

Article

Synergistic Enhancement of Photoresponse and Humidity Response in PPy/TiO₂ Heterostructures

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Abstract

This study investigates the responses in the resistance of polypyrrole (PPy) and titanium dioxide (TiO₂) single layers and PPy/TiO₂ heterostructures to rectangular pulses of monochromatic LED illumination under controlled relative humidity. Exposure to moisture increases the resistance of PPy while rapidly decreases that of TiO₂, reflecting opposite effects of electron donation from hydroxyl (–OH) groups in adsorbed H₂O on the majority carrier densities of the two materials. Under monochromatic illumination, the resistance of PPy decreases, whereas that of TiO₂ increases accompanied by a brief transient at excitation wavelengths near its optical edge (367 nm and 398 nm). This photoresponse is attributed to photoinduced modifications of carrier density through two opposing processes: photogeneration, which enhances charge carriers, and H₂O photodesorption, which reduces them. A combination of illumination and moisture exposure results in an intensified photoresponse of PPy, thereby enhancing its humidity response. The PPy/TiO₂ heterostructure demonstrates a mixed photoresponse arising from contrasting behaviors of its p-type PPy and n-type TiO₂ components, coupled with charge exchange across the p–n junction. When simultaneously exposed to moisture and monochromatic light, the heterostructure undergoes contrasting photoinduced carrier generation in its two components, which in turn modulates the depletion region in inverse phase with carrier density, thereby intensifying the overall photoresponse. This complementary “push–pull” interaction synergistically enhances both the photoresponse and the humidity response of the PPy/TiO₂ heterostructure.

Keywords: TiO₂; PPy; PPy/TiO₂ heterostructure; photocatalysis; photoresponse



Academic Editor: Zizhong Zhang

Received: 27 July 2026

Revised: 2 September 2026

Accepted: 6 September 2026

Published: 10 September 2026

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1. Introduction

Many nanostructured wide-bandgap semiconductors ranging from inorganic compounds such as TiO₂, ZnO, SnO₂, WO₃, SiO₂, Nb₂O₃, Fe₂O₃, CdS to organic compounds such as semiconducting polymers of PANi, PPy, PEDOT, etc., exhibit unique photoactive features [1–5]. Upon exposure to light, these materials generate electron–hole pairs that function as potent redox agents, subsequently initiating the formation of diverse reactive free radicals [1,2]. Owing to high activity, the radical species can drive electrochemical

processes such as water splitting for hydrogen production, pollutant degradation, and microbial sterilization [5–11]. Building on this mechanism, photocatalysis has emerged as a promising, sustainable approach for addressing energy and environmental challenges such as air pollution and wastewater contamination. Accordingly, the development of highly effective semiconductor photocatalysts is being pursued at both fundamental and applied levels.

Titanium dioxide (TiO_2) is widely regarded as a cornerstone photocatalyst owing to its chemical stability, affordability, low toxicity, and favorable band-edge positions. However, its photocatalytic activity is confined to the UV region (<400 nm), and it suffers from high electron–hole recombination rates and limited surface absorption. To overcome these limitations, heterostructures formed by coupling TiO_2 , an inorganic semiconductor, with counterparts possessing complementary electronic properties have been developed as one of the most effective strategies for improving the photocatalytic performance [12–16]. Among prospective materials, semiconducting polymers such as PANi and PPy are particularly attractive due to their narrow and tunable bandgaps, strong visible-light absorption, and efficient charge transport [17–23]. PPy was selected over PANi in this study owing to its better environmental stability, improved interfacial compatibility with TiO_2 , and its ability to form uniform thin layers, all of which are advantageous for heterostructure fabrication. When integrated with TiO_2 , PPy extends the absorption range into the visible spectrum while simultaneously facilitating charge separation and reducing recombination losses. As a result, TiO_2 /PPy nanocomposites used as photocatalysts have demonstrated greater efficiency in degrading methylene blue, rhodamine B, methyl orange dyes, shown significantly improved catalytic activity in the photoreduction of CO_2 , and been applied in the development of self-cleaning/antibacterial paints [22,23]. Nevertheless, most studies on photocatalysts in general, and on PPy/ TiO_2 in particular, have emphasized synthesis methodologies and overall photocatalytic performance. In contrast, mechanistic studies of photocatalytic processes within the structure remain scarce and demand further experimental validation to substantiate existing concepts or to propose alternative mechanistic pathways for future advancement.

From a photoelectrochemical perspective, the photocatalytic activity of semiconductor nanostructures such as TiO_2 proceeds through a sequence of fundamental processes. Upon photon absorption, electron–hole (e^- – h^+) pairs are generated, subsequently separated, and migrate to the semiconductor surface, where they initiate chemical redox reactions with adsorbed O_2 , H_2O , and other species. These reactions yield secondary reactive species (e.g., $\bullet\text{OH}$, $\text{O}_2\bullet^-$, H^+), which further propagate the photocatalytic process. The formation of these radicals is governed by the local availability of oxygen and moisture; for instance, the photocatalytic performance in ambient air is strongly humidity-dependent and differs markedly from that in aqueous environments. Beyond environmental factors, photocatalytic activity in semiconductor nanostructures is fundamentally governed by their electronic configuration, encompassing carrier type, bandgap, and the relative positions of the conduction and valence bands. Accordingly, the deliberate tailoring of electronic structure has emerged as a pivotal strategy for optimizing and enhancing photocatalytic performance. In heterostructures, the coupling of complementary semiconductors (e.g., n-type TiO_2 with p-type PPy) induces modifications in the electronic structure, which are manifested in altered conductance characteristics. In turn, the conductance/resistance response of such heterostructures to light excitation under controlled humidity conditions can serve as an essential and informative parameter for probing photoelectrochemical processes—particularly in ambient air, where humidity and oxygen play critical roles in photoinduced processes and, more broadly, in catalytic activity.

Motivated by this rationale, the present study investigates the resistance response of PPy and TiO₂ single layers and PPy/TiO₂ heterostructures to rectangular pulses of monochromatic LED illumination under controlled humidity. This experimental framework is expected to enable a systematic exploration of moisture-induced electronic effects and charge-transfer mechanisms. By correlating the time-resolved resistance response with the underlying photoelectrochemical processes, the synergistic modulation of photocatalytic processes in the PPy/TiO₂ heterostructure by humidity and illumination can be deduced and evaluated. The findings are expected to provide new insights into design principles for photocatalytic and optoelectronic materials responsive to coupled light-and-moisture stimuli.

