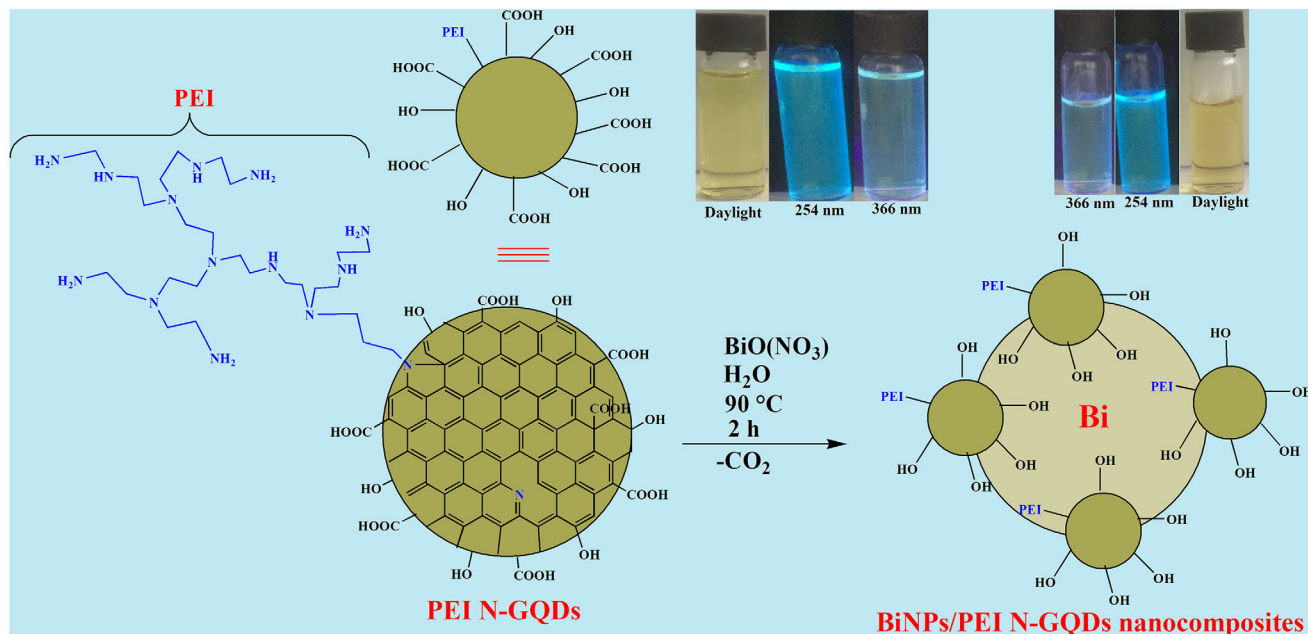


FIGURE 1 | Synthesis of BiNPs&PEI N-GQDs nanocomposite.

passivation. For example, GQDs/ZnO heterojunctions have achieved self-powered UV detection by minimizing surface trap states [3], while Si/GQDs structures improved photon absorption and carrier separation efficiency [4, 5]. Likewise, porous-Si-based photodetectors incorporating GQDs showed multiple-fold enhancement in responsivity and detectivity compared with undoped counterparts [6].

Further improvements have been realized through surface functionalization and heteroatom doping, which allow tuning of the electronic and optical properties of GQDs. In particular, polyethyleneimine (PEI) functionalization and nitrogen doping have yielded high rectification ratios and adjustable barrier heights [7, 8], while rare-earth or metallic dopants such as gadolinium and lanthanum have modulated charge transport and diode behavior [9, 10]. These functionalization strategies demonstrate the versatility of GQDs in designing high-performance and broadband photodetectors [11, 12].

In parallel, bismuth-based nanostructures have emerged as another promising material class for optoelectronic applications because of their high carrier mobility, low toxicity, and broadband absorption. Studies on Bi quantum dots (BiQDs) and thin films have reported strong photoresponse extending from the UV to near-IR regions, along with self-driven operation and rapid response times [13–15].

At the same time, GQDs-based photodetectors have demonstrated promising performance, with reported detectivity values exceeding 10^{11} Jones under optimized device architectures and operating conditions [16]. Incorporating GQDs into porous-Si heterostructures has proven to enhance photoresponse by several orders of magnitude [6]. Moreover, scalable hydrothermal synthesis enables large-area production of GQDs with high external quantum efficiencies [17].

However, despite the remarkable progress in GQDs- and Bi-based photodetectors, reports on silicon heterojunction photodetectors incorporating Bi-doped PEI N-GQDs remain very limited [18–20]. To address this gap, in this study, a green-synthesized and solution-processed Bi-doped PEI N-GQDs/p-Si heterojunction photodetector was fabricated. The structural, optical, electrical, and photodetection properties of the heterojunction were systematically investigated under dark and illuminated conditions. Moreover, the influence of Bi incorporation was clarified through comparative analyses with an undoped PEI N-GQDs/p-Si reference device. In addition, the long-term stability of the fabricated heterojunction was evaluated through aging measurements after 24 months of storage under ambient conditions.

2 | Materials and Methods

2.1 | Materials

All chemicals were obtained from commercial sources and used without further purification. The citric acid (CA), Polyethyleneimine (PEI) (M_w : 1300, 50 wt.% in H_2O) and $\text{BiO}(\text{NO}_3)_3$ were purchased from Sigma–Aldrich.

2.2 | Synthesis of Nanocomposites

For the synthesis of BiNPs&PEI N-GQDs nanocomposites a solution of PEI N-doped GQDs [8, 21] (1.00 g) in 50 mL water was added to a 250 mL round bottom flask. Then 50 mL of 1.00 g $\text{BiO}(\text{NO}_3)_3$ solution was added to the PEI N-doped GQDs mixture. The mixture was heated at 90°C for 2 h to complete the reduction process of Bi (III) cation to Bi (0) nanoparticles (BiNPs).

This synthesis route was carried out in an aqueous medium without the use of additional hazardous reducing agents,

representing a simple and environmentally friendly approach for the preparation of the BiNPs&PEI N-GQDs nanocomposite.

After this time, the color of the solution changed and the BiNPs&PEI N-GQDs nanocomposites solution was centrifuged at 12 000 rpm for 10 min and the supernatant was collected. BiNPs&PEI N-GQDs nanocomposites were washed once with deionized distilled water and ethanol. They were stored in a vacuum desiccator for later use (Figure 1).

2.3 | Characterization Techniques

To investigate the structural and chemical properties of the prepared BiNPs&PEI N-GQDs nanocomposite, a comprehensive set of characterization techniques was employed, including Ultraviolet-Visible Spectroscopy (UV-Vis), Fourier Transform-Infrared Spectroscopy (FT-IR), x-ray Photoelectron Spectroscopy (XPS), Ultraviolet Photoelectron Spectroscopy (UPS), Photoluminescence (PL) spectroscopy, and Transmission Electron Microscopy (TEM).

UV-Vis spectra were measured using a PG Instruments T+80 UV-Visible spectrophotometer. FT-IR spectra were obtained from a Perkin Elmer BX II spectrometer in KBr discs and were reported in cm^{-1} units. Elemental compositions of the PEI N-doped GQDs and BiNPs&PEI N-GQDs nanocomposites materials were analyzed using XPS (PHI 5000 Versa Probe spectrometer). UPS using He (I) radiation (21.22 eV) was employed to determine the work function of the heterostructure.

BiNPs&PEI N-GQDs nanocomposites were morphologically characterized by TEM (FEI Technai G2 STwin) at an accelerating voltage of 200 kV. The nanocomposites in aqueous suspensions were treated in an ultrasonic bath before dropping to reduce aggregation. A 10 μL of distributed nanostructures was dropped on carbon-coated 200 mesh copper grids and dried under ambient conditions. PL was conducted by an excitation of a Kimmon IK series He-Cd continuous wave laser with 325 nm wavelength focused on the desired point collimated at 45° of incident light by 50X lens of optical microscope that equipped with a camera, while a HORIBO Jobin Yvon iHR550 monochromator adopted for differentiating the PL spectrum with 1800 Grooves/mm of VIS holographic grating in extended data collection mode with an end-point of a CCD detector.

2.4 | Device Fabrication

In the fabrication of the BiNPs&PEI N-GQDs nanocomposite-based device, a p-type Si wafer (100) with a resistivity range of 1 to 10 $\Omega\text{ cm}$ and a thickness of 350 μm was used. After completing the cleaning steps, a 100 nm thick layer of high-purity gold (Au) (99.999%) was sputtered onto the unpolished side of the wafer to achieve an ohmic contact. Next, the BiNPs&PEI N-GQDs nanocomposite solution was coated onto the polished surface of the wafer using the spin-coating method. The coating process was carried out at a rotation speed of 3000 rpm for 30 s, resulting in a thin film with a thickness of 30 nm. Finally, the BiNPs&PEI N-GQDs/p-Si heterojunction structure was completed by depositing circular Au contact points, each with a thickness of 125 nm,

using a circular metal mask with a diameter of 0.5 mm. Figure 2 illustrates the schematic structure of the device.

