Scalable-Production, Self-Powered TiO₂ Nanowell–Organic Hybrid UV Photodetectors with Tunable Performances

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Supporting Information

ABSTRACT: Hybrid inorganic–organic photoelectric devices draw considerable attention because of their unique features by combining the tunable functionality of organic molecules and the superior intrinsic carrier mobilities of inorganic semiconductors. An ordered thin layer of TiO₂ nanowells is formed in situ with shallow nanoconcave patterns without cracking with scalable production by a facile and economic strategy, and these layers are used as building blocks to construct hybrid UV photodetectors (PDs). Organic conducting polymers (polyaniline (PANI) with various morphologies) have been exploited as p-type materials, enabling tunable photodetection performances at zero bias. The thin layer of n-type TiO₂ nanowells is favorable for electron transport and light absorption with respect to their conventional nanotubular counterparts, while PANI acts as a hopping state or bridge to largely enhance the transition probability of the valence electrons in TiO₂ to its conduction band, resulting in an increase in photocurrent in a self-powered mode. In particular, the lowest polyaniline loading sample (TP1) exhibits the highest responsivity (3.6 mA·W⁻¹), largest on–off switching ratio (≈10³), excellent wavelength selectivity, fast response speed (3.8/30.7 ms), and good stability under 320 nm light illumination (0.56 mW·cm⁻²) without an external energy supply. This work might be of great value in developing tunable UV photoresponse materials with respect to low cost and a large area for future energy-efficient optoelectronic devices.

KEYWORDS: self-powered photodetectors, polyaniline, TiO₂, inorganic–organic, fast response

1. INTRODUCTION

To meet the great demand in a large variety of applications, including optical communications, biological and chemical sensing, imaging, and optoelectronic circuits, self-powered UV photodetectors (PDs), without consuming an external energy supply, are attracting much attention nowadays. Great efforts in fabricating self-powered devices have been demonstrated the potential to build independent, sustainable, and zero-maintenance nanosystems through the construction of p–n junctions, Schottky junctions, and heterojunctions due to the efficient separation ability of photogenerated electron–hole pairs by the photovoltaic effect. Unfortunately, it is still costly and sophisticated to fabricate highly crystalline junctions and thus not suitable for practical large-scale devices. Therefore, it would be greatly advantageous to explore novel junction configurations of self-powered PDs via a simple and low-cost strategy with high detecting performance.

Junctions between p-type and n-type semiconductor materials have built-in potential difference that acts as a driving force to direct the movement of photogenerated electrons and holes. To date, various inorganic semiconductor nanomaterials, such as TiO₂, ZnO, SnO₂, Nb₂O₅, and GaN, have been extensively studied as p-type semiconductors during the past decade in low-cost heterojunctions for UV and visible photodetection. In particular, TiO₂ has been extensively studied as an important n-type semiconductor in visible-blind UV light sensors owing to its distinct UV absorption characteristics with a wide bandgap. Anatase TiO₂ films are proven to exhibit wider bandgaps (~3.2 eV), larger electron mobility, and lower defect concentration at the film surface, which is promising for UV detectors. Among numerous synthetic strategies, anodization represents the most elegant and versatile solution-based approach to growing one-dimensional TiO₂ nanotubes (NTs) in an entirely self-organized manner at a large scale. Owing to their good biocompatibility, high stability, abundant availability, and superior performance, e.g., excellent light-trapping, large specific surface area, well-defined charge-carrier transport pathway and so on, anatase TiO₂ NTs attracted considerable interest in optoelectronic devices. For example, with a large surface area, TiO₂ NT-based PDs were found to demonstrate a high responsivity of 13 A·W⁻¹ at a 2.5 V bias.

Because p-type oxide semiconductors are rare, full oxide p–n junction photodetectors are hard to achieve. One promising solution is to adopt organic semiconducting polymers with p-type conductivity to construct hybrid inorganic and organic heterojunction devices. The emergence of organic conducting polymers for photovoltaic devices has opened a new area in designing new materials for energy conversion,
owing to their unique properties that conventional inorganic materials do not possess, such as ease of processing, large device area, low cost, and high flexibility. In particular, polyaniline (PANI) is a well-studied p-type conducting polymer that is desirable for hole collection and transport layer in p–n junction configuration. For instance, Wu J. et al. accomplished a highly efficient p–n heterojunction diode composed of p-type PANI microrods and n-type ZnO nanowires by a controlled electrochemical deposition method. Deng Y. et al. demonstrated a sandwich-structured UV PD based on one layer of PANI nanowires and two layers of n-type ZnO nanorods with high photocurrent (∼1.4 × 10⁻³ A) and photosensitivity (∼10⁵) at zero bias. Yang S. et al. reported that the PANI functionalized MnO₂ nanocomposite-based PD exhibited a reversible and highly efficient photoresponse. These studies suggested that the p-type conducting PANI can function synergistically in the detection of optical signals in the inorganic–organic heterojunction devices.