2. Results and Discussion

FESEM images of the surface morphology and cross-sections of PPy, TiO₂, and the PPy/TiO₂ heterostructure are presented in Figure 1. The PPy single layer, with a thickness of approximate 90–110 nm, consists of uniformly distributed grains with mean sizes of 20–30 nm, deposited on the surface of glass substrates (Figure 1a,b). On the other hand, the TiO₂ single layer, with a thickness of 360 nm, is composed of 15–20 nm grains forming clusters that randomly cover the surface of the glass plate (Figure 1c,d). The PPy/TiO₂ heterostructure consists of two distinct layers—TiO₂ and PPy—each with a thickness corresponding to its respective component (Figure 1e,f). Notably, the presence of an air gap at the PPy–glass interface indicates weak mechanical adhesion, which may limit the stability of the PPy layer when deposited directly on glass. However, the continuous and smooth PPy/TiO₂ interface demonstrates strong bonding, suggesting that TiO₂ acts as an effective intermediate layer that promotes heterostructure formation. This improved interfacial contact is expected to enhance electronic coupling between PPy and TiO₂, thereby contributing to better charge transport across the interface.

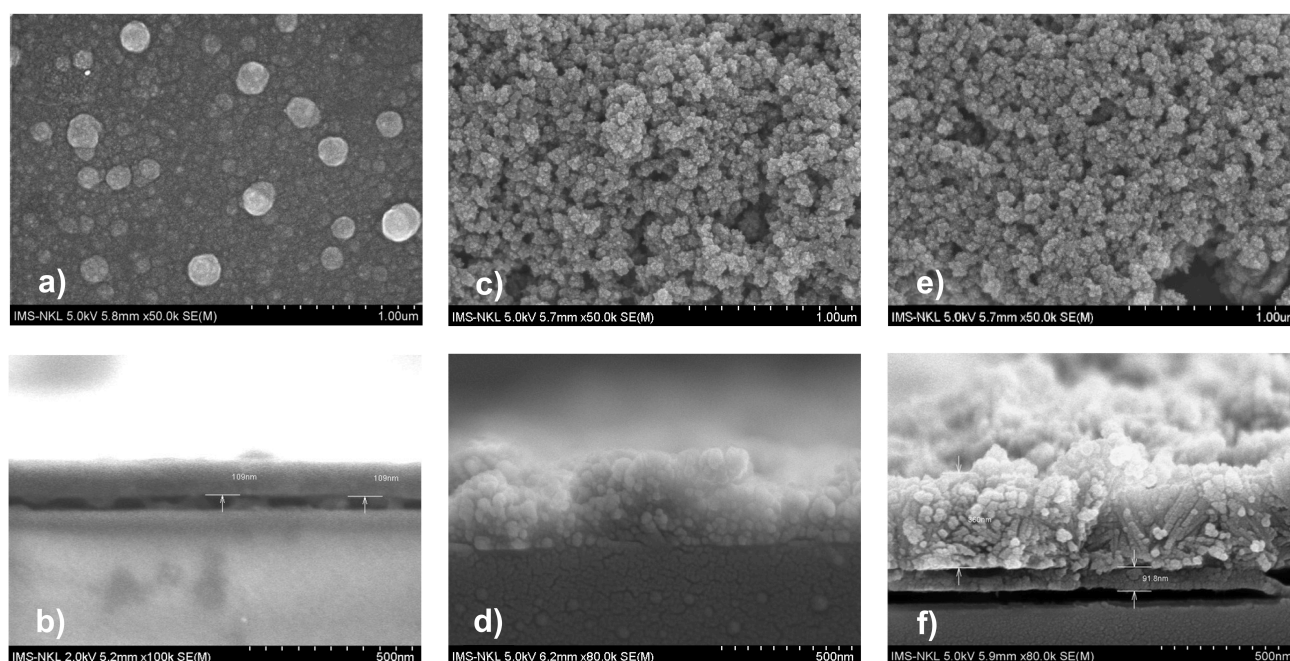


Figure 1. SEM images of (a) PPy thin-layer surface, (b) PPy layer cross-section, (c) TiO₂ layer surface, (d) TiO₂ cross-section, (e) PPy/TiO₂ heterostructure surface, and (f) PPy/TiO₂ heterostructure cross-section.

The XRD spectrum shown in Figure 2 confirms the predominance of the rutile phase in TiO₂ deposited from the reaction solution. The diffraction pattern exhibits all characteristic

peaks of rutile; notably, the most intense peak at $2\theta = 27.35^\circ$ corresponds to the (110) plane, while additional peaks at $2\theta = 36.14^\circ$, 41.30° , 54.32° , 56.48° , 63.59° , and 68.84° are assigned to the (101), (111), (211), (220), (002), and (301) planes, respectively (JCPDS No. 00-021-1276) [24]. The predominance of the rutile phase in the resulting deposition is attributed to the presence of additional HCl in the medium during pyrolysis of the precursor [24,25].

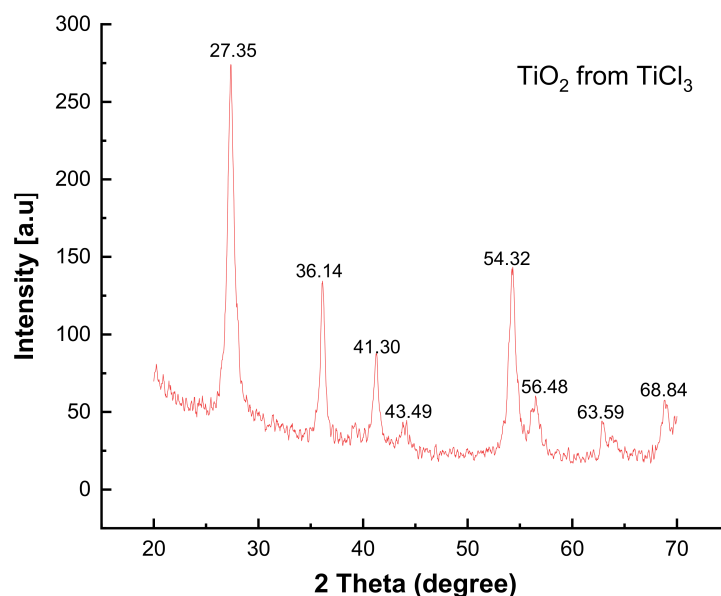


Figure 2. XRD spectrum of TiO_2 .