2.5 | Experimental Setup and Measurement Conditions

The device structure was fabricated by depositing Bi-doped N-GQDs nanocomposites onto a p-Si wafer to assess its electrical and photodetection properties. The electrical measurements were performed using a source-measure unit (Keithley 4200 SCS) in a vertical (top-bottom) configuration, where the bias voltage was applied between the circular Au electrode on the BiNPs&PEI N-GQDs layer (top contact) and the Au back electrode on the p-Si substrate (ohmic contact). Forward bias was defined as applying a positive voltage to the top electrode relative to the back contact, while reverse bias corresponded to the opposite polarity. During illumination, the light spot ($\sim 1\text{ mm}$ in diameter) completely covered the 0.5 mm-diameter Au electrode, ensuring that the entire active device area was exposed to light. I - V characteristics were recorded under both dark and illuminated conditions to evaluate the optoelectronic performance of the heterojunction diode. A light intensity controller was used to vary the intensity of white light (450–2400 nm spectral range) from a supercontinuum light source (SuperK Compact by NKT Photonics) to analyze photocurrent behavior under different light levels. The I - V behaviors of the device were examined under dark and light intensities ranging from 48 to 240 mW cm^{-2} .

3 | Results and Discussion

3.1 | Characterizations of PEI N-GQDs and BiNPs&PEI N-GQDs Using UV-vis, FT-IR, XPS, PL, UPS, and TEM

The UV-Vis absorption spectra of PEI N-GQDs and BiNPs&PEI N-GQDs nanocomposites were measured in water and are presented in Figure 3a. In the UV-Vis spectrum of PEI N-GQDs, two bands assigned to π - π^* transitions of $\text{C}=\text{C}$ at 258 nm and n - π^* transitions of $\text{C}=\text{N}$ and $\text{C}=\text{O}$ at 353 nm were observed. In BiNPs&PEI N-GQDs nanocomposites, π - π^* and n - π^* transitions were found at 251 and 349 nm, respectively. Furthermore, a shoulder at 376 nm was assigned to the plasmon resonance in BiNPs&PEI N-GQDs nanocomposites.

The FT-IR spectra of PEI N-GQDs and BiNPs&PEI N-GQDs nanocomposites were measured and are presented in Figure 3b. In the FT-IR spectrum of PEI N-GQDs, the frequencies of the characteristic functional groups are: $\nu[\text{OH}+\text{NH}_2+\text{NH}+\text{COOH}]$: 3431–3244 cm^{-1} (s-br), $\nu\text{C}-\text{H}$: 2974–1302–1250 cm^{-1} (s), $\nu\text{C}=\text{O}$: 1690 cm^{-1} (s), $\nu\text{C}=\text{N}$ pyridinic: 1655 cm^{-1} (s), $\nu\text{C}=\text{C}$: 1556 cm^{-1} (s), $\nu\text{C}-\text{N}$: 1442 cm^{-1} (m), $\nu\text{C}-\text{O}$: 1397 cm^{-1} . In the spectrum, $\text{OH}+\text{NH}_2+\text{NH}+\text{COOH}$ peaks were observed to overlap. In addition, the characteristic $\text{C}=\text{O}$ (carboxylic acid) and $\text{C}=\text{N}$ (pyridinic) vibrations in PEI N-GQDs were observed at different frequencies.

In BiNPs&PEI N-GQDs nanocomposites, OH , NH_2 , NH , $\text{C}-\text{H}$, $\text{C}=\text{N}$, $\text{C}=\text{C}$, $\text{C}-\text{N}$ and $\text{C}-\text{O}$ vibration bands are observed at

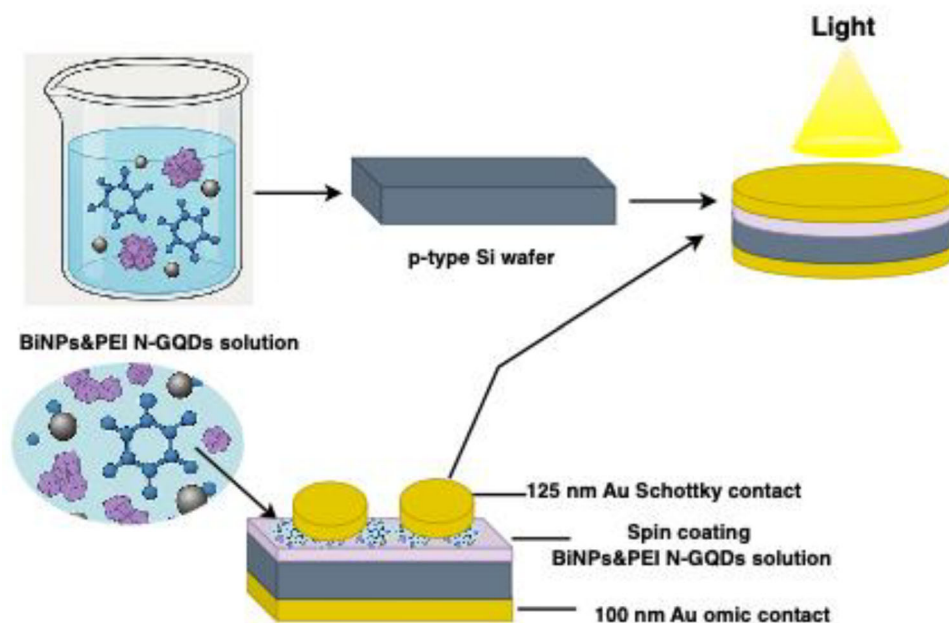


FIGURE 2 | Schematic structure of BiNPs&PEI N-GQDs/p-Si heterojunction device.

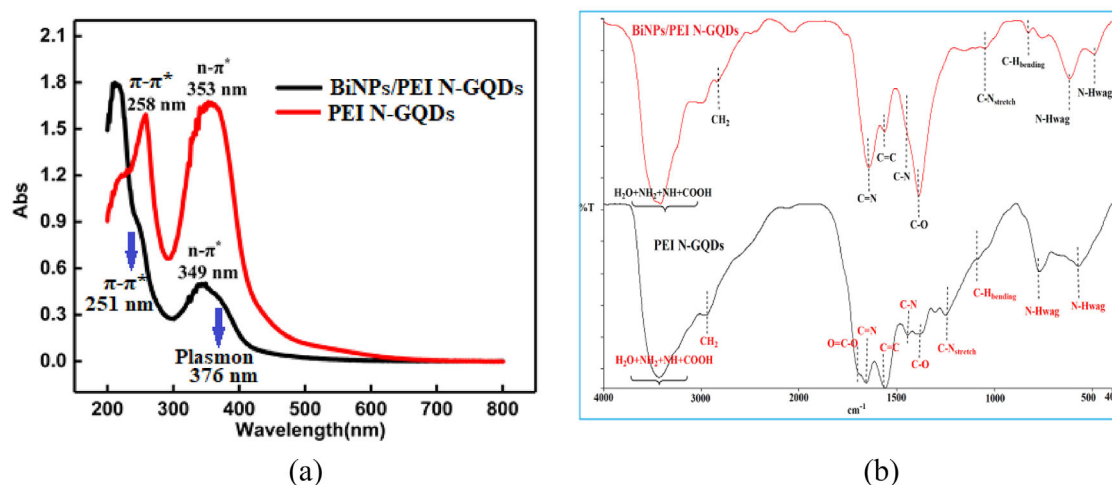


FIGURE 3 | (a) UV-Vis spectra and (b) FT-IR spectra of the PEI N-GQDs and BiNPs&PEI N-GQDs nanocomposites.

3417–3240–3013 cm^{-1} , 2837–1153 cm^{-1} , 1641 cm^{-1} , 1561 cm^{-1} , 1432 and 1384 cm^{-1} , respectively. The $\text{OH}+\text{NH}_2+\text{NH}$ overlapped in BiNPs&PEI N-GQDs nanocomposites. No $\text{O}=\text{C}-\text{O}$ vibrations were observed in the BiNPs&PEI N-GQDs nanocomposite. This indicates that, during the reduction of Bi(III), the entire $\text{O}=\text{C}-\text{OH}$ group was oxidized to CO_2 , resulting in the formation of a phenolic-OH structure. In addition, for both materials, the $\text{C}-\text{N}_{\text{stretch}}$, $\text{C}-\text{H}_{\text{stretch}}$ and $\text{N}-\text{H}_{\text{wag}}$ vibrations were observed at 1250, 1149, 768 and 570 cm^{-1} for PEI N-GQDs, and 1153, 1049, 615 and 491 cm^{-1} for BiNPs&PEI N-GQDs (Figure 3b).