Herein, we report the development and application of novel heterojunctions consisting of n-type TiO₂ nanowells and p-type PANI with tunable morphologies in PD devices. An array of ordered TiO₂ nanowells is used as the pathway for electron transport and light-scattering structure, while p-type PANI nanostructures act as the hole transport layer. The results demonstrate that the incorporation of PANI into TiO₂ system successfully realizes highly efficient self-powered PDs with high on-off switching ratios, excellent wavelength dependence, fast photoresponse speed, and good stability. Moreover, the photocurrent and responsivity greatly decrease with the increasing amount of PANI, owing to the dramatically reduced effective junction area under irradiation between TiO₂ and PANI together with the decreased active sites of TiO₂. The innovative strategy of constructing TiO₂-based p–n junction configuration with scalable production into optoelectronic devices might envisage a strong impact in future energy-efficient optoelectronic applications.

2. METHODS

Preparation of Anatase TiO₂ Nanowells. The Ti foils (99.7% purity, 0.25 mm thick, Sigma-Aldrich) were ultrasonically cleaned in acetone, ethanol, and deionized water successively and then dried in a desiccator at room temperature. The Ti foils were anodized at 45 V for 7.5 h in the electrolyte containing 0.35 wt % NH₄F (85% lactic acid) and 10 vol % DMSO (dimethyl sulfoxide, ≥99%, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) with a Keithley 2450 Sourcemeter. To obtain the anatase TiO₂ nanowells, the as-anodized film was ultrasonicated in water to remove the nanotube layer and surface debris, leaving an ordered concave pattern (namely, nanowells on the substrate). To increase the crystallinity of TiO₂, the as-exposed nanowell substrate was thermally treated at 450 °C in air for 2 h at a rate of 3 °C/min.

Synthesis of TiO₂−PANI Hybrids. The detailed fabrication process is illustrated in Scheme 1. The polymerization was carried out in an ice-water bath at a temperature of 10 and −5 °C, respectively, to yield TiO₂−PANI hybrids with different PANI loading (denoted as TP1 and TP2, respectively). At 10 °C, anatase TiO₂ nanowell substrate was immersed into a 1 M H₂SO₄ (20 mL) aqueous solution containing aniline monomer (ANI, 27.39 μL) and stirred for 10 min to ensure complete dispersion of the ANI onto the TiO₂ nanowells. Then, another 20 mL of 1 M H₂SO₄ aqueous solution containing ammonium persulfate (APS, 68.48 mg) was rapidly added, and the mixture was stirred for 30 s. The molar ratio of ANI to APS was 1:1. After 24 h of reaction, the TiO₂−PANI hybrid (TP1) was taken out and washed with deionized water for several times. Sample TP2 was fabricated under similar conditions but at a temperature of −5 °C. To study the extreme case (the most loading amount of PANI), sample TP3 was prepared by performing in situ polymerization at −5 °C twice (i.e., we used TP2 as the substrate and immersed it in ANI monomer acid solution), and then APS acid solution was added to react for another 24 h. Finally, the substrate was washed with distilled water and ethanol, respectively, and dried at 60 °C for 6 h to produce TiO₂−PANI hybrids (TP3).

Characterizations. Sample morphologies were characterized using field-emission scanning electron microscopy (FESEM, Zeiss Sigma). X-ray diffraction (XRD) patterns were collected on a Bruker D8-A25 diffractometer using Cu Kα radiation (λ = 1.5405 Å). Raman spectroscopy (Horiba Jobin Yvon XploRA, France) with a 532 nm Nd:YAG laser was employed to verify chemical bonding characteristics. The optical properties were investigated by optical diffuse absorption spectra using a UV–vis spectrophotometer (Hitachi U-3900H) with an integrating sphere attachment.