Raman profiles taken from the PPy and TiO_2 layers and PPy/ TiO_2 heterostructure show identical vibrational modes corresponding to PPy and TiO_2 as presented in Figure 3. The Raman spectrum of the TiO_2 layer exhibits three strong bands at 252 , 438 , and 608 cm^{-1} , consistent with the rutile phase, along with a weak band at 149 cm^{-1} indicating a minor trace of anatase [26,27]. The Raman spectrum of the PPy layer exhibits distinct vibrational modes at 1589 , 1348 , and 986 cm^{-1} , indicating that certain sites of the PPy chain remain in the benzoid form (reduced state). The vibrational mode at $938\text{--}945\text{ cm}^{-1}$ assigned to C–C ring deformation in the quinoid form, corresponds to oxidized sites of PPy (bipolaron) [28–31]. The bands at 1054 and 1086 cm^{-1} that appear in the PPy and PPy/ TiO_2 spectrum, are respectively assigned to the C–H in-plane deformation corresponding to the polaron and bipolaron state of PPy. In addition, coupling TiO_2 and PPy in the PPy/ TiO_2 heterostructure causes changes in relative intensity and a shift in the vibrational bands associated with each component. Regarding the PPy component in PPy/ TiO_2 , the vibrational modes of the C=C bond exhibit a blue shift from 1348 and 1589 cm^{-1} to 1338 and 1590 cm^{-1} respectively, indicating that PPy transitions toward a higher oxidized structure, i.e., the PPy component is partly oxidized as a result of coupling with TiO_2 .

UV–Vis absorbance spectra of PPy, TiO_2 , and the PPy/ TiO_2 heterostructure are depicted in Figure 4a. The TiO_2 layer shows a broadened absorption edge between 380 and 420 nm , reflecting contributions from the predominant rutile band and possible traces of transient rutile–anatase phases. Both UV–Vis spectra of PPy and PPy/ TiO_2 , spreading over the UV–Vis region, contain three broad bands centered around 415 nm , 476 nm , and 670 nm , which correspond to the typical absorption bands of PPy. The 415 nm absorption band represents the $\pi\text{--}\pi^*$ transition, while the 476 nm and 670 nm absorption bands correspond to allowed polaronic and bipolaronic transitions, respectively, characteristic of the oxidized state of the PPy component (Figure 4b) [32–34]. As seen from the spectra, when TiO_2 is introduced, the $\pi\text{--}\pi^*$ band (VB to CB) undergoes a slight shift from 415 to

417 nm, while the transition bands at 476 nm and 670 nm increases in intensity indicating an increase in polaron and bipolaron levels in the PPy bandgap, respectively. In addition to the conclusions derived from Raman analysis, the UV–Vis spectrum further corroborates that, upon coupling with TiO₂, the oxidative state of PPy is enhanced.

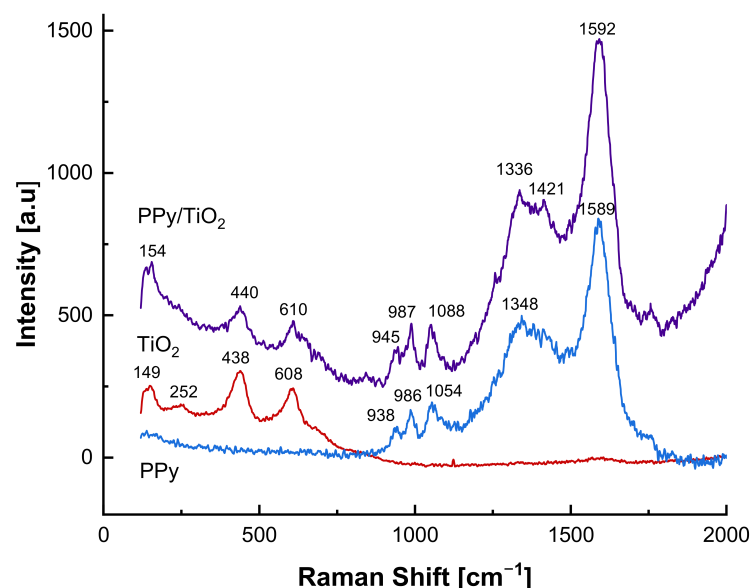
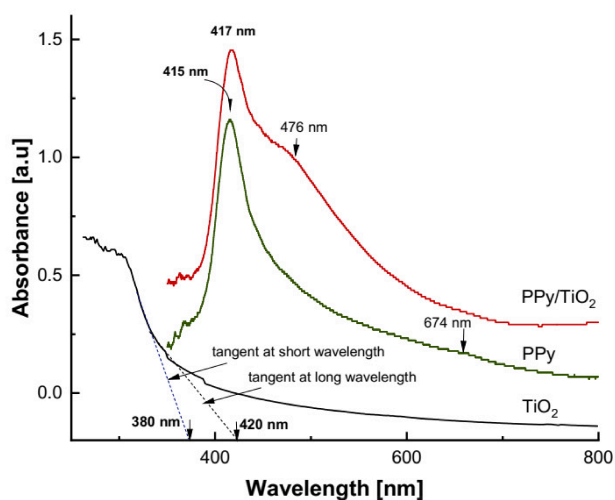
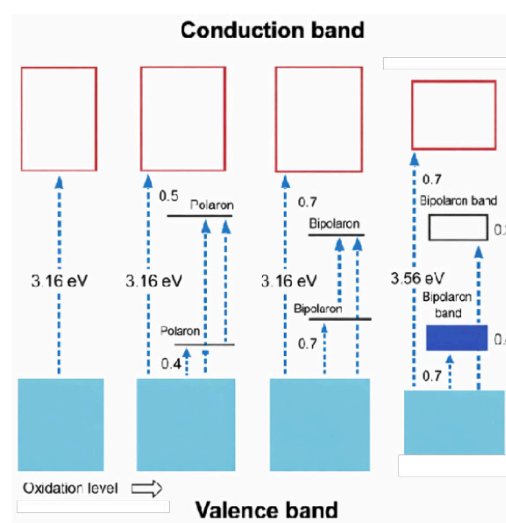


Figure 3. Raman profiles of TiO₂, PPy and PPy/TiO₂ heterostructure.