When the vibrations in the FT-IR spectra of BiNPs&PEI N-GQDs nanocomposites are compared with the spectrum of pure PEI N-GQDs, the vibrations of all functional groups in the metal nanocomposites are shifted to lower frequencies. From these results, it is seen that GQDs are oxidized while metals are reduced.

The energy values giving information about the chemical and binding environment of BiNPs&PEI N-GQDs nanocomposites were determined using XPS, and the XPS spectrum of BiNPs&PEI N-GQDs nanocomposite is shown in Figure 4a,b. The chemical composition and nature of nanocomposite structures containing metallic Bi and Bi_2O_3 were investigated by recording high-resolution XPS spectra using Al K α radiation. In this context, for Bi_2O_3 nanostructures, Bi 4f spectra with two symmetric binding energy values of 163.7 and 158.4 eV, and spin-orbit separation of 5.3 eV were observed [22]. In brief, the shape of the Bi 4f peaks in the spectrum reveals whether the bismuth present in the composite is metallic or oxidized. Accordingly, for bismuth metal, asymmetric peaks with lower values are observed, whereas for bismuth compounds such as oxides, symmetric peaks with higher values are observed, with a spin-orbit separation of 5.3 eV. It is seen from Figure 4a that the binding energies are 158, 163, 441

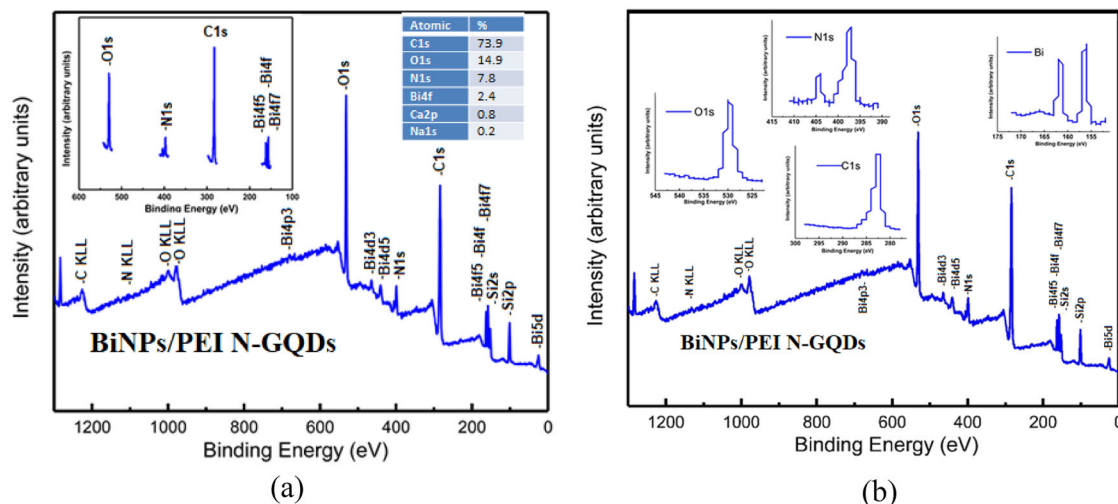


FIGURE 4 | (a) Normal XPS spectrum and (b) Extended XPS of BiNPs&PEI N-GQDs nanocomposites.

and 465 eV for Bi 4f7/2, Bi 4f5/2, Bi 4d5 and Bi 4d3, respectively. The peaks observed at 158 and 163 eV for Bi 4f7/2 and Bi 4f5/2 are evidence that Bi is present in the composite in the metallic state [22]. In the studies, binding energies of 159.8 and 164.1 eV were observed for Bi 4f7/2 and Bi 4f5/2 in Bi₂O₃ materials [22]. Furthermore, as can be seen from Figure 4a,b, the peaks observed at 284, 399 and 531 eV can be attributed to the binding energies of C 1s, N 1s and O 1s, respectively. The broad spectra observed for O, N and C in XPS indicate that these elements are in different bonding types in the material (Figure 4b). That is, C—O and C=O for O, N—C and N—O for N, and C—C and C=C for C. Quantitative XPS analysis yielded atomic concentrations of 73.5 at.% C, 14.9 at.% O, 7.8 at.% N, and 2.4 at.% Bi, confirming the presence of Bi in the BiNPs&PEI N-GQDs nanocomposite (Figure 4a).

The PL spectra shown in Figure 5a exhibit two distinct emission bands centered at approximately 2.95 and 2.42 eV, suggesting the presence of multiple radiative recombination pathways within the BiNPs&PEI N-GQDs system. These emissions may be associated with defect-related states, surface states, and other localized energy levels, consistent with previous reports on GQDs [23]. The UPS spectrum shown in Figure 5b yielded a work function value of 2.21 eV for the BiNPs&PEI N-GQDs nanocomposite. Moreover, the valence band maximum (VBM) was determined to be 3.43 eV from the extrapolation of the valence band edge, providing information on the electronic structure of the nanocomposite. The optical bandgap values were obtained from the Tauc plots shown in Figure 5c,d. Direct and indirect optical band gaps of 2.95 and 2.49 eV, respectively, were determined from the extrapolation of the linear regions of the corresponding plots. The high-energy emission band (~2.95 eV) coincides with the direct optical bandgap, whereas the lower-energy emission band (~2.42 eV) is close to the indirect optical bandgap value (~2.49 eV). Based on the experimentally determined energy-level positions, the Si band edges appear to be located within the bandgap of the BiNPs&PEI N-GQDs layer, suggesting a Type-I band alignment configuration for the heterojunction. In this configuration, the band edges of one semiconductor are encompassed within the bandgap of the other, resulting in a straddled energy-level alignment [24].

Also, the morphology of BiNPs & PEI N-GQDs nanocomposites was evaluated by TEM analysis and is presented in Figure 6a,b. As shown in the high-magnification TEM image (Figure 6a), the Bi/PEI N-GQDs exhibit a relatively uniform spherical morphology with limited agglomeration, and the particle size is in the range of 2–8 nm, which is consistent with the structural features observed in the lower magnification image (Figure 6b).

3.2 | Electrical Characterization

The *I*–*V* behavior of the BiNPs&PEI NGQDs/p-Si heterojunction structure was analyzed in the dark and under different light intensities ranging from 48 to 240 mW cm^{−2}. During the *I*–*V* measurements, voltage was applied to the BiNPs&PEI N-GQDs layer, while the Si substrate was grounded. Device parameters were initially determined using thermionic emission (TE) theory [25, 26].

In the TE theory, the dynamics of current and voltage can be delineated by the following equation:

$$I = I_0 \left[\exp \left(\frac{q(V - IR_s)}{nkT} \right) - 1 \right] \quad (1)$$

with I_0 , n , V , k , q , IR_s , and T the reverse saturation current at zero bias, the ideality factor, the applied bias voltage, the Boltzmann constant, the electronic charge, the voltage drop across series resistance (R_s), and the temperature in Kelvin, respectively. Subsequently, it is possible to utilize I_0 in order to extract the Schottky barrier height (ϕ_B) from the equation [27].

$$I_0 = AA^*T^2 \exp \left(-\frac{q\phi_B}{kT} \right) \quad (2)$$

where A^* is the Richardson constant (≈ 32 A cm^{−2} K^{−2} for p-Si at room temperature) and A is the area of the interfacial layer. The ideality factor, n , can be determined through analysis of the slope of the semi-log *I*–*V* curve at low forward bias (i.e., at negative

