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Optimizing reaction time in hydrothermal synthesis of nanocomposites $V_2O_5/PANI$ for improved photodetector applications performance

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Original Research

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Abstract:

This study assesses the photodetection efficacy of a nanocomposite heterojunction photodetector utilizing V₂O₅, PANI, and V₂O₅/PANI thin films. The nanocomposites were manufactured by a hydrothermal approach for 6 and 8 hours, then coated onto silicon (Si) substrates using a spray-coating technique. X-ray diffraction (XRD) examination verified the orthorhombic crystalline structure of V₂O₅ and the semi-crystalline characteristics of PANI. The nanocomposite synthesis led to noticeable alterations in both structures, with the reaction duration markedly affecting the crystallinity. Raman spectroscopy identified unique vibrational modes for each component, and the composite spectra exhibited distinctive changes indicative of robust molecular interactions. FESEM and AFM investigations revealed improved surface texture and suitable roughness in the sample synthesized at 6 hours and 180 °C, facilitating optimal morphology for effective photocarrier production and transport. Photoluminescence (PL) experiments verified that the active spectrum response of the nanocomposite photodetector ranges from 300 to 700 nm. The device constructed with a 6-hour response time demonstrated optimum performance, with a responsivity of 0.383 μA/W, a detectivity of 1.77×10^{20} Jones, and an external quantum efficiency of 153.2% at a 2 V bias and 10 mW/cm² light intensity. The reaction and recovery durations were 0.62 and 0.59 seconds, respectively. The results indicate the structural and functional dependability of the V₂O₅/PANI nanocomposite, presenting a viable avenue for constructing efficient optoelectronic devices.

Keywords: Hydrothermal; Time rection; Nanocomposite; Visible light photodetector; V₂O₅/PANI; Spray coting

1. Introduction

Recently, there has been significant interest in microelectronic and optoelectronic devices utilizing vanadium pentoxide (V_2O_5), a crucial transition-metal oxide semiconductor [1]. V_2O_5 is a potential material for photodetection applications owing to its direct bandgap in the visible-light spectrum ($E_g = 2.2 - 2.9$ eV) and its classification as an n-type metal oxide semiconductor [2]. Crystalline V_2O_5 exhibits a distinctive orthorhombic layered structure, a direct optical energy gap, advantageous chemical stability, thermal resistance, and elevated specific energy [3]. These characteristics render it appealing for several applications, such as solar cell windows, catalysts [4], infrared detectors [5], gas

sensors [6], and optoelectronic devices [7]. Despite its outstanding photovoltaic properties, V_2O_5 has comparatively worse electrical conductivity and an elevated electron-hole recombination rate in comparison to other conductive substances. Consequently, the amalgamation of V_2O_5 with additional components is frequently essential to augment its efficacy in practical applications [8]. The primary function of a photodetector is to produce electron-hole pairs in response to input light; hence, the photovoltaic performance of V_2O_5 can be enhanced by integrating nanoscale elements into its matrix to customize its features for particular applications. Polyaniline (PANI), in its emeraldine salt form, stands out among traditional conducting polymers. It has a wide range of desirable properties, such as being

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sensitive to visible light (bandgap: 2.5 - 3 eV), being easily synthesized at a low cost, being redox tunable via acid/base doping, having adjustable conductivity, and being environmentally stable [9–12]. Nanoscale materials embedded in a polymer matrix to make polymeric nanocomposites have found extensive application in performance enhancement. Composites made of PANI have been engineered using a wide range of additives, including organic molecules, carbon nanostructures, metal oxides, and other polymers [13]. To add to its sensitivity in the visible-light spectrum, PANI exhibits a HOMO-LUMO energy gap below 2.8 eV [14, 15]. So, a V₂O₅/PANI heterojunction could be a good choice for developing multicolor photodetectors (PDs) since it could provide novel optoelectronic features neither material could provide. Flexible V₂O₅/PANI heterojunctions for UV and visible light detection have not been described in any prior investigations as far as we are aware. Here, we detail the process of creating and studying V₂O₅/PANI heterojunctions that can detect many colors when exposed to ultraviolet and visible light. The electrical and optical characteristics of the suggested devices were examined by measuring the current voltage (I-V) and analyzing the photocurrent response.

2. Experimental

2.1 Materials

The materials such as aniline (99.9%) monomer, ammonium persulfate (APS), hydrochloric acid (HCl), ammonium metavanadate (NH $_4$ VO $_3$) ethanol and deionized water were purchased from sigma Aldrich.

2.2 Synthesis of PANI

Polyaniline (PANI) in its emeraldine salt (ES) form was created using chemical oxidative polymerization of aniline in an acidic environment. The synthesis entailed the formulation of two distinct solutions: Solution 1 comprised 10 mL of hydrochloric acid (HCl), 20 mL of deionized water, and 3 mL of aniline; Solution 2 included 4 g of ammonium persulfate (APS) mixed in 30 mL of deionized water.

After 40 minutes of individual agitation, Solution 2 was incrementally introduced to Solution 1 while maintaining continuous stirring. A progressive color transition from blue to dark green was noted, signifying the synthesis of PANI by oxidative polymerization. The reaction mixture was stirred for another 3 hours to finalize the polymerization process. The green precipitate of PANI was recovered via filtering, extensively rinsed with deionized water to eliminate contaminants, and dried in an oven at 60 °C for 6 hours.

2.3 Synthesis of V₂O₅

Vanadium pentoxide (V_2O_5) nanostructures were produced through the thermal breakdown of 2 g of ammonium metavanadate (NH₄VO₃) in a sealed autoclave at a temperature range of $500-550\,^{\circ}\text{C}$ for 2 hours. During breakdown, water and ammonia gasses were generated as byproducts and evaporated due to the high temperature, as indicated by the following reaction:

$$2NH_2VO_3 \xrightarrow{500-550 \text{ °C}} V_2O_5 + H_2O + 2NH_3$$
 (1)

Following thermal treatment, the resultant V_2O_5 powder was solubilized in deionized water to provide a concentrated working solution, which was then utilized to synthesize the nanocomposite.

2.4 Synthesis of V₂O₅/PANI nanocomposites

V₂O₅/PANI nanocomposites were manufactured via a straightforward, economical, surfactant-free hydrothermal technique. Two samples, VP-6h and VP-8h, were produced with an identical weight ratio 1:3 (V₂O₅:PANI). Precisely, 0.125 g of V₂O₅ powder and 0.375 g of polyaniline (PANI) were allocated into individual tubes. Each tube received 25 mL of deionized water, followed by ultrasonic treatment for 25 minutes to achieve uniform dispersion of the components.

After ultrasonication, each combination was placed into a Teflon-lined stainless-steel autoclave for hydrothermal processing. The VP-6h sample was heated in an oven at 180 °C for 6 hours, whereas the VP-8h sample underwent identical conditions for 8 hours. After the heat procedure, the autoclaves were allowed to cool naturally to ambient temperature, and the resultant nanocomposites were gathered for further examination.