(a)



(b)

Figure 4. (a) UV–Vis absorbance spectra of TiO₂, PPy and PPy/TiO₂ heterostructure; (b) allowed transitions in PPy adsorption band [32,34].

Figure 5a,b illustrate the resistance response of the PPy and TiO₂ single layers to humidity, exhibiting opposite trends. As relative humidity rises from 60% to 100%, the resistance of the TiO₂ drops sharply by more than two orders of magnitude, from $\sim 10^9 \Omega$ to $\sim 5 \times 10^7 \Omega$. In contrast, under the same conditions, the resistance of PPy increases modestly by about 20–30%, from $\sim 35 \text{ k}\Omega$ to $\sim 40 \text{ k}\Omega$ —significantly smaller than the change observed in the TiO₂. These opposing resistance changes are attributed to electron transfer (donation) from hydroxyl (–OH) groups in adsorbed water molecules to TiO₂ and PPy, two materials distinguished by their distinct electronic structures. In TiO₂, an n-type semiconductor, electron donation enhances the majority carrier (electron) density, thereby lowering the resistance. In contrast, in the p-type PPy layer, electron donation reduces the majority

carrier (hole) concentration, leading to an increase in resistance. The rapid recovery in resistance in both TiO₂ and PPy to the baseline upon returning from 100% to 60% RH indicates that the interactions between hydroxyl (–OH) groups and these materials are reversible, namely that H₂O adsorption and desorption on the surfaces of TiO₂ and PPy are reversible processes. This reversibility suggests that at the equilibrium the adsorption bondings between hydroxyl (–OH) groups and TiO₂ and PPy are balanced with the thermal kinetic energy of molecules ($\sim kT$).

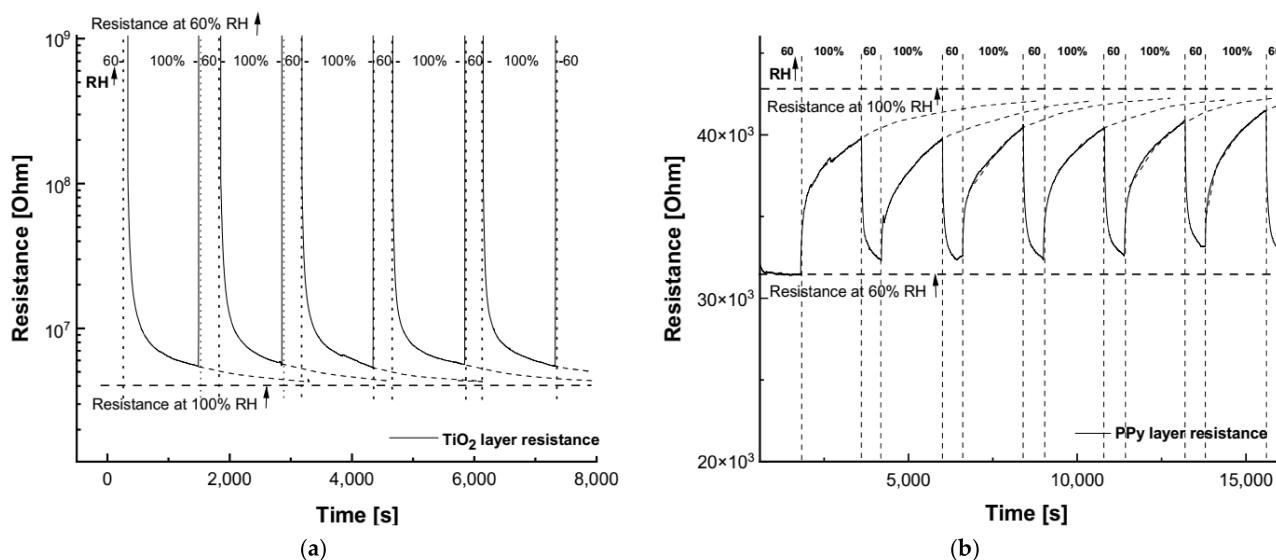


Figure 5. Resistance response of: (a) single-layer TiO₂, and (b) PPy under relative humidity (RH) conditions shifting between 60% and 100%. The dash lines indicate the separation of RH condition and resistance.

Upon irradiation with monochromatic light in 60 and 100% RH, the electrical resistances of TiO₂, PPy, and the PPy/TiO₂ heterostructure exhibit distinct and mixed light response modes. For PPy, the resistance decreases when the light is switched on and returns to its baseline value when the light is switched off, indicating a negative photoresponse. However, the magnitude of this response depends on both the excitation wavelength and the moisture level. The most intensive response is observed under 367 nm illumination and gradually diminishes at longer wavelengths. This behavior can be attributed to the wavelength dependence of allowed electronic transitions, as evidenced in the UV–Vis spectra. As the relative humidity increases from 60% to 100%, the response magnitude of the PPy layer reduces from approximately -0.16 ($\sim -16\%$) to -1.20 ($\sim -120\%$) under 367 nm illumination as shown in Figure 6a,b, representing an order-of-magnitude drop in resistance. This prompt resistance drop suggests an abnormal charge transfer, which is interpreted as an increase in the photocatalytic process of PPy, a reductive photocatalyst. For the TiO₂ layer, the resistance at 60% RH is extremely high, exceeding the instrument range, so the light response could not be measured. However, when the relative humidity increases from 60% to 100% RH, the resistance of the TiO₂ layer decreases sharply to around $5 \times 10^7 \Omega$ from an initially near-infinite value ($\sim 10^9 \Omega$), consistent with the observation in Figure 5a. At 100% RH, upon light exposure, the TiO₂ layer exhibits a wavelength-dependent transitional behavior with a response contracting to that of the PPy, as shown in Figure 6c. Under long-wavelength excitation (664 and 505 nm), the TiO₂ response simply increases when the light is on and decreases when the light is off. However, under short-wavelength excitation (447, 398, and 367 nm), the TiO₂ layer exhibits a transient response characterized by a brief decrease before increasing during on/off switching, with the most pronounced effect observed under 367 nm illumination. The transient response is attributed to fluctuations