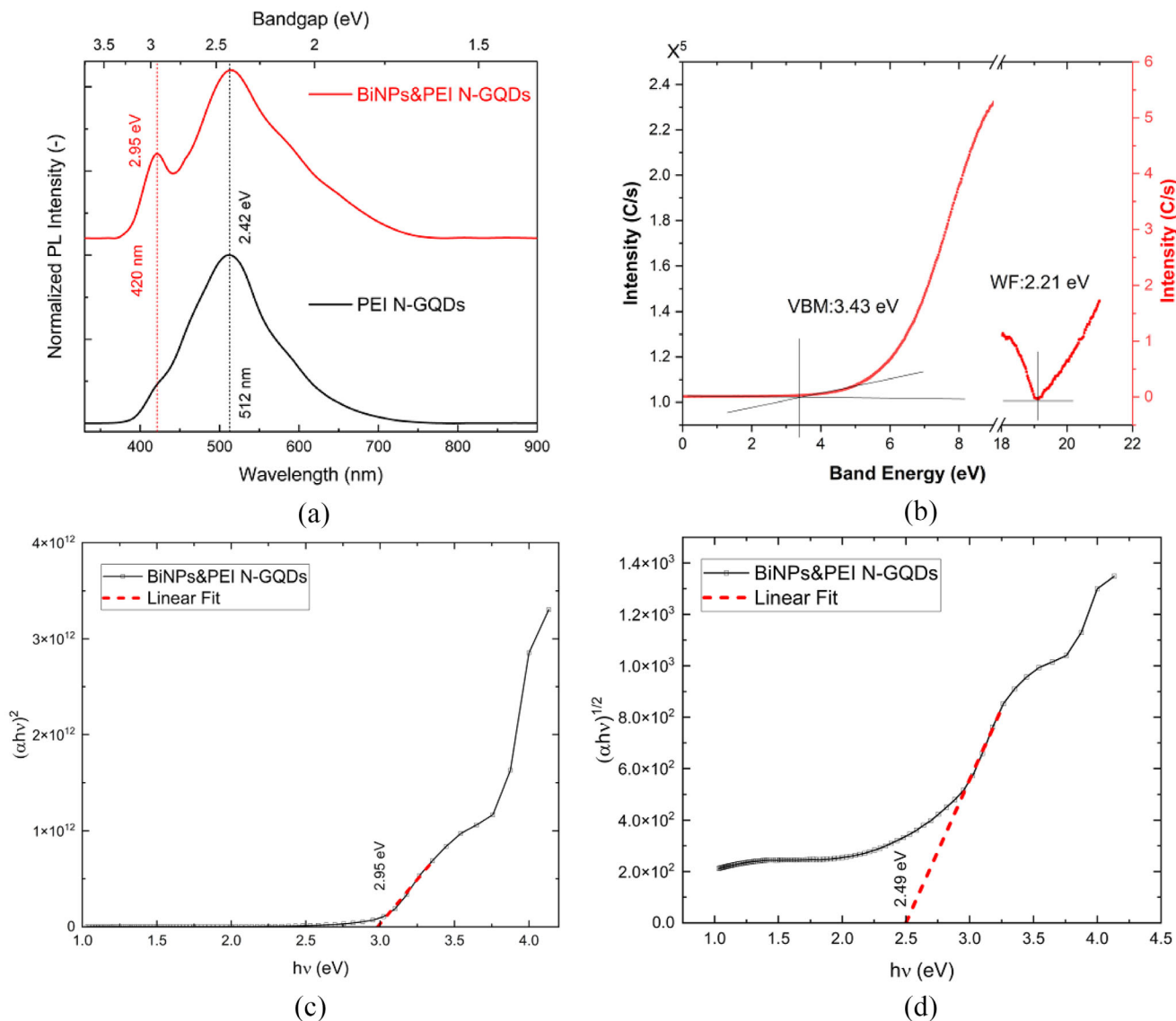


FIGURE 5 | (a) PL spectra of PEI N-GQDs (black) and BiNPs&PEI N-GQDs (red) vs. both bandgap (eV) and wavelength (nm). (b) UPS spectrum of BiNPs&PEI N-GQDs. Tauc plots of the nanocomposite indicating a (c) direct bandgap and (d) indirect bandgap.

voltages in our case), as follows:

$$n = \frac{q}{kT} \left(\frac{dV}{d \ln I} \right) \quad (3)$$

Using Equations (1)–(3) and the $\ln(I)$ – V characteristics, the barrier height and the ideality factor were estimated as 0.72 and 2.45 eV, respectively. The rectification ratio (RR), defined as the ratio of the forward to reverse current, was calculated as 7.52×10^4 under dark conditions at a voltage bias of ± 5 V. The barrier height of 0.72 eV is suitable for promoting efficient carrier transport without excessive leakage, supporting thermionic emission across the heterojunction. The ideality factor of 2.45 suggests the involvement of recombination mechanisms, likely due to Bi-induced mid-gap states and interface trap levels. Meanwhile, the high rectification ratio (7.52×10^4) confirms strong diode-like behavior under dark conditions, indicating a well-formed junction capable of unidirectional current flow.

Figure 7a presents the I – V characteristics of the BiNPs&PEI N-GQDs/p-Si heterojunction device under dark and illuminated conditions, with incident light intensities ranging from 48 to 240 mW cm^{-2} , where the y-axis is plotted on a logarithmic scale to clearly display the order of magnitude of the current. This format facilitates the comparison between forward and reverse bias regions and highlights the rectification behavior of the device. In the dark, the device exhibits diode-like rectification, validating the formation of a functional heterojunction. Upon illumination, a significant enhancement in photocurrent is observed, with the current increasing as light intensity rises—indicating efficient photogeneration and carrier separation. The minor fluctuations observed in the forward-bias region are likely associated with interface-related trapping/de-trapping processes, local junction inhomogeneities, and the increased uncertainty of current measurements near the low-current regime [28].

Figure 7b shows the dark I – V characteristics of the Au/BiNPs&PEI N-GQDs/p-Si/Au diode measured immediately

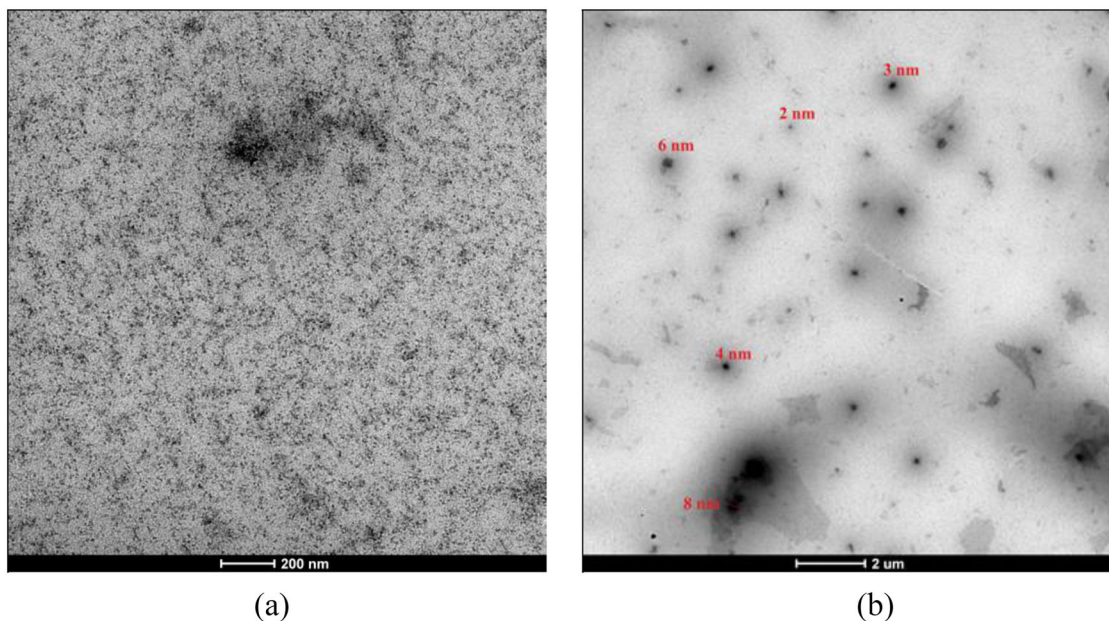


FIGURE 6 | TEM images (a) high-magnification and (b) lower-magnification of the BiNPs&PEI N-GQDs nanocomposites.

after fabrication and after 24 months of storage. Both curves exhibit clear rectifying behavior over the investigated voltage range. Although differences in current magnitude are observed, particularly under forward bias, the overall shape of the dark I - V characteristics remains similar after storage.

The initial and aged diode parameters extracted using the TE model are summarized in Table 1. Comparison of the initial and aged diode parameters indicates that changes in the rectification ratio and ideality factor occurred during aging, whereas the barrier height remained nearly unchanged. Although the rectification ratio decreased over time, it remained on the order of 10^3 . Overall, these results indicate that the BiNPs&PEI N-GQDs/p-Si heterojunction retained its essential diode characteristics after prolonged storage under ambient conditions.

Figure 7c shows the estimated energy level diagram of the BiNPs&PEI N-GQDs/p-Si heterojunction constructed from UPS and optical bandgap analyses. The valence band maximum (VBM) position was determined from the UPS measurements, while the conduction band minimum (CBM) was estimated using the direct optical bandgap obtained from Tauc analysis.

Table 1 also includes the undoped PEI N-GQDs/p-Si reference device fabricated using the same procedure. Compared with the undoped device, the incorporation of Bi nanoparticles increases the rectification ratio from 2.78×10^4 to 7.52×10^4 reduces the ideality factor from 3.58 to 2.45, and increases the barrier height from 0.68 to 0.72 eV. Furthermore, the dark current decreases from 4.45×10^{-7} A to 1.04×10^{-7} A at 5 V. These changes suggest that Bi nanoparticle incorporation modifies the interfacial electronic properties of the heterojunction, improves the rectifying characteristics, and contributes to the suppression of leakage current.