2.5 Fabrication of the photodetector device

Nanocomposites $V_2O_5/PANI$ were deposited onto p-type silicon substrates to fabricate the photodetector device. Before deposition, the substrates underwent a comprehensive cleaning process involving sequential cleaning with deionized water, acetone, and ethanol, in addition to one hour of sonication in a water bath to eliminate dust, fingerprints, and residual surface contaminants. The substrates were then dried with a nitrogen gas stream. Nanocomposite films were deposited using spray-coating techniques. As shown in (figure 1), the cleaned silicon substrates were positioned on a hot plate from $80~^{\circ}C$ to $85~^{\circ}C$. 50~ spray cycles were conducted, each lasting 5~ seconds and a 25~ second interval for drying between consecutive sprays. This technique facilitated the creation of uniform thin films with thicknesses that varied according to the parameters of the spray application

Moderately thick films are generally ideal for photodetector applications, as they effectively balance electrical conductivity and light absorption, ensuring sufficient charge carrier mobility while facilitating adequate interaction with incident photons to produce electron-hole pairs. Conversely, skinny films generally demonstrate increased electrical conductivity owing to reduced carrier transport distances; however, they may exhibit diminished light absorption, leading to lower photocurrent and elevated noise levels. Excessively thick films can absorb significant amounts of light and generate more photogenerated carriers. However, this may increase recombination rates and diminished carrier collection efficiency, attributed to longer transport distances and elevated bulk resistance [16]. Following film deposition, silver electrodes were applied to the surface of the nanocompositecoated substrates through an electrodeposition technique, thus finalizing the fabrication of the photodetector device.

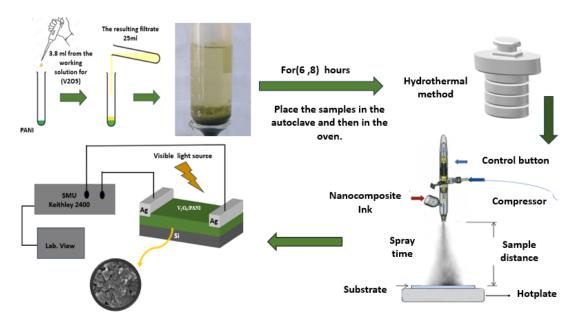


Figure 1. The experimental steps for preparation of V₂O₅, PANI and V₂O₅/PANI nanocomposite thin films and fabrication processes photodetector.

2.6 Characterization techniques

Several techniques were employed to characterize the V_2O_5 , PANI, and V₂O₅/PANI nanocomposites. The structural investigation of nanoparticles was done by applying a Shimadzu-6000 X-ray apparatus. The gadget used a Cu-K α radiation source at 0.15406 nm. The operational current was 40 mA at 40 kV. The samples were scanned from 5 to 70 degrees. The study utilized an advanced Field Emission Scanning Electron Microscope (FESEM) from ARYA Electron Optic, equipped with energy-dispersive X-ray (EDX) capabilities. This device provides elemental and topographical data with significantly enhanced image clarity, reduced electrostatic distortion, and three to six times higher resolution than traditional SEMs. Using an AFM, the nanoparticles' topography, surface morphology, and particle size distribution were examined (Mountains SPIP Expert 8.2.9621). This phenomenon is used to examine the energy structure of semiconductor materials. With an excitation wavelength of 320 nm, the FS-1401004 instrument was utilized to detect photoluminescence within a scanning range of 350 to 700 nm. Using a Horiba JOBIN YVON HR800, the Raman spectra were examined. To analyze the bonding structure, a (SUNSHINE-V2-86) device was used to measure the Raman spectrum. Finally, the I-V characteristics of the fabricated based-visible light photodetectors were analyzed via Keithley 237 SMU with 10 s on/off switching period and variety of illumination power intensity (AM 1.5 G filter).

3. Results and discussion

3.1 Structural analysis

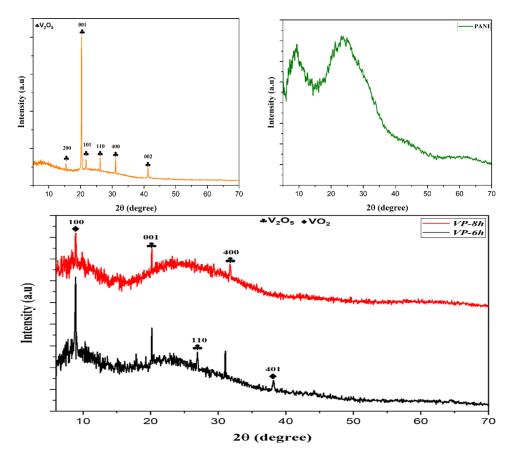
X-ray diffraction (XRD) analysis was utilized to examine the crystallinity, phase composition, and structural evolution of as-deposited V_2O_5 , polyaniline (PANI), and V_2O_5 /PANI nanocomposite thin films synthesized through spray coating on silicon substrates. Figure 2 (a) illustrates the XRD pattern of pure V_2O_5 , showcasing notable diffraction peaks at $2\theta = 15.3^\circ$, 20.3° , 21.7° , 26.9° , 31.1° , and 41.2° , which

align with the (200), (001), (101), (110), (400), and (002) crystallographic planes, respectively. The observed peaks correspond to the orthorhombic phase of V_2O_5 (JCPDS 00-009-0387) [17], with the prominent (101) reflection highlighting its layered structure, which is essential for the improvement of semiconducting properties. The distinct, impurity-free peaks affirm a high degree of crystallinity and phase purity, aligning with the principles of thermal decomposition synthesis.

Conversely, figure 2 (b) exhibits a broad peak of PANI centered at $2\theta=23.16^\circ$, which is ascribed to scattering from semi-crystalline polyaniline chains alongside a low-angle feature ($2\theta=6.0-10^\circ$) peaking at 9.25°, suggesting the presence of ordered PANI chains in the emeraldine salt form. As previously documented, the semi-crystalline behavior emerges from oxidative polymerization conducted in acidic media without cooling [18, 19].

The V_2O_5 /PANI nanocomposites figure 2 (c), synthesized over reaction durations of 6 h (VP-6h) and 8 h (VP-8h), demonstrate structural alterations attributed to the intercalation of PANI and the redox processes involving vanadium. VP-6h maintains the principal orthorhombic V₂O₅ peaks, albeit with diminished intensity, and exhibits two broadened PANI peaks, in addition to novel (001) reflections at $2\theta \approx 8.38^{\circ}$ corresponding to monoclinic VO₂ (JCPDS 01-071-0288) [20]. This indicates an expansion of the interlayer spacing from 0.43 nm in pristine V₂O₅ to 1.42 nm, thereby confirming the intercalation of PANI into the (002) planes. The VP-8h sample exhibits additional structural changes, characterized by a reduction in V₂O₅ peak intensity, significant broadening of the PANI peak, and a faint monoclinic VO₂ peak at $2\theta = 38.13^{\circ}$. The observed alterations indicate an extended reaction-driven reduction of vanadium ($V^{+5} \rightarrow V^{+4}$) alongside lattice strain, wherein V⁺⁴ ions facilitate the polymerization of PANI and contribute to the stabilization of intercalated H₂O-V₂O₅-PANI structures [21].