in charge transfer arising from photoinduced process within the TiO_2 layer. On the other hand, the PPy/ TiO_2 heterostructure (Figure 6d) exhibits the resistance characteristics of TiO_2 , but the light response combines features of both components, showing a wavelength- and cycle-dependent behavior. Like the TiO_2 single layer, its resistance decreases sharply from an initially extremely high value as the relative humidity increases from 60% to 100% RH. Under long-wavelength light at 664 nm, the heterostructure response resembles that of the PPy, characterized by a simple decrease and an increase respectively following the light on and off. Under shorter-wavelength excitation (505, 447, 398, and 367 nm), the heterostructure exhibits a transient response during the initial on/off cycles before stabilizing into TiO_2 -like behavior with increasing magnitude. For example, after four cycles under 447 nm illumination, the heterostructure's response increases from 0.4 to 1.83, exceeding the TiO_2 response of 1.14 by approximately 50% (Figure 6c,d). This behavior can be attributed to photoinduced charge-transfer processes within the PPy/ TiO_2 heterostructure, occurring both in the individual TiO_2 and PPy components and across the p–n junction.

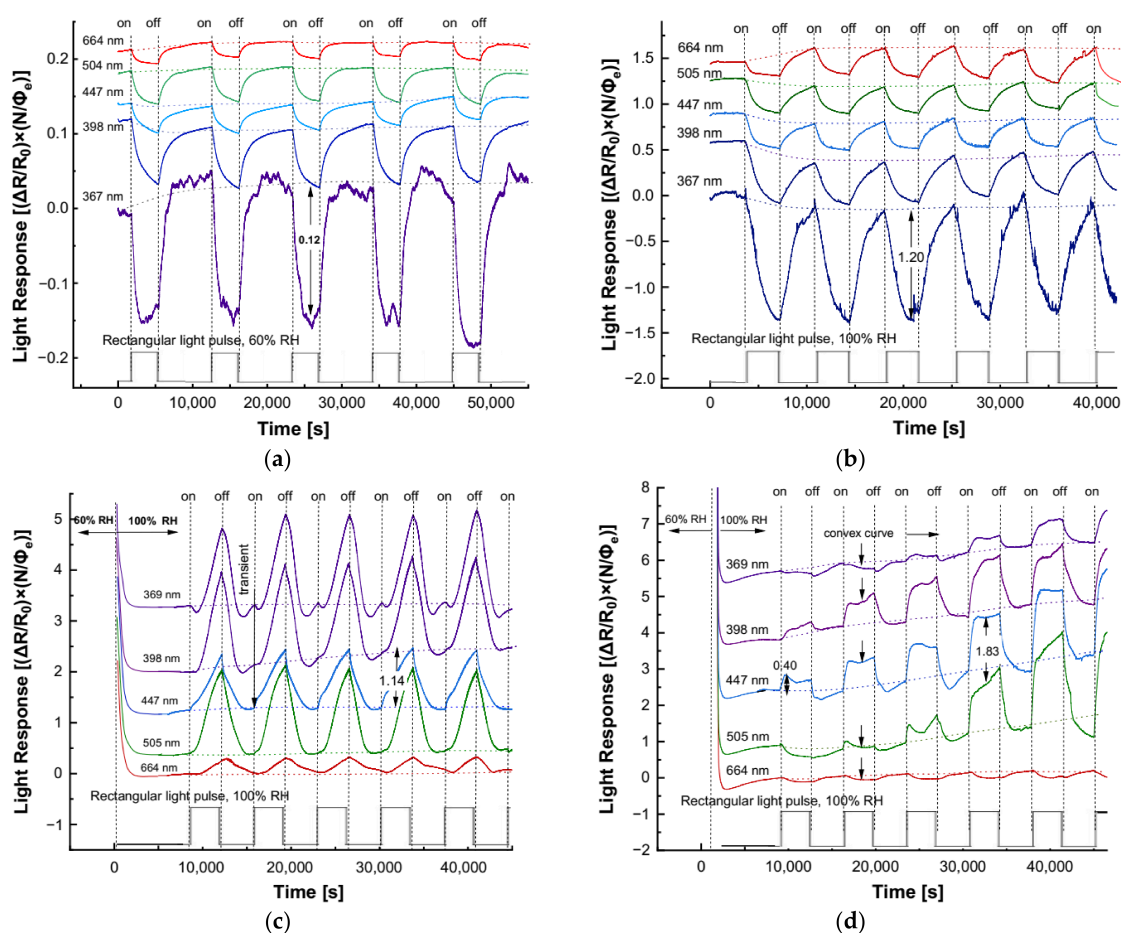


Figure 6. (a) Light response of PPy layer under 60% RH; (b) PPy layer under 100% RH; (c) TiO_2 layer under 100% RH; and (d) PPy/ TiO_2 heterostructure under 100% RH. The colored dashed lines along the response curves represent the baseline of the material's resistance.

The changes in resistance of PPy, TiO_2 , and the PPy/ TiO_2 heterostructure under moisture and light exposure can be attributed to photoelectrochemical processes involving charge exchange and transfer within the materials. As individual components, the PPy and TiO_2 exhibit intrinsic conductivity characteristics of p-type and n-type semiconductors, respectively, and their conductance is further modified by agents or processes that function as secondary dopants. For instance, oxidative or reductive species in the surrounding environment, such as O_2 and H_2O , can share or transfer electrons with the conduction and

valence bands of PPy and TiO_2 , thereby influencing their conductance. The physical adsorption of oxidative or reductive gases or moisture available in ambient air affects the PPy conductance, which enables the development of various gas and humidity sensors [35–37].

With respect to moisture interaction, H_2O molecules (via hydroxyl $-\text{OH}$ groups) tend to share a portion of electrons during adsorption and desorption, respectively, thereby modulating the conductance of p-type PPy and n-type TiO_2 in opposite directions. In macroscale, these modulations exhibit a change in overall conductance/resistance of the layers. A proposed mechanism of charge exchange within the individual PPy and TiO_2 layers during H_2O sorption and desorption, together with their corresponding longitudinal resistances illustrated in Figure 7a,b, provides a coherent explanation for the resistance responses observed in Figures 5 and 6. By partially sharing electrons with TiO_2 and PPy through physical bonding, likely via dipole–dipole interactions, the absorbed H_2O molecules increase the majority carrier (electron) density in the n-type TiO_2 layer while reducing the majority carrier (hole) density in the p-type PPy layer, thereby enhancing the conductance of TiO_2 and decreasing that of PPy. Because the physical bonding is weak and reversible, the photoinduced removal of moisture leads to H_2O desorption, which reverses the process and consequently restores the conductance of both PPy and TiO_2 to their original values.