3.3 | Key Performance Metrics of the Photodetector

In this study, the photodetector characteristics of BiNPs&PEI N-GQDs/p-Si devices were investigated. All measurements were performed within the applied bias range of 0–5 V. Figure 8a illustrates the transient photocurrent ($I_{\text{transient}}$) response of the heterojunction incorporating Bi-doped PEI N-GQDs. As shown in Figure 8a, the transient photocurrent response displays sharp and reproducible switching with a stable dark current baseline (~ 10 nA). The signal-to-noise ratio (SNR) was estimated as $I_{\text{signal}}/I_{\text{noise}}$, where I_{signal} corresponds to the photocurrent amplitude and I_{noise} to the dark current fluctuation. The estimated SNR values range from ~ 70 (37 dB) at 48 mW cm^{-2} to ~ 350 (51 dB) at 240 mW cm^{-2} , confirming the high signal-to-noise ratio and reliable operation of the solution-processed BiNPs&PEI N-GQDs/p-Si photodetector.

The transient photoresponse behavior of the BiNPs&PEI N-GQDs/p-Si photodiode was evaluated using photocurrent-time (I - t) measurements. The rise and fall times were determined from the transient photocurrent curves shown in Figure S1 using the commonly adopted 10%–90% and 90%–10% criteria for photodetector response analysis [29, 30]. As summarized in Table 2, the rise times ranged from 2.02 to 2.11 s, while the fall times ranged from 1.10 to 1.13 s. The extracted values show only minor variations under different illumination conditions.

Photocurrent (I_{photo}) is defined as $I_{\text{light}} - I_{\text{dark}}$, i.e., the difference between the current under illumination and in the dark; this metric emphasizes the device's light-to-current conversion capability. Figure 8b shows the variation of photocurrent with applied voltage for the BiNPs&PEI N-GQDs/p-Si heterojunction under different illumination intensities. In all cases, the photocurrent

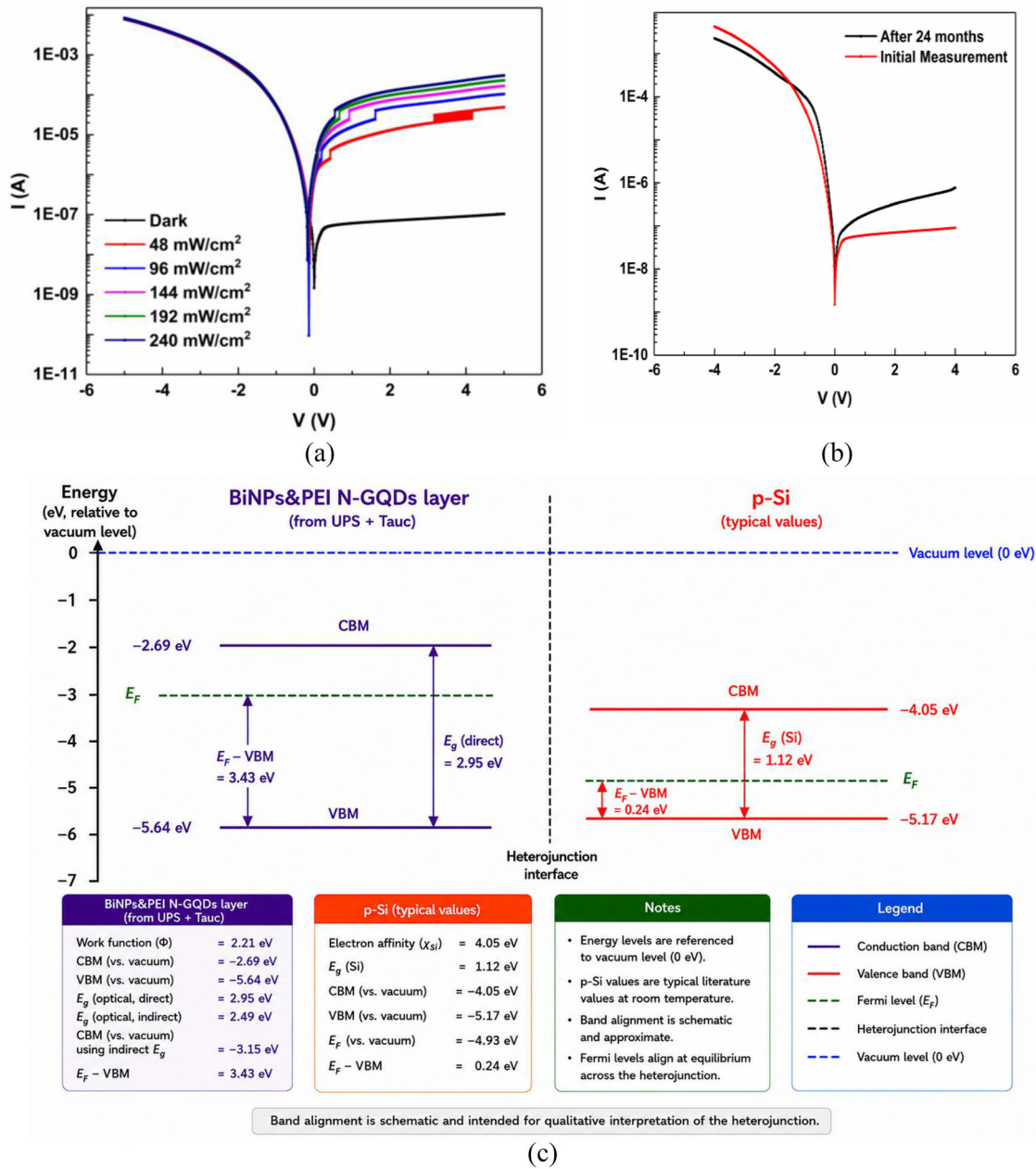


FIGURE 7 | (a) I - V characteristics of the Au/BiNPs&PEI N-GQDs/p-Si diode under dark and illuminated conditions. (b) Dark I - V characteristics of BiNPs&PEI N-GQDs/p-Si heterojunction measured immediately after fabrication and after 24 months of storage. (c) Estimated energy level diagram of BiNPs&PEI N-GQDs/p-Si heterojunction based on UPS and Tauc analyses.

TABLE 1 | Comparison of the dark electrical characteristics of the undoped and Bi-doped devices fabricated using the same experimental procedure.

Diode	n	ϕ_B (eV)	RR	References
Undoped PEI N-GQDs/p-Si (Reference photodetector)	3.58	0.68 (TE)	2.78×10^4 at ± 5 V	Present work
Bi NPs&PEI N-GQDs/p-Si (Initial)	2.45	0.72 (TE)	7.52×10^4 at ± 5 V	Present work
Bi NPs&PEI N-GQDs/p-Si (After 24 months)	2.90	0.70 (TE)	2.95×10^3 at ± 4 V	Present work