The quantitative analysis of crystallography, as presented in



 $\textbf{Figure 2.} \ \, \textbf{XRD} \ \, \textbf{patterns of (a)} \ \, \textbf{V}_2\textbf{O}_5, \textbf{(b)} \ \, \textbf{PANI}, \ \, \textbf{and (c)} \ \, \textbf{nanocomposite} \ \, \textbf{V}_2\textbf{O}_5/PANI \ \, \textbf{thin films synthesized with reaction times of 6 hours and 8 hours.}$

Table 1, employs Scherrer's equation (the crystalline size), dislocation density, and macro strains were obtained by applying equations (2), (3), and (4), respectively [22, 23]:

$$D = \frac{0.9\lambda}{\beta\cos\theta} \tag{2}$$

$$\delta = \frac{1}{D^2} \tag{3}$$

$$\eta = \frac{\beta}{4\tan\theta} \tag{4}$$

where D is the crystallite size, K is the form factor (often 0.9), λ is the X-ray wavelength (1.5406 Å for Cu K α), β is the full width at half maximum (FWHM) of the diffraction peak in radians, and θ is the Bragg angle.

Elucidating notable trends. Pristine V_2O_5 demonstrates crystallite dimensions ranging from 35.5 to 111.6 nm, with dislocation densities between 0.07 and 0.80×10^{-3} nm $^{-2}$, alongside microstrains varying from 1.34 to 5.01×10^{-3} nm $^{-1}$, indicative of a moderate degree of lattice distortion. VP-6h exhibits diminished crystallite dimensions (61.3 nm for monoclinic VO₂) and an increased dislocation density $(0.27 \times 10^{-3} \text{ nm}^{-2})$, indicating structural perturbation due to PANI intercalation. VP-8h exhibits additional crystallite refinement (27.5 nm for VO₂) and an increase in defects, as evidenced by dislocation density and microstrain values of 1.33×10^{-3} nm $^{-2}$ and 17.65×10^{-3} nm $^{-1}$, respectively. This phenomenon can be linked to the prolonged reaction time, which facilitates vanadium reduction and contributes

to lattice disorder. The observed trends support the transition from orthorhombic to monoclinic phases, which is influenced by redox interactions occurring during the polymerization of PANI [24]. The heightened microstrain in VP-8h corresponds with similar oxide-polymer systems, wherein extended synthesis intensifies lattice distortion [25]. The intercalation mechanism, driven by V⁴⁺ ions and the resulting expansion of interlayer spacing, facilitates the customization of structural and electronic properties in V₂O₅/PANI nanocomposites, thereby establishing them as noteworthy contenders for semiconductor applications.

3.2 Raman spectroscopy analysis

Figure 3 displays Raman spectroscopy of vanadium pentavalent oxide (V₂O₅), polyaniline (PANI), and the hydrothermally synthesized V₂O₅/PANI nanocomposite exhibited unique spectrum fingerprints indicative of the structural and molecular interactions among the constituents. Figure 3 (a) distinct peaks for V₂O₅ were 103, 148, 308, 360, 512, 590, 695, 780, 940, and 1073 cm⁻¹. Lower peaks $(< 400 \text{ cm}^{-1})$ signify lattice vibrations and bending of V-O-V bonds, whereas the $500 - 700 \text{ cm}^{-1}$ range corresponds to in-plane vibrations related to bond coordination in the orthorhombic structure [26]. The peak at 940 cm^{-1} indicates the V=O terminal bond stretching, signifying the level of crystallinity and the existence of highly symmetric terminal bonds [27, 28]. The high-frequency Raman signal at around 1073 cm⁻¹ corresponds to the vanadyl oxygen stretching mode (V=OV) [29]. The observed splitting probably results

 $\textbf{Table 1.} \ Shows \ 2\theta, \ full \ width \ at \ half \ maximum, \ crystal \ size, \ dislocation \ density, \ micro \ strains \ of \ V_2O_5 \ and \ V_2O_5/PANI \ (VP-6h, \ VP-8h).$

Code sample	2θ	FWHM	Miller indices	Crystalline size (nm)	Dislocation density $(\delta) \times 10^{-3}$	Micro strains $(nm^{-2}) \times 10^{-3}$	Crystal system	Chemical formula
V_2O_5	15.3	0.143	200	56.05	0.3182	4.64	Orthorhombic	V_2O_5
	20.3	0.094	001	85.85	0.135	2.29	Orthorhombic	V_2O_5
	21.7	0.22	101	36.76	0.73	5.008	Orthorhombic	V_2O_5
	26.1	0.23	110	35.45	0.79	4.32	Orthorhombic	V_2O_5
	31.1	0.173	400	47.66	0.44	2.71	Orthorhombic	V_2O_5
	41.2	0.086	002	35.45	0.79	4.32	Orthorhombic	V_2O_5
Vp-6h	8.2	0.13	100	61.29	0.26	7.37	Monoclinic	VO ₂
	20.2	0.135	001	59.77	0.27	3.30	Orthorhombic	V_2O_5
	26.9	0.0732	110	111.58	0.08	1.33	Orthorhombic	V_2O_5
	31.1	0.067	400	123.07	0.06	1.051	Orthorhombic	V_2O_5
	38.1	0.1282	401	65.56	0.232	1.61	Orthorhombic	V_2O_5
Vp-8h	8.2	0.29	100	27.46	1.32	17.65	Monoclinic	VO ₂
	20.2	0.123	110	65.46	0.233	3.013	Orthorhombic	V_2O_5
	31.7	0.25	400	32.94	0.92	3.84	Orthorhombic	V ₂ O ₅

from local structural distortions or fluctuations in the bonding environment inside the V_2O_5 lattice.

Figure 3 (b) exhibits the polyaniline spectra displayed significant peaks at 447, 512, 587, 705, 762, 876, 965, 1065, 1194, 1275, 1321, 1480, 1562, and 1605 cm⁻¹, indicative of the polymer chain structure in the semi-oxidized state (emeraldine salt) [30, 31]. The peaks at 447 – 762 cm⁻¹ result from C–H wagging and C–N–C bending vibrations, but the peaks at 876 – 1065 cm⁻¹ signify out-of-plane ring vibrations, demonstrating the uniformity of the polymer chain. The peaks at 1194 – 1321 cm⁻¹ correspond to C–N and C=N vibrations, indicative of polaron-type local charges, whereas the peaks at 1480 – 1605 cm⁻¹ signify C=C stretching in the aromatic rings, which are linked to the oxidation state and electrical conductivity within the chain [32, 33].