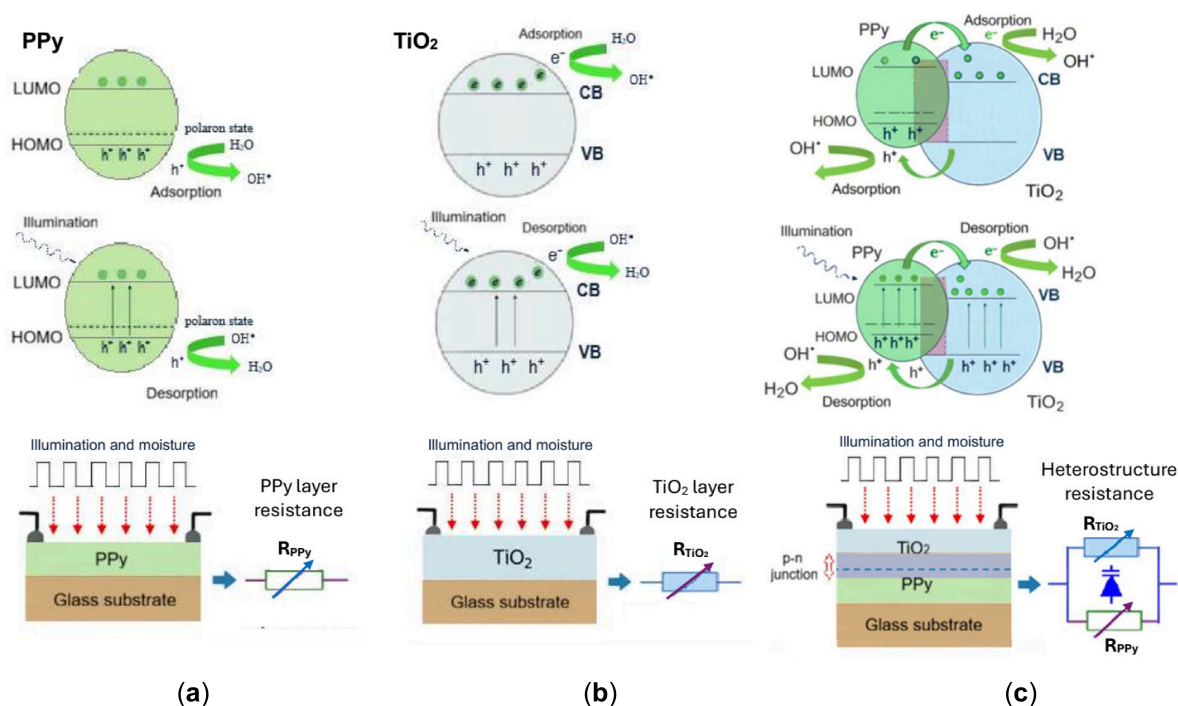


Figure 7. Schematic illustration of charge exchange processes in PPy (a), TiO_2 (b), and PPy/ TiO_2 heterostructure (c) upon exposure to illumination and moisture, along with their equivalent longitudinal resistances.

Upon exposure to excitation light, the photoinduced modifications in PPy, TiO_2 , and the heterostructure exhibit a common pattern synchronized with light on/off switching but differ significantly in the mode and magnitude depending to light wavelength, giving rise to a mixed photoresponse. In PPy, the overlap between the absorption band of the PPy layer (Figure 4) and the emission spectra of the monochromatic LEDs (Figure 8) facilitates electron transitions from the valence band into polaron and bipolaron states, thereby simply increasing hole density and enhancing the electrical conductance of the PPy layer. In terms of photocatalysis, photoexcited PPy can function as a reductive photocatalyst, donating electrons to oxygen in ambient air and thereby increasing its majority carrier. On the other

hand, illumination is also assumed to induce the photodesorption of physisorbed H_2O molecules (with weak bonding strength on the order of thermal energy, $\sim kT$) from the PPy surface; the removal of these electron-donating adsorbates elevates the hole concentration in p-type PPy, further augmenting its conductance. The fast response in the PPy resistance observed in Figure 6 is attributed to the combined effects of the rate of allowed electronic transitions, photocatalysis, and photoinduced desorption within the PPy layer.

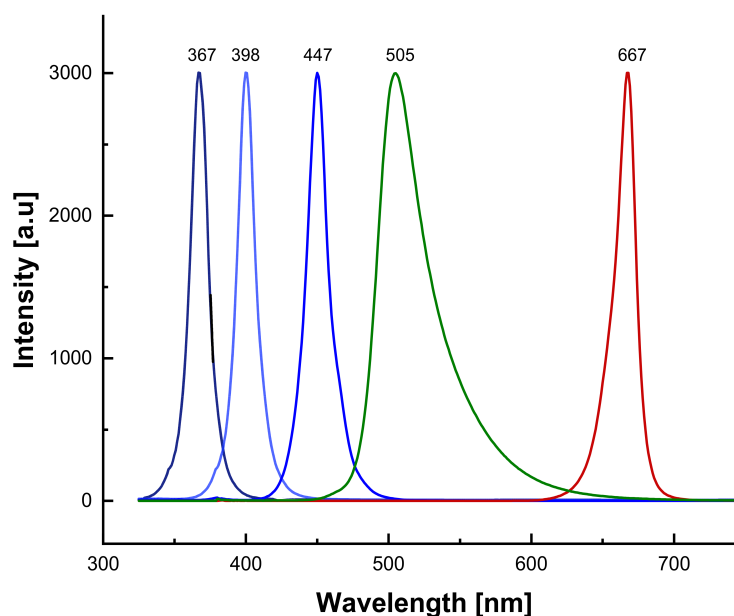


Figure 8. Spectral profiles of monochromatic LED sources used for illumination.