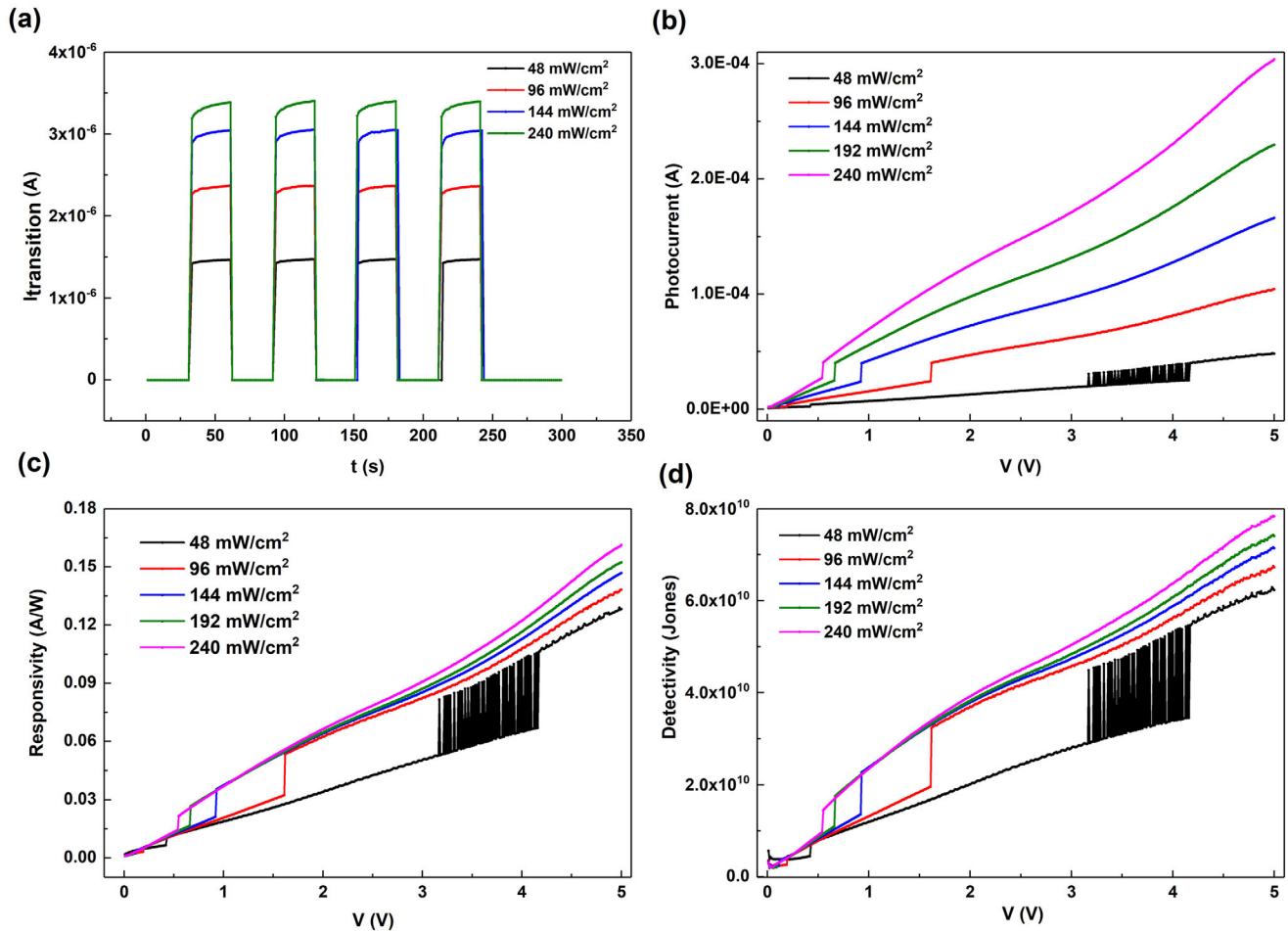


FIGURE 8 | (a) $I_{\text{transient}}$ vs. t at 0 V under varying illuminations, (b) sensitivity, (c) responsivity (d) detectivity vs. voltage under varying illuminations.

TABLE 2 | Rise and fall times of the BiNPs&PEI N-GQDs/p-Si photodetector under different illumination conditions.

Illumination conditions	Rise time (10%–90%) (s)	Fall time (90%–10%) (s)
I25	2.02	1.10
I50	2.05	1.10
I75	2.09	1.12
I90	2.11	1.13

increases with increasing bias voltage and illumination intensity. The photocurrent remains positive throughout the investigated voltage range and exhibits a nonlinear dependence on the applied voltage. Furthermore, no saturation behavior is observed up to 5 V, and higher illumination intensities result in larger photocurrent values.

Responsivity ($R = \frac{I_{\text{photo}}}{P_{\text{opt}}} = \frac{I_{\text{light}} - I_{\text{dark}}}{E_{\text{inc}} \cdot A_d}$) is defined as the ratio of the photocurrent generated by the device to the incident light power, where I_{photo} is the photocurrent, E_{inc} is the incident irradiance (mW cm⁻²), and A_d is the illuminated device area (cm²). This is equivalent to using the total incident optical power $P_{\text{opt}} = E_{\text{inc}} \cdot A_d$. It indicates how efficiently the detector converts incoming light

into electrical current, with higher responsivity representing better light-to-current conversion performance. Figure 8c shows the variation of responsivity as a function of applied bias for the BiNPs&PEI N-GQDs/p-Si heterojunction under different illumination intensities. The responsivity increases with increasing bias voltage and illumination intensity, reaching a maximum value of approximately 0.16 A W⁻¹ at 5 V under 240 mW cm⁻² illumination. At low bias voltages, the responsivity values are relatively close to each other for different illumination intensities, whereas a more pronounced separation between the curves is observed at higher bias voltages.

The specific detectivity (D^*) was calculated using [31, 32]:

$$D^* = \frac{\sqrt{A_d \Delta f}}{NEP} = R \frac{\sqrt{A_d \Delta f}}{i_{\text{noise}}} \quad (4)$$

where R is the responsivity, A_d is the photosensitive area of the photodetector, and Δf is the bandwidth (taken as 1 Hz). In the present study, the detectivity values were estimated under the commonly adopted shot-noise-limited assumption, where the theoretical noise current was calculated as $(2qI_{\text{dark}})^{1/2}$, with q being the elementary charge and I_{dark} the dark current. Since frequency-dependent noise spectral density measurements were not performed, the reported D^* values should be regarded as

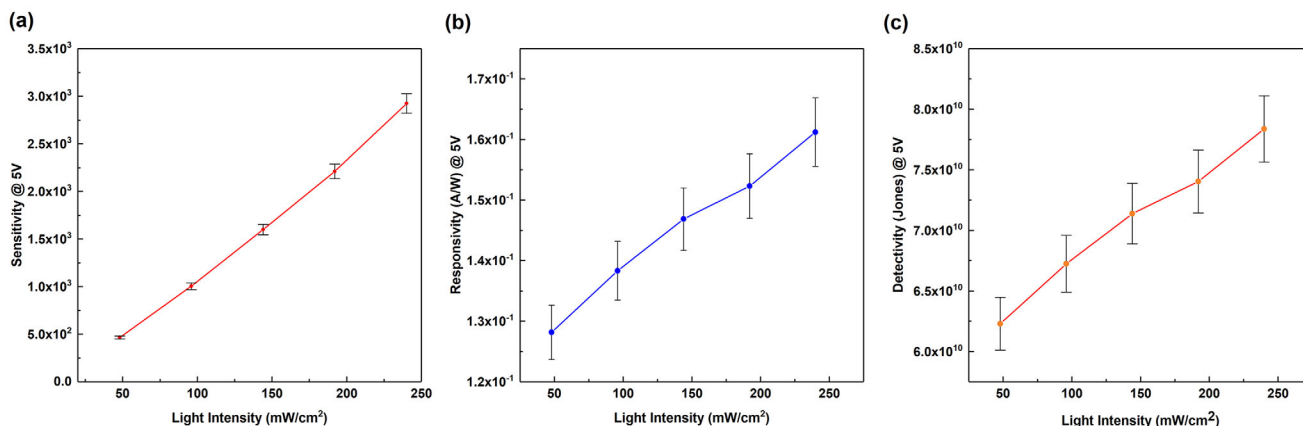


FIGURE 9 | Variation of (a) sensitivity (b) responsivity, (c) specific detectivity with illumination intensity at 5 V. Error bars indicate the estimated uncertainties associated with the measurements.

estimated rather than experimentally verified values and interpreted within the limitations of the shot-noise approximation.

D^* (expressed in Jones, $\text{cm} \cdot \text{Hz}^{1/2} \cdot \text{W}^{-1}$) is a key figure of merit that quantifies the minimum detectable optical signal relative to noise. Across all illumination intensities, detectivity increases steadily with applied voltage. Figure 8d presents the variation of D^* for the BiNPs&PEI N-GQDs/p-Si heterojunction photodiode. The maximum detectivity reaches 7.84×10^{10} Jones at 5 V under 240 mW cm^{-2} illumination. The photodetector maintained a high detectivity on the order of 10^{10} Jones over a wide range of illumination intensities ($48\text{--}240 \text{ mW cm}^{-2}$) and applied bias voltages, with a slight decrease to the 10^9 Jones range only at very low bias voltages (Figure 8d).

Figure 9 shows the variation of sensitivity, responsivity, and specific detectivity with illumination intensity at an applied bias of 5 V. As the illumination intensity increases, all three parameters exhibit an increasing trend. In particular, the responsivity exhibits a lower rate of increase at the highest illumination intensities.

The uncertainties associated with the calculated photodetector parameters were estimated by considering the combined contributions of light-source stability ($\pm 1.0\%$), measurement repeatability based on three independent measurements ($\pm 2.5\%$), optical alignment variations ($\pm 1.5\%$), and instrumental noise ($\pm 1.5\%$). Using the root-sum-square (RSS) method, the overall uncertainty was estimated to be approximately $\pm 3.5\%$. Accordingly, the error bars presented in Figure 9 represent this estimated uncertainty.

To evaluate device-to-device reproducibility, nine individual photodiodes fabricated on the same substrate were characterized under identical measurement conditions. The electrical and photodetector parameters were extracted using an in-house Python-based analysis program developed in our previous study [33]. The average values obtained from the nine devices were $n = (2.45 \pm 0.04)$, $R = (0.16 \pm 0.01) \text{ A W}^{-1}$, and $D^* = (7.84 \pm 0.05) \times 10^{10}$ Jones. The relatively small standard deviations indicate good device-to-device reproducibility and fabrication uniformity.