Figure 3 (c) illustrates the amalgamation of V_2O_5 and PANI by hydrothermal treatment resulted in a nanocomposite that displayed a characteristic spectrum, indicating a structural interaction between the two substances, with peaks seen at 110, 147, 360, 470, 587, 695, 775, 870, 940, 1075, 1200, $1262, 1321, 1502, \text{ and } 1569 \text{ cm}^{-1}$. The existence of peaks characteristic of V_2O_5 (e.g., 310, 360, 940 cm⁻¹) signifies partial preservation of the crystalline architecture of the inorganic component, whereas the peaks linked to PANI $(587, 695, 1262, 1321, 1502, 1569 \text{ cm}^{-1})$ denote successful interpenetration of the polymer chains within the crystalline framework. Moreover, supplementary peaks were detected at 310 and 508 cm⁻¹ in the nanocomposite, ascribed to a secondary phase of vanadium oxide, VO₂, in the monoclinic configuration. These peaks signify distinct vibrations of the VO₂ structure, contrasting with those of V₂O₅, showing

the emergence of minor quantities of this phase due to the hydrothermal environment's heat and pressure reaction conditions. This transition signifies a change in oxidation state from V^{5+} to V^{4+} , influencing the electrical and structural characteristics of the composite [34, 35]. Upon comparison of the two samples with varying reaction periods (6 and 8 hours), the VP-6h sample exhibits sharper and more distinct peaks, signifying a greater degree of crystallinity and enhanced structural regularity. The VP-8h sample subjected to an extended reaction duration (8 hours) demonstrates minor blue changes towards elevated frequencies at the peaks of 870, 940, 1075, 1200, 1262, 1321, 1502, and 1569 cm⁻¹. The observed shifts can be attributed to the prolonged reaction time, which facilitates chemical bond rearrangements and enhances interlocking between the PANI chains and vanadium ions, resulting in bond shortening (notably V=O and C=N bonds) and an elevation in their vibrational energy [36], manifesting spectrally as a shift toward higher values [37]. Moreover, prolonged excessive reaction may result in the formation of secondary crystals or irregular partial recrystallization, diminishing the purity of the parent structure and impacting the Raman spectrum. From a chemical standpoint, the ideal reaction duration (6 hours) establishes an equilibrium between the rate of crystal growth and the development of interfacial bonds between V₂O₅ and PANI while avoiding "interfacial saturation" that may result in adverse compositional alterations. From a physical standpoint, preserving nanoscale dimensions and uniform distribution of components in a reduced timeframe improves the clarity of spectral peaks and diminishes the impact of random structural interference, resulting in enhanced electrical and

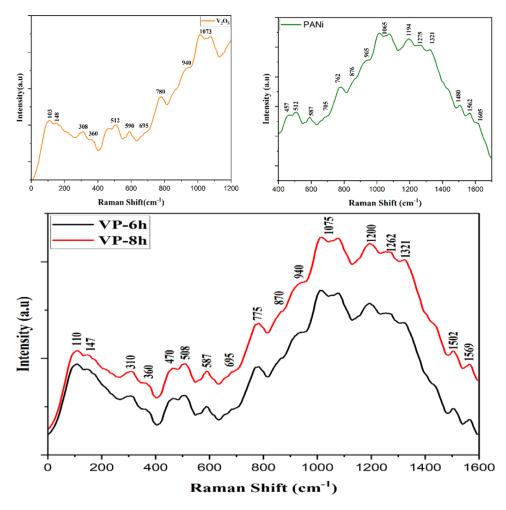


Figure 3. Raman spectroscopy of (a) V₂O₅, (b) PANI, and (c) V₂O₅/PANI synthesized with reaction times of 6 hours and 8 hours.

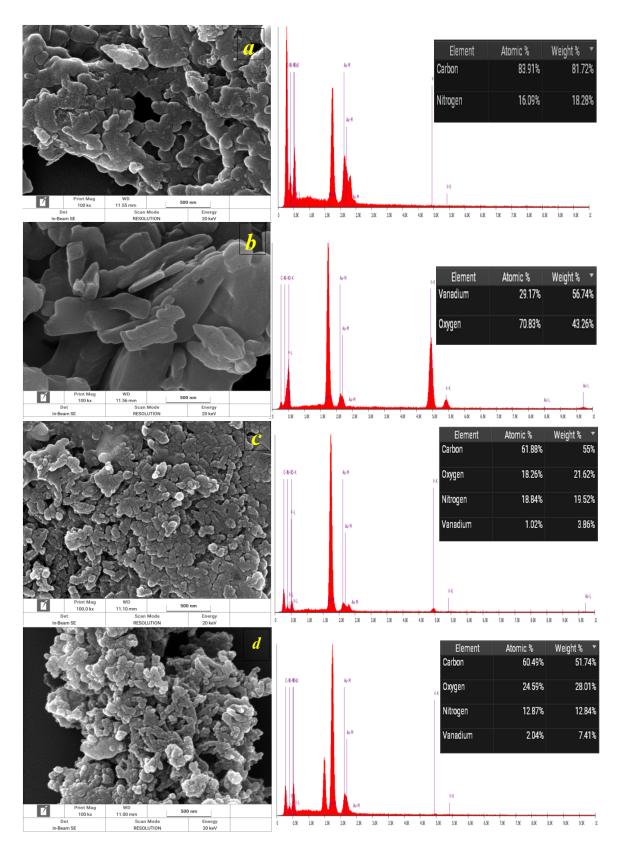
optical properties due to the facilitation of charge transfer within a more orderly structure [38].

3.3 Field emission scanning electron microscopy (FE-SEM) and EDX

The surface morphology of vanadium pentoxide (V_2O_5) , polyaniline (PANI), and their nanocomposites were examined using field-emission scanning electron microscopy (FE-SEM), as seen in figure 4. Pure PANI (figure 4 a) has a fibrous and foamy morphology with considerable porosity, marked by a rough surface that improves its detection efficacy by auguring active sits [39]. Energy-dispersive X-ray (EDX) examination verifies the elemental composition, revealing atomic percentages of carbon (C) at 83.91% and nitrogen (N) at 16.09%, consistent with the polymer's organic backbone. Conversely, V2O5 (figure 4 b) exhibits a hybrid morphology of nanorods and nanosheets, dictated by the synthesis temperature, characterized by a uniform surface and EDX-derived atomic percentages of vanadium (V) and oxygen (O) at 29.17% and 70.83%, respectively, aligning with its stoichiometric composition [25].