In the TiO_2 layer, illumination can induce both the photodesorption of absorbed moisture, like the process observed in the PPy layer, and the photogeneration of charge carriers, with the rate depending on the wavelength. Among the monochromatic LEDs employed in this study (Figure 9), the spectra of the 367, 398, and 447 nm LEDs lie fully or partially below the optical absorption edge of TiO_2 (Figure 4), thereby enabling excitation of electrons from the valence band to the conduction band and generating electron–hole pairs within the TiO_2 layer. Consequently, upon exposure to illumination, TiO_2 generally exhibits a positive photoresponse, with mixed transient features under short-wavelength excitation, as shown in Figure 6c. The transient feature observed at the onset of illumination then reflects the competition between electron generation by photoexcitation and electron removal through photoinduced desorption of H_2O from the TiO_2 surface, whereas the delayed hysteresis following light-off corresponds to enhanced reabsorption of H_2O beyond the baseline level, likely attributable to photoinduced superhydrophilicity of the TiO_2 surface.

When PPy and TiO_2 layers are combined, the couple typically forms a p–n heterojunction, where a depletion region and an internal electric field are established because of diffusion and neutralization of opposite charge carriers across the junction. A proposed mechanism of photoelectrochemical processes in the PPy/ TiO_2 heterostructure, together with a simplified sketch of the corresponding longitudinal resistance, is presented in Figure 7c. The depletion region behaves like a capacitor [38], with its capacitance determined by the contact area, depletion width, and dielectric constant of the material, where PPy is polarized as the positive electrode and TiO_2 as the negative electrode. Since the depletion region extends into both sides, with its width in each component inversely proportional to the carrier density and directly proportional to the dielectric constant ($\epsilon \approx 2\text{--}5$ for PPy, $\epsilon \approx 80\text{--}240$ for TiO_2), it preferentially penetrates more deeply into TiO_2 than into PPy. Upon exposure to illumination and moisture, the resistance/conductance

of PPy and TiO₂ changes in opposite directions, as does their carrier density. An increase in carrier density within TiO₂ is accompanied by a decrease in carrier density within PPy, and vice versa. As a result, the depletion width on the TiO₂ side is further reduced by the “pull” effect from the PPy side, while the depletion width on the PPy side expands more significantly due to the “push” effect from TiO₂. This complementary behavior underlies the “push–pull” concept applied to this heterostructure. Although the individual components respond in opposite ways, their coupling—enabled by modulation of the depletion layer—amplifies the overall response of the PPy/TiO₂ heterostructure, producing a synergistic transfer. Consequently, the heterostructure’s response reflects the combined photoinduced processes occurring in the PPy and TiO₂ components, along with electronic modulations at the junction, resulting in a complex wavelength- and cycle-dependent behavior (Figure 6d). Modulation of the depletion width alters the resistance of the PPy and TiO₂ layers as well as the junction capacitance, effectively functioning as variable resistors and varicap diode, as denoted in Figure 7c. As moisture rises from 60% to 100% RH, the heterostructure displays a humidity response closely resembling that of the TiO₂ layer as shown in Figure 6c, a behavior attributable to the dominant contribution of TiO₂ arising from its greater thickness and its upper position within the heterostructure. Under 664 nm illumination at 100% RH moisture, the light response of the heterostructure is negative, consistent with the mode of the PPy (Figure 6b). Since 664 nm lies well below the optical absorption edge of TiO₂, photoexcitation occurs in the PPy layer and is negligible in the TiO₂, making the response primarily governed by the PPy. In the short-wavelength range of illumination (447, 398, and 367 nm), the gradual shift from negative to positive response mode, together with the intensification of response magnitude, indicates a synergistic transfer from PPy to TiO₂ within the heterostructure, similar to that observed in the PANi/TiO₂ heterostructure [39,40]. The transient response remains observable under 505 nm illumination, indirectly suggesting that the PPy/TiO₂ coupling enables the extension of photoinduced processes within the heterostructure into the visible region. In summary, the interaction of opposite responses from both components, together with the inverse modulation of the depletion width relative to carrier density, operates analogously to a “push–pull amplifier,” leading to a synergistic enhancement of both the photoresponse and humidity response in the heterostructure.

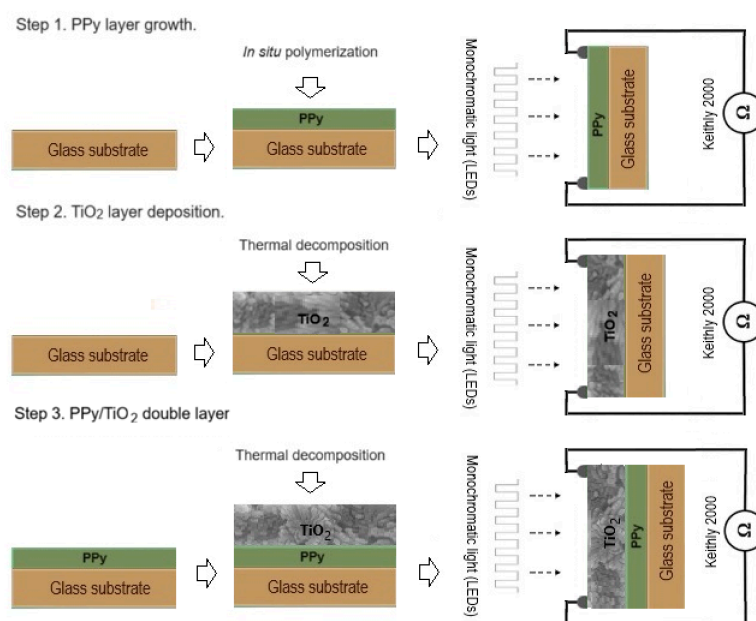


Figure 9. Schematic representation of the experimental procedure used to fabricate PPy, TiO₂, and PPy/TiO₂ heterostructure and to determine their light response.

3. Experimental Section

TiO₂ and PPy layers were synthesized by chemical methods following routine procedures [38,41]. TiO₂ was prepared via thermal decomposition of a TiCl₃ precursor (Aldrich Corp., Milwaukee, WI, USA), while PPy was synthesized by oxidation of pyrrole (Py, 99.5%, Aldrich Corp., Milwaukee, WI, USA) using ammonium persulfate (APS, Kanto Chemical Co., Inc., Tokyo, Japan) as the oxidant. The test samples were fabricated as thin layers on glass substrates, as described below:

PPy Layer: Synthesized by oxidation of pyrrole (Py, 99.5%, Aldrich Corp., Milwaukee, WI, USA) using ammonium persulfate (APS). A glass plate was immersed in an acidic solution of 0.1 M HCl and 0.1 M pyrrole. A 0.1 M APS solution was added dropwise, initiating pyrrole oxidation and deposition onto the plate surface.