Table 3 compares the photodetection performance of the present BiNPs&PEI N-GQDs/p-Si heterojunction with previously reported Bi-based and Bi-doped photodetectors. The reported responsivity and specific detectivity values vary significantly depending on the device architecture, active material, illumination intensity, wavelength, applied bias, and measurement configuration. Among the compared devices, the layered $\text{Bi}_2\text{Se}_3/\text{n-Si}$ topological insulator heterostructure exhibits exceptionally high performance, with responsivity and detectivity values reaching 2.60 A W^{-1} and 4.39×10^{12} Jones, respectively. Most of the compared Bi-based and Bi-doped heterojunction photodetectors exhibit responsivity values in the mA W^{-1} range and detectivity values between 10^8 and 10^{10} Jones. Although the $\text{Bi}_2\text{Se}_3/\text{n-Si}$ heterostructure exhibits superior responsivity and detectivity values, the detectivity of the present device is comparable to most of the reported Bi-based photodetectors. Further improvement may be achieved through optimization of the Bi nanoparticle loading and interfacial engineering strategies to suppress carrier recombination. Nevertheless, the present BiNPs&PEI N-GQDs/p-Si photodetector provides a favorable combination of competitive photodetection performance, fabrication simplicity, environmentally friendly synthesis, and good long-term stability.

Compared with the undoped PEI N-GQDs/p-Si reference device, the incorporation of Bi nanoparticles leads to an improved rectification ratio, a lower ideality factor, a higher barrier height, and a reduced dark current. In particular, the dark current decreases from $4.45 \times 10^{-7} \text{ A}$ to $1.04 \times 10^{-7} \text{ A}$ at 5 V. These results indicate that Bi incorporation effectively modifies the electrical characteristics of the heterojunction and contributes to improved diode behavior.

4 | Conclusion

In this study, a BiNPs&PEI N-GQDs/p-Si heterojunction photodetector was successfully fabricated via a green solution-based approach, and its structural, optical, electrical, and photoreponse properties were systematically investigated. Spectroscopic analyses provided insight into the electronic structure of the BiNPs&PEI N-GQDs nanocomposite, and the corresponding

TABLE 3 | Comparison of the photodetection performance of the present device with representative Bi-based photodetectors.

Device/Structure	Responsivity (R) (AW^{-1})	Specific Detectivity (D^*) (Jones)	Notes/Conditions	Refs.
PEI N-GQDs/p-Si (Bi free)	~ 0.20	2.10×10^{11} At -5 V; $100 \text{ mW} \cdot \text{cm}^{-2}$	Bi NPs-free (reference photodetector)	Present work
BiNPs&PEI GQDs/p-Si	~ 0.16	7.84×10^{10} at 5 V; $240 \text{ mW} \cdot \text{cm}^{-2}$	Bi NPs-doped	Present work
$\text{Bi}_2\text{Se}_3/\text{n-Si}$	2.60	4.39×10^{12} at 0 V; $60 \mu\text{W} \cdot \text{cm}^{-2}$	Layered topological insulator film	[18]
$\text{Bi}_2\text{Se}_3/\text{a-Ga}_2\text{O}_3/\text{p-Si}$	$\sim 1.38 \times 10^{-3}$	3.22×10^{10} at 0 V; $39.2 \mu\text{W} \cdot \text{cm}^{-2}$	Bi_2Se_3 powder	[20]
Bi NPs (PEC- type)	$\sim 4.98 \times 10^{-3}$	3.71×10^{10} at 0 V; $5 \text{ mW} \cdot \text{cm}^{-2}$	Bi NPs	[19]
$\text{Bi}_2\text{Se}_3/\text{a-Ga}_2\text{O}_3/\text{p-Si}$	$\sim 1.38 \times 10^{-3}$	3.22×10^{10} at 0 V; $39.2 \mu\text{W} \cdot \text{cm}^{-2}$	Bi_2Se_3 powder	[20]
CuO/n-Si	$\sim 1.91 \times 10^{-3}$	3.73×10^8 at 5 V; $100 \text{ mW} \cdot \text{cm}^{-2}$	Bi-free (reference photodetector)	[34]
1% Bi:CuO/n-Si	$\sim 1.15 \times 10^{-3}$	3.57×10^8 at 5 V; $100 \text{ mW} \cdot \text{cm}^{-2}$	with 1% Bi doped	[34]
2% Bi:CuO/n-Si heterojunction PD	$\sim 3.71 \times 10^{-3}$	4.00×10^8 at 5 V; $100 \text{ mW} \cdot \text{cm}^{-2}$	with 2 wt % Bi doped (best-performing sample)	[34]
3% Bi:CuO/n-Si	$\sim 0.28 \times 10^{-3}$	2.51×10^8 at 5 V; $100 \text{ mW} \cdot \text{cm}^{-2}$	with 3 wt % Bi doped (the lowest performance)	[34]
Al/CdO/p-Si	$\sim 1 \times 10^{-3}$	1.62×10^8 at 1.7 V; $100 \text{ mW} \cdot \text{cm}^{-2}$	Bi-free (reference photodetector)	[35]
Al/Bi: CdO/p-Si	$\sim 5.35 \times 10^{-3}$	1.15×10^9 at 1.7 V; $100 \text{ mW} \cdot \text{cm}^{-2}$	0.5 wt.% Bi-doped (optimum Bi doping)	[35]

energy-level diagram was established based on UPS and optical bandgap measurements.

The fabricated heterojunction exhibited rectifying behavior in the dark and a stable photoresponse under illumination, achieving a responsivity of 0.16 A W^{-1} and a specific detectivity of 7.84×10^{10} Jones at 5 V under an illumination intensity of 240 mW cm^{-2} . The electrical characteristics were largely preserved after 24 months of storage under ambient conditions, confirming the long-term stability of the device.

Combined UV-Vis, PL, UPS, and electrical analyses revealed that Bi nanoparticle incorporation modifies the optical absorption behavior and energy-level alignment at the heterointerface, leading to an increased barrier height, reduced ideality factor, enhanced rectification ratio, and suppressed dark current. Comparison with previously reported Bi-based photodetectors demonstrated that the proposed device exhibits comparable performance within the reported literature range.

Overall, the results demonstrate that BiNPs&PEI N-GQDs can be effectively integrated into Si-based heterojunction photodetectors through an environmentally friendly, solution-processable route. The simple fabrication strategy, reduced processing complexity, and potential scalability highlight the potential of this approach for sustainable optoelectronic and photosensing applications.

Author Contributions

E. O. and A. D. B. conceptualized the study and supervised the overall work. M. Y. contributed to the interpretation of results and refinement of the manuscript. Z. B. and A. K. carried out the experiments, performed data analysis, and wrote the original draft. S. S. performed the PL measurement. İ. Y. performed UPS measurement. All authors reviewed and approved the final version of the manuscript.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

All data included in this study are available upon reasonable request from the corresponding author.

References

1. N. Kumar, R. Dhyani, B. S. Rawat, P. S. Rawat, D. Roy, and D. Singh, "A Review on Synthesis, Challenges as Well as Future Prospects of Graphene Quantum Dot (GQD)," *Pramana* 98 (2024): 42, <https://doi.org/10.1007/s12043-023-02690-2>.