The nanocomposite VP-6h (figure 4 c), produced hydrothermally at 180 °C for 6 hours, has a semi-crystalline morphology characterized by spherical nanoclusters and a porous, agglomerated granular structure. The morphology, linked to homogeneous V_2O_5 dispersion and polaronic interactions.

tions, corresponds with EDX data indicating 60.49% C, 24.59% O, 12.87% N, and 2.04% V. The increased oxygen concentration (24.59%) and vanadium (2.04%) indicate partial preservation of the V_2O_5 structure in conjunction with PANI incorporation. In contrast, the VP-8h composite (figure 4 d), synthesized under the same circumstances but with an 8-hour reaction duration, demonstrates supplementary nanofiber development overlaid over porosity clusters. This structural development correlates with diminished electrical conductivity, presumably attributable to bipolaron formation and inadequate grain dispersion. EDX analysis for VP-8h reveals 61.88% carbon, 18.26% oxygen, 18.84% nitrogen, and 1.02% vanadium, demonstrating a significant reduction in oxygen and vanadium levels relative to VP-6h, coupled with an increase in nitrogen (18.84%), indicative of heightened PANI prevalence and suggesting accelerated PANI polymerization and vanadium reduction $(V^{5+} \rightarrow V^{4+})$ during prolonged reaction durations. These patterns validate XRD results, indicating that extended synthesis facilitates PANI intercalation, vanadium reduction, and phase transition, affecting the nanocomposite's electronic and morphological characteristics [40]. The reduction of vanadium and oxygen levels in VP-8h and nitrogen enrichment highlights the redox-mediated interaction between PANI and V₂O₅ during composite synthesis, essential for optimizing functional performance in sensing applications. Ibrahim et al. JTAP**19** (2025) -192543 7/17



 $\textbf{Figure 4.} \ \textbf{FESEM} \ images \ and \ EDX \ spectra \ of (a) \ PANI \ (b) \ V_2O_5 \ (c) \ VP-6h \ and \ (d) \ VP-8h \ nanocomposite \ V_2O_5/PANI \ Synthesis \ with \ various \ reaction time 6h \ and 8h \ respectively.$

3.4 Atomic Force Microscopy (AFM)

The 3D AFM micrographs and V₂O₅, PANI and V₂O₅/PANI histograms displayed in figure 5 (a) reveal a homogeneous rough high porosity surface morphology of PANI with RMS roughness 3.31375 nm, and the average particle size was 13.1465 nm. The rough, heterogeneous surface enhances the effective surface area, with the nanoparticle structure arising from the emeraldine salt form of polyaniline, which is semi-crystalline. The polymer's interwoven chains create porosity, indicating a semihomogeneous distribution and possible voids or pores. Figure 5 (b) porosity-free morphology with homogeneity and uniformity on the sample surface of V₂O₅ pure was shown by the atomic force microscopy investigation. The surface of the film showed no signs of cracking. The grains' surface was covered in enormous, exquisitely divided conical columnar development, with some columnar grains clumping together in specific places. Its RMS roughness was 19.3263 nm, which was attributed to the polycrystalline structure of the film. Moreover, its average particle size was 101.843 nm. It should be mentioned that because rough surfaces have a significantly larger total surface area than smooth surfaces, significant sample roughness is necessary for photovoltaic applications [41]. The micrograph displays a uniform distribution of high-quality VP-6h particles with an average size of 32.8338 nm and RMS roughness (Sq) of 4.59369 nm at a reaction time of 6 hours figure 5 (c). The nanoparticles were observed to form spherical aggregates with a unique porosity. Nevertheless, the VP-8h prepared at a reaction time of 8 hours exhibited a distinct morphological feature. The VP-8h was observed to form as rough particles with irregular cylindrical shapes and an average size of 28.7720 nm and RMS roughness (Sq) of 4.60817 nm figure 5 (d). This is by the results of the FESEM. This result shows the substantial impact of reaction time on the hydrothermal process, suggesting that producing fine particles with a high surface area is feasible under shorter reaction periods.

3.5 Photoluminescence spectroscopy analysis

The photoluminescence (PL) spectra of PANI, V_2O_5 , and nanocomposite samples (VP-6h and VP-8h) are displayed in figure 6. The excitation wavelength is 320 nm. As shown in figure 6 (a), four peaks of PANI may be attributable to a minimal difference in wavelength. A $\pi^* - \pi$ transition of the benzoic units and de-excitation from the polaron band was responsible for the genesis of the peak centered about 426 nm and 536 nm, respectively, as stated in reference [42]. Nothing is known about the source of the peak assigned to 608 nm. An association may be made between the bipolaron de-excitation and the faint peak at 724 nm. Additionally, the relative strength of the peak produced due to the de-excitation from the polaron band increases in proportion to the concentration of Hcl acid [43].

Additionally, the PL spectra of the V_2O_5 nanostructure can be seen due to four peaks. There are three peaks in the PL spectrum: around 414 nm, 501-580 nm, and 752 nm. The band-edge transition of V_2O_5 is responsible for the significant peak that occurs around 580 nm. In comparison, the

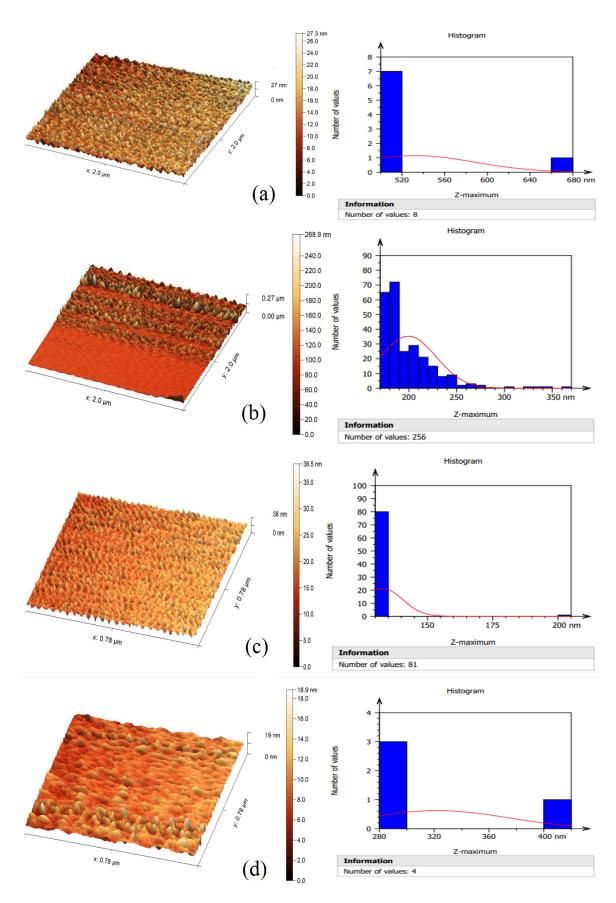
peak around 411 nm results from the transition from the top of the conduction band to the valance band of the material [44]. The extrinsic transition created by oxygen vacancies due to the annealing process is responsible for the emission that occurs at 752 nm [45].

As seen in figure 6 (b), the interaction between V_2O_5 and PANI resulted in the appearance of new peaks in the fundamental ranges of both materials and enhancements in the physical properties of each of the materials individually. It can be seen that the VP-8h has the look of on account of the $\pi - \pi^*$ transition of a benzenoid unit of PANI, the initial emission peak was seen at a wavelength of 351 nm [46]. The emission peak sites have demonstrated peak shifting, while the strength has steadily dropped with increasing excitation wavelength in VP-6h, which appears to have its peak at 386 nm. In samples, the peaks at 463 nm and 434 nm are present. A shift and a drop in intensity are seen in the VP-8h and VP-6h samples, respectively, when compared to the V_2O_5 and PANI samples [47]. The fact that it is connected with the polaron and bipolaron band transitions of PANI, respectively, suggests the interaction between PANI and V₂O₅. When conducting PANI, the charge carriers are essentially the polaron and the bipolaron. These interactions lead to the introduction of new electronic transitions and the rearranging of energy levels, both of which are not present in the materials in their natural state [48]. Because of this, electronic transit is improved, and the emission qualities are converted into something other. A range encompasses the third peak for VP-8h and VP-6h, as well as their respective peaks at 565 nm and 567 nm. The band-edge transition of V₂O₅ is responsible for the principal peak that can be found at around 580 nm [49]. This transition displays a slight change in intensity while retaining levels almost equal to those found in the pure sample of carbon dioxide. Sample VP-8h exhibits a shift and an increase in the intensity of the unknown peak at 660 nm, in contrast to the strength of the peak at 608 nm associated with pure PANI [50]. It is possible that the prolonged duration led to the formation of crystalline structural faults or distortions, in addition to interactions within the chain of the PANI molecule. As for the weak peaks that appear at 702 - 739 nm in VP-8h and 762 nm in VP-6h, these peaks indicate the extrinsic transition created by oxygen vacancies as a result of the annealing process. In association with the bipolaron de-excitation, these faint peaks were seen. The relative strength of the peak that was formed owing to the de-excitation from the polaron band increases as the reaction time increases [51].