Photoelectric Measurements. To construct a detector device, small amounts of silver paste with areas of ∼0.005 cm² were dropped onto the sample as electrodes. The irradiated sample area is estimated to be ∼0.8 mm². The photoelectric performance was analyzed with an Xe lamp, monochromator, and a program-controlled semiconductor characterization system (Keithley 4200). The light intensity was measured with a NOVA II power meter (OPHIR photonics). The temporal response of the photodetector was measured by a Nd:YAG 355 nm pulsed laser (Continuum Electro-Optics, MINILITE II) with pulse width of 3−5 ns and an oscilloscope (Tektronix DPO S140B).
All of the measurements were performed at room temperature under ambient conditions.

3. RESULTS AND DISCUSSION

Figure 1 reveals the typical scanning electron microscopy (SEM) images of different TiO$_2$-based nanostructures. Self-ordered one-dimensional TiO$_2$ NT arrays are obtained as shown in Figure 1a with outer tube diameters ranging from 160 to 250 nm. The inset indicates that all the nanotubes are vertically aligned on the Ti substrate with a film length of $\sim 2.5 \mu$m. Figure 1b shows that the TiO$_2$ nanowells exhibit two-dimensional periodicity in a large scale without cracking, which are formed in situ with shallow nanoconcave patterns in the Ti substrate. The average diameters are found to be $\sim 200$ nm, the same as the top tube’s diameters. The thin layer of TiO$_2$ nanowells ($\sim 150$ nm thick; Figure S1a) ensures a shorter diffusion path in contrast to TiO$_2$ NTs counterparts$^{36}$ but maintains the self-ordered features with large area. Moreover, it is worth noticing that the scale of the nanoconcaved structural basis can be readily adjusted by the size of Ti starting material for anodization, which guarantees its feasibility for scale-up in large area PD devices via a facile and low-cost route. Figure 1c,d presents the structural morphology of sample TP1 with the lowest loading of PANI. Small PANI nanofibers with diameters ranging from 30 to 65 nm are randomly grown on top surface of TiO$_2$ nanowells. Note that the biggest part of the TiO$_2$ layer
is exposed to the environment, which is favorable for UV light harvest by TiO$_2$. 

Figure 2a shows that a continuous film of PANI forms on top with the same porous morphology as the beneath TiO$_2$ nanowells for sample TP2 (i.e., the PANI film mostly covers the edges of each TiO$_2$ nanowell), leaving the bottom of the nanowell exposed to the environment, which is favorable for light absorption by TiO$_2$ nanowells. The thickness of the thin layer PANI is approximately 25 nm (inset in Figure S1b). At the extreme case for sample TP3, uniform small PANI nanoclusters film are found to fully cover the TiO$_2$ underlayer. The layer thickness of PANI in TP3 is approximately 350 nm, as revealed by the cross-sectional SEM image in Figure S1c,d. Therefore, sample TP1 has the largest part of TiO$_2$ layer exposed to the environment with respect to samples TP2 and TP3, which takes most advantages of UV light absorption by TiO$_2$ and is promising for the photoresponse properties.

XRD patterns were studied to examine the structural features of TiO$_2$ nanowells and three TiO$_2$–PANI hybrids (Figure 3a).

![Figure 3](image-url) 

**Figure 3.** (a) XRD patterns and (b) Raman spectra of pristine TiO$_2$ nanowells and samples TP1–TP3. The inset in (b) shows the Raman spectrum of TiO$_2$ nanowells in the 100–1000 cm$^{-1}$ region.

A major peak centered at 25.3°, assigned to the (101) facet of anatase TiO$_2$ (JCPDS card no. 21-1272), can be observed for TiO$_2$ and TiO$_2$–PANI hybrids. Other peaks agreed well with Ti metal (JCPDS no. 44-1294) are so strong and sharp that the signals for PANI species (Figure S2) in the TiO$_2$–PANI hybrids are undetectable. Raman spectroscopy was performed to further examine the existense of PANI in the three hybrids. As shown in Figure 3b, all the three samples (TP1–TP3) exhibit the same pattern in the 1000–2000 cm$^{-1}$ region, while no obvious peaks for TiO$_2$ nanowells can be observed, revealing the successful incorpration of PANI species into the TiO$_2$–PANI hybrids. The characteristic peaks located at 1164, 1236, 1337, 1507, and 1594 cm$^{-1}$ for samples TP1–TP3 can be attributed to the C−H bending of the quinoid ring, the C−N vibration of the benzene diame units, the C=N vibration of the quinoid nanoprotonated diimine units, the C=C vibration of the quinoid rings, and the C−C stretching of the benzoid ring, respectively, owing to the presence of PANI. The inset in Figure 3b shows the Raman spectrum for TiO$_2$ nanowells in the 100–1000 cm$^{-1}$ region and the three characteristic peaks, ascribed to O−Ti−O symmetric deformation vibration and Ti−O stretching vibration, further confirming the anatase phase of TiO$_2$ and consistent with the XRD data in Figure 3a.