2. Y. Cui, L. Liu, M. Shi, et al., "A Review of Advances in Graphene Quantum Dots: From Preparation and Modification Methods to Application," *Journal of Carbon Research* 10 (2024): 1–40.
3. M. Li, J. Liu, T. Zhang, et al., "Enhanced Performance of Self-Powered ZnO-Based PEC Type UV Photodetectors by Loading GQDs to Construct Heterojunctions," *Materials Research Bulletin* 172 (2024): 112657, <https://doi.org/10.1016/j.materresbull.2023.112657>.
4. M.-L. Tsai, W.-C. Tu, L. Tang, et al., "Efficiency Enhancement of Silicon Heterojunction Solar Cells via Photon Management Using Graphene Quantum Dot as Downconverters," *Nano Letters* 16 (2016): 309–313, <https://doi.org/10.1021/acs.nanolett.5b03814>.
5. P. Gao, K. Ding, Y. Wang, et al., "Crystalline Si/Graphene Quantum Dots Heterojunction Solar Cells," *The Journal of Physical Chemistry C* 118 (2014): 5164–5171, <https://doi.org/10.1021/jp412591k>.
6. F. Kalantari, M. Amirmazlaghani, and S. Olyaei, "Enhanced UV-Sensing Properties by Utilizing Solution-Processed GQD in GQDs/Porous Si Heterojunction Near-UV Photodetector," *Materials Science in Semiconductor Processing* 163 (2023): 107560, <https://doi.org/10.1016/j.mssp.2023.107560>.
7. D. H. Shin, S. Kim, J. M. Kim, et al., "Graphene/Si-Quantum-Dot Heterojunction Diodes Showing High Photosensitivity Compatible With Quantum Confinement Effect," *Advanced Materials* 27 (2015): 2614–2620, <https://doi.org/10.1002/adma.201500040>.
8. Z. Berktaş, M. Yıldız, E. Seven, E. O. Orhan, and Ş. Altındal, "PEI N-Doped Graphene Quantum Dots/p-Type Silicon Schottky Diode," *FlatChem* 36 (2022): 100436, <https://doi.org/10.1016/j.flatc.2022.100436>.
9. E. Orhan, A. Anter, M. Ulusoy, et al., "Effect of Gadolinium on Electrical Properties of Polyethyleneimine Functionalized and Nitrogen-Doped Graphene Quantum Dot Nanocomposite Based Diode," *Advanced Electronic Materials* 9 (2023): 2300261, <https://doi.org/10.1002/aeml.202300261>.
10. A. Anter, E. Orhan, M. Ulusoy, et al., "Lanthanum(III)Hydroxide Nanoparticles and Polyethyleneimine-Functionalized Graphene Quantum Dot Nanocomposites in Photosensitive Silicon Heterojunctions," *ACS Applied Materials & Interfaces* 16 (2024): 22421–22432, <https://doi.org/10.1021/acsami.4c02102>.
11. H. Tetsuka, "Nitrogen-Functionalized Graphene Quantum Dots: A Versatile Platform for Integrated Optoelectronic Devices," *The Chemical Record* 20 (2020): 429–439, <https://doi.org/10.1002/tcr.201900063>.
12. I. Mihalache, A. Radoi, R. Pascu, C. Romanitan, E. Vasile, and M. Kusko, "Engineering Graphene Quantum Dots for Enhanced Ultraviolet and Visible Light p-Si Nanowire-Based Photodetector," *ACS Applied Materials & Interfaces* 9 (2017): 29234–29247, <https://doi.org/10.1021/acsami.7b07667>.
13. Z. Dang, W. Wang, J. Chen, et al., "Vis-NIR Photodetector With Microsecond Response Enabled by 2D Bismuth/Si (111) Heterojunction," *2D Materials* 8 (2021): 035002.
14. C. Xing, W. Huang, Z. Xie, et al., "Ultrasmall Bismuth Quantum Dots: Facile Liquid-Phase Exfoliation, Characterization, and Application in High-Performance UV-Vis Photodetector," *ACS Photonics* 5 (2018): 621–629, <https://doi.org/10.1021/acsp Photonics.7b01211>.
15. J. Yao, Z. Zheng, J. Shao, and G. Yang, "Promoting Photosensitivity and Detectivity of the Bi/Si Heterojunction Photodetector by Inserting a WS₂ Layer," *ACS Applied Materials & Interfaces* 7 (2015): 26701–26708, <https://doi.org/10.1021/acsami.5b08677>.
16. C. O. Kim, S. W. Hwang, S. Kim, et al., "High-Performance Graphene-Quantum-Dot Photodetectors," *Scientific Reports* 4 (2014): 4–9, <https://doi.org/10.1038/srep05603>.
17. S. Gupta, J. Walden, A. Banaszak, and S. B. Carrizosa, "Facile Synthesis of Water-Soluble Graphene Quantum Dots/Graphene for Efficient Photodetector," *MRS Advances* 3 (2018): 817–824, <https://doi.org/10.1557/adv.2018.14>.
18. H. Zhang, X. Zhang, C. Liu, S.-T. Lee, and J. Jie, "High-Responsivity, High-Detectivity, Ultrafast Topological Insulator Bi₂Se₃/Silicon Heterostructure Broadband Photodetectors," *ACS Nano* 10 (2016): 5113–5122, <https://doi.org/10.1021/acsnano.6b00272>.
19. S. Yang, S. Jiao, Y. Nie, et al., "Facile Synthesis of Bismuth Nanoparticles for Efficient Self-Powered Broadband Photodetector Application," *Journal of Materials Science & Technology* 126 (2022): 161–168, <https://doi.org/10.1016/j.jmst.2022.03.019>.
20. Y. Han, S. Jiao, J. Jing, et al., "A Self-Powered Solar-Blind UV-Enhanced Bi₂Se₃/a-Ga₂O₃/p-Si Heterojunction Photodetector for Full Spectral Photoresponse and Imaging," *Nano Research* 17 (2024): 2960–2970, <https://doi.org/10.1007/s12274-023-6082-3>.
21. Z. Berktaş, E. Orhan, M. Ulusoy, M. Yildiz, and Ş. Altındal, "Negative Capacitance Behavior at Low Frequencies of Nitrogen-Doped Polyethyleneimine-Functionalized Graphene Quantum Dots-Based Structure," *ACS Applied Electronic Materials* 5 (2023): 1804–1811, <https://doi.org/10.1021/acsaeml.3c00011>.
22. S. Singh, R. K. Sahoo, N. M. Shinde, et al., "Asymmetric Faradaic Assembly of Bi₂O₃ and MnO₂ for a High-Performance Hybrid Electrochemical Energy Storage Device," *RSC Advances* 9 (2019): 32154–32164, <https://doi.org/10.1039/C9RA06331E>.
23. İ. Yıldız, "Electrical Properties of ZnO Nanoparticle-Embedded/Polyethyleneimine-Functionalized Nitrogen-Doped Graphene Quantum Dot Nanocomposites," *ACS Omega* 11 (2026): 15269–15282, <https://doi.org/10.1021/acsomega.5c12583>.
24. J. Kistner-Morris, A. Shi, E. Liu, et al., "Electric-Field Tunable Type-I to Type-II Band Alignment Transition in MoSe₂/WS₂ Heterobilayers," *Nature Communications* 15 (2024): 4075, <https://doi.org/10.1038/s41467-024-48321-1>.
25. A. Di Bartolomeo, "Graphene Schottky Diodes: an Experimental Review of the Rectifying Graphene/Semiconductor Heterojunction," *Physics Reports* 606 (2016): 1–58, <https://doi.org/10.1016/j.physrep.2015.10.003>.
26. G. Luongo, A. Di Bartolomeo, F. Giubileo, C. A. Chavarin, and C. Wenger, "Electronic Properties of Graphene/p-silicon Schottky Junction," *Journal of Physics D: Applied Physics* 51 (2018): 255305, <https://doi.org/10.1088/1361-6463/aac562>.
27. A. Di Bartolomeo, K. Intonti, L. Peluso, et al., "Metal-Semiconductor Schottky Diode With Landauer's Formalism," *Nano Express* 6 (2025): 022501.
28. S. M. Sze and K. K. Ng, *Physics of Semiconductor Devices* (John Wiley & Sons, 2006).
29. Z. Bielecki, K. Achtenberg, M. Kopytko, J. Mikołajczyk, J. Wojtas, and A. Rogalski, "Review of Photodetectors Characterization Methods," *Bulletin of the Polish Academy of Sciences Technical Sciences* 70, no. 2 (2022): e140534, <https://doi.org/10.24425/bpasts.2022.140534>.
30. C. Xie, C. Mak, X. Tao, and F. Yan, "Photodetectors Based on Two-Dimensional Layered Materials beyond Graphene," *Advanced Functional Materials* 27 (2017): 1603886, <https://doi.org/10.1002/adfm.201603886>.
31. J. Fu, C. Nie, F. Sun, G. Li, and X. Wei, "Photodetectors Based on Graphene–Semiconductor Hybrid Structures: Recent Progress and Future Outlook," *Advanced Devices & Instrumentation* 4 (2023): 0031, <https://doi.org/10.34133/adi.0031>.
32. J. Fu, Z. Guo, C. Nie, et al., "Schottky Infrared Detectors With Optically Tunable Barriers Beyond the Internal Photoemission Limit," *The Innovation* 5 (2024): 100600, <https://doi.org/10.1016/j.xinn.2024.100600>.
33. A. Öter, B. Ersöz, Z. Berktaş, H. İ. Bülbül, E. Orhan, and Ş. Sağiroğlu, "An Artificial Intelligence Model Estimation for Functionalized Graphene Quantum Dot-Based Diode Characteristics," *Physica Scripta* 99 (2024): 1–11, <https://doi.org/10.1088/1402-4896/ad3515>.
34. G. Sutcu, G. SY, S. Baturay, and H. Kilic, "Enhanced Opto-Electronic Properties of Bi:CuO/n-Si Heterojunctions for Photodetector Application,"

tions,” *Acta Physica Polonica A* 145 (2024): 3–15, <https://doi.org/10.12693/APhysPolA.145.3>.

35. M. Soylu and Z. Tahiroglu Kose, “Effect of Bi Doping Level on Optoelectronic Functionality of CdO in Si-Based Heterojunctions,” *Journal of Materials Science: Materials in Electronics* 37 (2026): 184.

Supporting Information

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