4. Photodetector characteristics

4.1 Current-voltage (I-V) characteristics

The current-voltage (I–V) characteristics of pure vanadium pentoxide (V_2O_5), polyaniline (PANI), and their hydrothermally synthesized nanocomposites (VP-6h and VP-8h) were assessed under dark and visible light circumstances with an illumination intensity of 10 mW/cm² at ambient temperature. The measurements were performed throughout a voltage range of -5 to +5 V, utilizing silver (Ag) as the electrode material, as seen in figure 7. The I–V characteristics of the pure devices demonstrate distinct rectifying



 $\textbf{Figure 5.} \ AFM \ 3-D \ images \ and \ histogram \ particles \ size \ of \ (a), \ PANI \ (b) \ V_2O_5 \ (c \ and \ d) \ V_2O_5/PANI \ NCPs \ synthesis \ with \ different \ reaction \ time \ 6h \ and \ 8h \ respectively.$

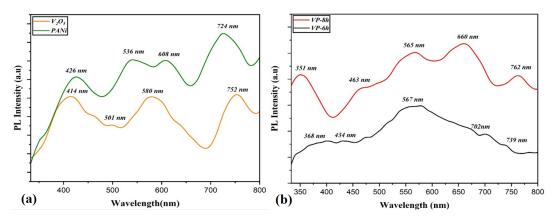


Figure 6. PL spectra of (a) V₂O₅ and PANI, (b) V₂O₅/PANI synthesized with different reaction time 6 hours (VP-6h) and 8 hours (VP-8h).

Table 2. Shows the bandgap energy of V	V ₂ O ₅ , PANI and V ₂ O ₅ /PANI NCPs.
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Sample	Wavelength (nm)	Energy gap (eV)
V_2O_5	414,501,580 and 752	2.9,2.4,2.1 and 1.64
PANI	426,536,608 and 724	2.9,2.3,2.04 and 1.7
V ₂ O ₅ /PANI (6 h)	368,434,567 ,702 and 739	3.3,2.8,2.1,1.7 and 1.6
V ₂ O ₅ /PANI (8 h)	351,463,565,660 and 762	3.5,2.6,2.1,1.8 and 1.6

behavior and enhanced current under light, signifying photosensitivity. For V_2O_5 , the photocurrent rose from 895.2 μA in darkness to 3543.4 μA under illumination at +5 V, but for PANI, it climbed from 816.8 μA to 3238.1 μA under the same circumstances. This improvement is due to the creation of electron-hole pairs when the energy of the incident photons surpasses the material's bandgap, and the relatively

low dark current indicates a modest degree of dark noise. Nonetheless, these pure materials continue to experience restrictions in responsivity because of Schottky barriers and surface imperfections. The I-V behavior changes markedly when integrating V_2O_5 and PANI into nanocomposite structures via hydrothermal treatment. The VP-6h nanocomposite exhibited superior optoelectronic performance under

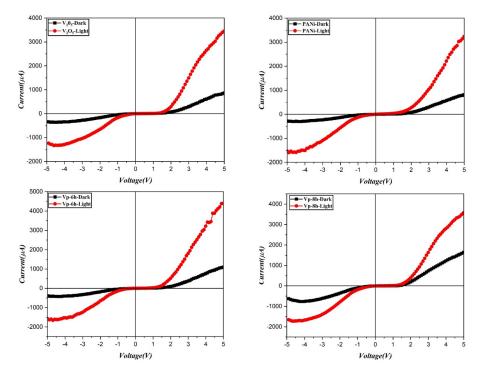


Figure 7. Current-voltage (I–V) characteristics of V_2O_5 , PANI and the nanocomposite synthesized with different reaction time 6 hours (VP-6h) and 8 hours (VP-8h), respectively.

dark and illuminated conditions, as confirmed by current voltage (I–V) measurements. At ± 5 V, VP-6h demonstrated significantly lower dark current values (387.4 μ A at -5 V and 1099.2 μA at +5 V) compared to VP-8h (620.8 μA at -5 V and 1677.7 μ A at +5 V), indicating reduced leakage current and minimal dark noise. This enhancement is primarily attributed to the improved crystallinity of VP-6h, as confirmed by X-ray diffraction (XRD) analysis, which correlates with a lower defect density and suppressed recombination of charge carriers. Furthermore, energy-dispersive X-ray spectroscopy (EDX) revealed a higher oxygen content in VP-6h, which facilitates electron trapping under dark conditions, contributing to the reduction of dark current [52]. Under illumination (10 mW/cm², visible light), VP-6h exhibited a significant increase in photocurrent, reaching 1571 μ A at -5 V and 4395.6 μ A at +5 V, which is considerably higher than that of VP-8h (1654.1 μA at -5 V and 3666.2 μ A at +5 V). The enhanced photocurrent in VP-6h is attributed to the efficient separation of photogenerated electron-hole pairs at the V₂O₅/PANI heterojunction. Illumination leads to narrowing the depletion layer, which reduces the barrier for carrier transport, facilitating a higher current flow. Moreover, applying a reverse bias enhances the internal electric field, promoting more effective separation of carriers and boosting photocurrent. In contrast, the VP-8h sample, which underwent extended hydrothermal synthesis (8 h at 180 °C), displayed higher dark current and lower photocurrent enhancement. This degradation in performance is likely due to increased structural disorder and defect density, which act as recombination centers, thus limiting carrier mobility and overall device efficiency. Additionally, the role of surface-adsorbed oxygen species is evident during light exposure; photogenerated holes interact with adsorbed oxygen ions, leading to the desorption of O⁻ species and injection of electrons into the conduction band, thereby enhancing the photocurrent response [53]. These findings underscore the importance of optimized synthesis conditions in achieving nanocomposites with high photoresponsivity and low noise levels for photodetector applications.