TiO₂ Layer: Prepared via thermal decomposition of a TiCl₃ precursor (Aldrich Corp., Milwaukee, WI, USA). A glass plate was dipped into a solution of 40 mM TiCl₃ and heated to 80 °C to initiate pyrolysis, resulting in TiO₂ deposition on the plate surface. After 2 h, the plate was washed, rinsed, and dried.

Heterostructure: PPy/TiO₂ heterostructure were made by combining the two procedures sequentially on the same glass plate.

Samples used for photoresponse testing were cut from material layers deposited on glass substrates. Silver electrodes were fabricated by silk-screen printing and connected to wires via spring-finger contacts.

Morphology and cross-sectional features of the layers were characterized using field-emission scanning electron microscopy (FESEM, Hitachi S-4800, Hitachi High-Tech Corp., Tokyo, Japan). The crystalline structure of TiO₂ deposited from solution was determined by X-ray diffraction (XRD, D8 Advance Bruker diffractometer, Billerica, MA, USA) employing Cu K α radiation ($\lambda = 0.154$ nm). The chemical and electronic structures were analyzed by Raman spectroscopy (Cary, Arlington, TX, USA) with 514 nm laser excitation, and UV-Vis absorbance spectroscopy (V-750, JASCO, Tokyo, Japan). Illumination was conducted using monochromatic LEDs at 367, 398, 447, 505, and 667 nm. Their spectral profiles and optical characteristics were determined with a RadOMA GS-1220 spectroradiometer (Gamma Scientific, San Diego, CA, USA) and are presented in Figure 8 and Table 1, respectively. In a closed, air-conditioned room maintained at 25 °C, the relative humidity was measured at 60% and remained stable throughout the experiment; this value was therefore chosen as a reference parameter. A relative humidity of 100%, representing saturated moisture conditions, was established based on thermodynamic vapor–liquid equilibrium over the liquid surface. Accordingly, a sealed glass chamber with a wetted cloth at the bottom generated an atmosphere saturated with moisture, corresponding to 100% RH at 25 °C. This condition was used as a principal parameter to evaluate the effect of moisture on the photoresponse of the test sample under light exposure.

Table 1. Spectral characteristics of monochromatic LEDs used for illumination.

LED Wavelength (nm)	Radiation Flux Φ_e (mW)	Half Width HW (nm)	Photon Energy $h\nu$ (1.6×10^{-19} J)	Photon Flux $\Phi_p = \Phi_e/h\nu$ ($\times 10^{16}$)
664	454.39	14.5	1.87	151.87
505	805.1	39.6	2.46	204.55
447	863.7	14.8	2.77	194.88
398	534.4	14.4	3.12	107.05
367	192.6	14.2	3.38	35.61

The overall experimental procedure used to make PPy, TiO₂ and the PPy/TiO₂ heterostructure and determine their responses are shown in Figure 9. Electrical resistance

was measured under ambient air conditions at 25 °C and relative humidity (RH) levels of approximately 60% and 100% using a programmable Keithley 2000 digital multimeter (Keithley Instruments, Cleveland, OH, USA). The excitation light was, in rectangular form, consecutively switched on/off alternatively in rectangular pulses with 3600 s duration. The photoresponse of the layers was normalized to the incident photon flux (Φ_e) listed in Table 1 and expressed as $(\Delta R/R_0) \times (N/\Phi_e)$. This formulation represents the relative change in resistance per photon within the incident flux, where positive values denote an increase and negative values denote a decrease. Here, $\Delta R = R - R_0$, with R_0 defined as the initial resistance at the onset of illumination and R the resistance measured under illumination. N is a constant normalization factor, set to 1.6×10^{16} in this study.

4. Conclusions

Upon exposure to moisture, the resistance of n-type TiO₂ decreases rapidly, whereas that of p-type PPy increases more gradually, and both processes are reversible. This inverse behavior results from electron exchange with hydroxyl (–OH) groups, which modify the majority carriers differently in PPy and TiO₂.

Under light excitation, the PPy layer exhibits a decrease in resistance, whereas TiO₂ shows an opposite tendency toward increased resistance. This contrasting behavior can be attributed to the combined effects of photogenerated carriers and photoinduced removal of moisture (H₂O photoinduced desorption). The PPy response demonstrates a straightforward wavelength dependence, as all excitation wavelengths employed lie below its optical band edge. In contrast, TiO₂ displays a brief transient response at shorter wavelengths, arising from the competition between excess charge carrier photogeneration near the optical band edge and charge-carrier elimination through H₂O photoinduced desorption. A combination of illumination and moisture exposure results in an intensified photoresponse of TiO₂, thereby enhancing its humidity response.

In the PPy/TiO₂ heterostructure, coupling between the p-type PPy and n-type TiO₂ layers establishes a p–n junction with a depletion region that is dynamically modulated by variations in carrier density within its components. Exposure to light and moisture alters the charge carrier in both the PPy and TiO₂ layer, leading to an inversely expanding depletion region relative to their majority carrier density. Under 664 nm excitation, the heterostructure response is dominated by PPy, reflecting in a negative mode. At shorter wavelengths, the heterostructure response undergoes a gradual shift from negative to positive mode, accompanied by an intensification of response magnitude, indicating a synergistic transfer from PPy to the TiO₂ component. The interplay between the contrasting photoinduced carrier generation, photodesorption and the modulation of the depletion region, occurring in inverse phase with carrier density, enhances the photoresponse of the PPy/TiO₂ heterostructure. This complementary “push–pull” interaction produces a synergistic effect, improving both the photoresponse and the humidity sensitivity of the heterostructure.

Author Contributions: H.D.N.: methodology, funding acquisition, conceptualization, supervision, writing—original draft, review, and editing; T.N.T.: software, investigation, visualization, validation; T.H.T.: investigation, visualization, validation; T.L.V.: supervision, data curation, review, and editing. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The raw data supporting the conclusions of this article will be made available by the authors on request.

Acknowledgments: The work is continued thanks to the basic research grant from Industrial University of Ho Chi Minh City (IUH).

Conflicts of Interest: The authors declare no conflict of interest.

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