4.2 Time-dependence characteristics

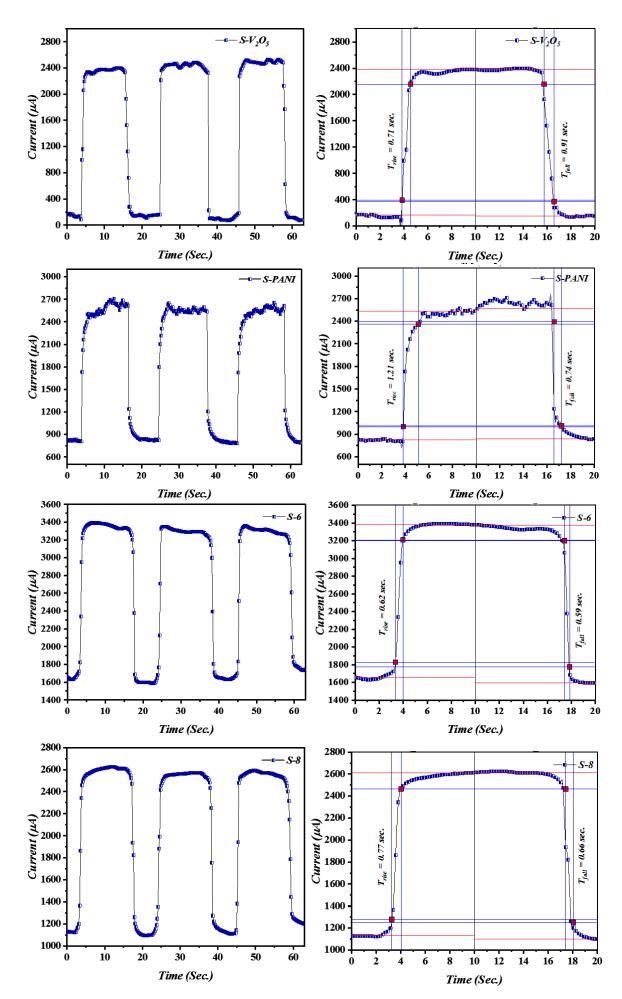
Photodetector behavior is influenced by key characteristics such as photo-switching and response/recovery time, which are critical for practical applications. As indicated in figure 8, The photo-switching behavior of the fabricated V₂O₅, PANI and nanocomposite (VP-6h, VP-8h) photodetectors was examined across multiple 10 mW/cm² illumination power cycles over three cycles of 10 s pulse with cycles at 2 bias voltages, indicating the device's durability and consistency. The apparatuses displayed the following response/recovery according. All four devices have excellent photoresponse, stability, and repeatability in each cycle. The current increased to the highest limit (light-ON) with an articulated response and diminished to its preliminary rate (light-OFF). The pure V₂O₅ device demonstrated a response and recovery time of 0.71 and 0.91 seconds, respectively, suggesting that the production rate of photogenerated electron-hole pairs is significantly quicker than the recombination rate. This characteristic is ascribed to the stratified orthorhombic configuration of V₂O₅, which provides elevated electron affinity and active surface spots that facilitate effective charge separation. Furthermore, terminal V=O bonds and inherent oxygen vacancies enhance electron mobility and reduce recombination. The comparatively porous structure and moderate surface roughness of the V₂O₅ layer promote light absorption and augment the effective surface area for carrier production, promoting better photoresponse efficiency.

Conversely, the pure PANI device exhibited extended response and recovery durations of 1.21/0.74 seconds. This indicates that the recombination rate exceeds the rate of electron-hole creation when illuminated. The reduced crystallinity, disordered molecular architecture, and restricted carrier mobility of PANI impede effective photocarrier production and transport. Moreover, the PANI film's comparatively smoother and denser surface, as seen by the AFM and FESEM pictures, leads to a diminished interfacial area and poorer light-matter interaction, constraining exciton dissociation and amplifying recombination losses [54]. The nanocomposite devices (VP-6h and VP-8h) demonstrated markedly enhanced response and recovery times of

The nanocomposite devices (VP-6h and VP-8h) demonstrated markedly enhanced response and recovery times of 0.62/0.59 s and 0.77/0.66 s, respectively. This improvement results from the synergistic interaction between the

Table 3. Represent the curent dark	cand light of	V_2O_5 , PANI and	V_2O_5 /PANI NCPs.
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Photodetector device	Voltage (V)	Dark-Curent (µA)	Light-Curent (µA)	
V.O	+5	870	3543.4	
V_2O_5	-5	339.1	1236.4	
PANI	+5	816.8	3238.08	
IANI	-5	284.6	1535	
VP-6h	+5	1099.2	4395.6	
V F-OII	-5	387.4	1571	
VP-8h	+5	1643	3666.2	
V1 -011	-5	620.8	1654.1	



inorganic V₂O₅ phase and the organic PANI matrix. The hybrid structure leverages the elevated carrier mobility of V₂O₅ and PANI's flexible, conductive framework, facilitating rapid separation and extraction of photogenerated carriers. The nanocomposite films have enhanced surface roughness and porosity, as AFM and FESEM investigations show [55, 56]. These textural characteristics augment light scattering and absorption, offering more active charge separation and transport sites. The coarse, porous texture enhances the interfacial contact area between the two phases, promoting interfacial charge transfer and diminishing the likelihood of recombination. Interestingly, different reaction times for nanocomposites result in varying conductivities, which contribute to diverse photovoltaic performance. This phenomenon indicates a rapid electron injection and relatively slow electron/hole recombination in the hybrid system [57].

4.3 Spectral dependency

Figure 9 illustrates the principal performance parameters of the photodetector, encompassing responsivity, detectivity, and external quantum efficiency (EQE) throughout an extensive spectrum range of 300 to 850 nm. This wavelength range encompasses the ultraviolet (UV), visible, and near-infrared (NIR) ranges, enabling a thorough assessment of the device's optoelectronic response. Spectral dependency (R_{λ}) is a crucial parameter for assessing photodetector performance, as it measures the device's sensitivity to various wavelengths of incident light and can be computed using

the equation.

$$R_{\lambda} = \frac{I_{\rm ph}}{P_{\rm light}} \tag{5}$$

where $I_{\rm ph}$ is the output photocurrent and $P_{\rm light}$ is the amount of incident illumination power [58]. Moreover, if the DC shot noise is the primary source of the produced noise, the photodetectivity (D^*), which is determined using equation (2), is another essential metric for estimating a photodetector's performance [59].

$$D^* = \frac{R_{\lambda}}{\sqrt{2qI_D}} \tag{6}$$

Here, q and I_D stand for the electron charge $(1.6 \times 10^{-19} \text{ C})$ and dark current, respectively. And to further quantify this gain, we measured the EQE of the PDs in reaction to light. EQE is an important measure for quantifying PD behavior and may be calculated as follows [60].

$$EQE = \frac{R_{\lambda} \times h \times c}{q \times \lambda} \times 100\% \tag{7}$$

where h is the Planck's constant, c is the light velocity, q is the electron charge, λ is the incoming light wavelength, and R_{λ} is the responsivity at the wavelength of λ nm. The spectral response of the fabricated photodetectors, illustrated in figure 9 (a–c), was examined under an illumination power of 10 mW/cm² at 2 bias voltage, demonstrating moderate sensitivity in the UV region and a notable increase in R_{λ} , D^* , and EQE values at visible wavelengths, especially between 450 nm and 600 nm, which aligns with the optical

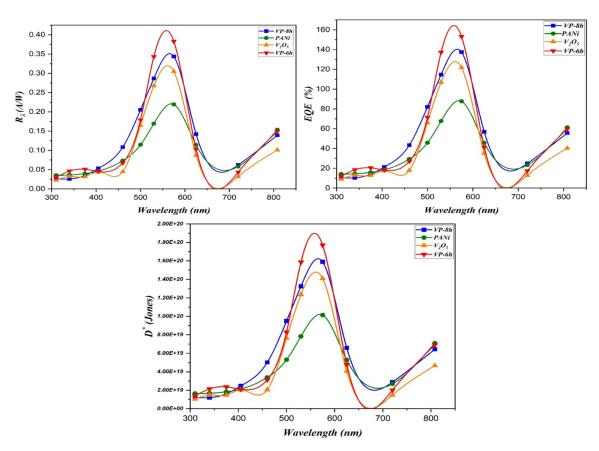


Figure 9. Photodetector responsivity, detectivity, and external quantum for PANI, V₂O₅, and V₂O₅/PANI nanocomposite synthesized with 6h (VP-6h) and 8h (VP-8h) reaction times, efficiency, respectively.

Photodetector device	$R(\lambda)$	$D^* \times 10^{20}$	EQE	REC-Time
V_2O_5	0.304	1.41	121.96	0.71/0.91
PANI	0.219	1.01	87.68	1.21/0.74
VP-6h	0.383	1.77	153.2	0.62/0.59
VP-8h	0.343	1.59	137.52	0.77/0.66

Table 4. Shows responsivity, detectivity external quantum efficency and recovery time.

bandgap analysis. A quantifiable reaction at wavelengths greater than 700 nm may indicate sub-bandgap transitions, maybe attributable to defect states or surface plasmonic effects caused by the hybrid nanostructures. The hybrid photodetector VP-6h, synthesized by 6 hours of hydrothermal treatment, had all investigated devices' greatest performance metrics (R_{λ}, D^*, EQE) , indicating its optimized crystalline structure and enhanced charge transport dynamics. In contrast, VP-8h, synthesized over 8 hours, exhibited intermediate values surpassing those of the unaltered V₂O₅ and PANI devices but inferior to VP-6h suggesting that extended reaction time may elevate structural flaws, thereby reducing carrier mobility. The results collectively indicate that the pronounced photoresponsivity and detectivity in the hybrid devices arise not solely from the mesoporous morphology but are also substantially affected by particular nanostructures characteristics, including V₂O₅ nanowires and platelets, which augment charge separation and current density, underscoring the significance of precise nanostructure fabrication in optimizing photodetector performance.

4.4 Photodetector mechanism of devices

The photo-response of V₂O₅/PANI nanocomposites (VP-6h, VP-8h) under visible light illumination and a 2 V applied bias results from synergistic charge transport kinetics and interfacial band engineering. The polaron lattice structure in PANI facilitates effective intra- and inter-chain hopping of delocalized π -electrons and holes, producing free photo-excitons inside its intermediate gap states via the aggregation of radical cations [14, 61]. Simultaneously, visible light irradiation stimulates electron-hole pairs in the mixed nanorod/nanosheet structure of V₂O₅, which are segregated by the intrinsic electric field at the V₂O₅/PANI interface. Photo-generated holes traverse the V₂O₅ valence band and transition to the HOMO level of PANI. At the same time, electrons are elevated to the conduction band of V₂O₅, aided by a cascade band-edge alignment (1.6 eV) that connects the LUMO of PANI with the conduction band of V_2O_5 figure 10 (c) [61]. The implemented bias expedites this process, amplifying carrier drift and reducing recombination. PANI serves as a conductive conduit,

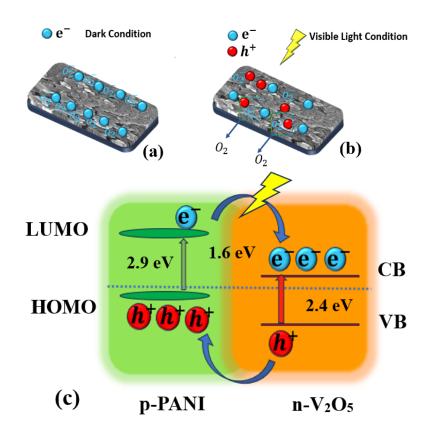


Figure 10. Illustrative schematic diagram of $V_2O_5/PANI$ in (a) dark and (b) light conditions (c) schematic energy band diagram of the $V_2O_5/PANI$ heterojunction.

enhancing photocurrent through polaron-mediated exciton generation. At the same time, figure 10 (a,b) illustrates adsorbed oxygen species on V₂O₅/VO₂ surfaces regulate depletion layers: upon illumination, trapped holes desorb oxygen $h^+ + O_2^-$ (ad) $\rightarrow O_2$ (g) diminishing barrier height and thickness, thus facilitating the occupation of unpaired electrons in the conduction band and increasing conductivity [52]. Following light removal, recombination through bipolaron states in PANI swiftly reinstates the dark current. In contrast, the restricted grains of V₂O₅ and the intermediate gap states of PANI guarantee stable on/off current ratios throughout cycles. The rectifying I-V characteristics and persistent photoresponse across different light intensities (Fig. 10) underscore the essential functions of interfacial charge separation, polaron dynamics, and bias-enhanced transport in attaining adjustable optoelectronic performance, differentiating this mechanism from self-powered systems that depend exclusively on built-in potentials.

5. Conclusion

A series of photodetectors employing pure V₂O₅, PANI, and hydrothermally produced V₂O₅/PANI nanocomposites (VP-6h and VP-8h) were effectively constructed by spray coating on silicon substrates. XRD analysis verified the existence of orthorhombic V₂O₅ and identified monoclinic VO₂ phases in the nanocomposites, demonstrating successful phase integration. FESEM and AFM analyses revealed that VP-6h exhibited a highly porous morphology and excellent surface roughness, conducive to improved photodetection, whereas VP-8h displayed nanorod production. Raman spectroscopy confirmed the practical synthesis by detecting distinctive vibrational modes of each component. Photoluminescence investigations established the detector's active spectral range as 450 to 650 nm, aligning with the high responsivity (0.383 A/W), detectivity $(1.77 \times 10^{20} \text{ Jones})$, and external quantum efficiency (153.2%) demonstrated by VP-6h under a 2 V bias and 10 mW/cm² illumination. Moreover, rapid response and recovery periods further illustrate its appropriateness for practical applications. The present research emphasizes the innovative application of hydrothermally produced V₂O₅/PANI nanocomposites with customized shape and phase composition, leading to markedly enhanced photodetector performance. These findings provide significant insights for developing sophisticated, economical hybrid optoelectronic devices.

Authors Contribution

The intellectual substance, idea, and design of this study, or the analysis and interpretation of the data (if applicable), as well as the manuscript's writing, were all sufficiently contributed to by each author

Availability of data and materials

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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