The optical properties are determined by UV−vis diffuse absorption spectra as shown in Figure 4. Interestingly, all of the samples exhibit strong light absorption in the visible range (400–700 nm) due to their selective light absorption of the photonic bandgaps (periodicity of nanoconcaved patterns in the Ti surface), leading to colorful sample appearances, and could be possibly useful in preparing photonic crystal materials. Samples TP1–TP3 exhibit distinctly different colors: purple, blue, and dark green, respectively, with increasing amount of PANI. For TP1, no obvious color change can be readily observed by the naked eye, and no additional peaks assigned to PANI are detected. Therefore, it has the same absorption characteristics as those of bare TiO$_2$ nanowells but with dramatically increasing light absorption intensity within UV range (200–400 nm), which suggests enhanced generation of electron−hole pairs after the introduction of PANI into TiO$_2$. The absorption intensities increase slightly for TP2 when the amount of PANI increases compared to that of TP1. A new peak centered at 215 nm emerges that can be assigned to the $\pi$−$\pi^*$ transition of the benzoid rings of PANI. Interestingly, the spectrum pattern of sample TP3 is different from those of TP1 and TP2 but similar to that of pure PANI sample, as displayed in the inset of Figure 4. The absorption peaks located at 223, 354, and 444 nm is attributed to the $\pi$−$\pi^*$ transition, the polaron band to the $\pi^*$ transition, and $\pi$ to the localized polaron band of PANI, respectively. These bands indicate that the PANI is in their conducting form (i.e., the emeraldine salt form of PANI, consistent with the dark-green appearance of TP3). However, the high absorption intensities of both TP2 and TP3 are induced by the upper thicker layer of PANI instead of TiO$_2$, as most of the portion of the light is absorbed by the continuous PANI film on top, and this nontransparent layer (≈350 nm thick) blocks the light to some extent; thus, only a very small portion of light can reach beneath the TiO$_2$ (SEM images are shown in Figure 2).

The photoelectrical and UV detection properties as photo-detector devices were carefully examined under ambient conditions and monochromatic illumination based on TiO$_2$–PANI hybrids. To construct the device, small silver pads were dropped onto the sample and directly used as the electrodes, as illustrated in Figure 5a. Figure 5b reveals the current−voltage ($I$−$V$) curves of device TP1 under dark and different conditions.

![Figure 4](image-url) 

**Figure 4.** UV−vis diffuse absorption spectra of TiO$_2$ nanowells and TiO$_2$–PANI hybrids TP1–TP3 and their corresponding optical graphs. The inset shows the spectrum of the pure PANI sample.
wavelengths of light source at 500, 400, 350, and 320 nm with the applied bias from −1 to 1 V. The dramatic photocurrent increase under 350 and 320 nm light illumination can be ascribed to the enhanced numbers of photoexcited electron–hole pairs when the photon’s energy is larger than the bandgap of TiO₂ and TP1. The nonlinearity of the I–V curves feature an excellent photovoltaic property with a short-circuit current of ∼34 nA and an open circuit voltage $V_{oc}$ = 0.15 V. Thus, the hybrid device TP1 can work in a self-powered mode without any external power supply. Because two types of junctions (Schottky junction and p–n junction) might exist in this hybrid device, more information needs to obtain to understand the origin of the self-powered response. PDs based on both pure TiO₂ nanowells and pure PANI samples were constructed, and the I–V curves were measured under dark conditions and upon 350 nm light illumination. As shown in Figure S3a, the symmetric I–V curves for pristine TiO₂ nanowells indicate that the Schottky junction from Ag–TiO₂ is unable to induce self-powered behavior, while the linear I–V curves for pure PANI devices in the dark indicates good ohmic contacts at Ag–PANI, and no photoresponse can be detected upon 350 nm light illumination (Figure S3b). Thus, it is safe to conclude that the built-in potential ($V_{oc}$) in the hybrid device TP1 are the main result of p–n junctions at the PANI–TiO₂ interface, which acts as a driving force to separate the photogenerated electron–hole pairs and produce large photocurrent, leading to a self-powered response. For the other two types of hybrid PDs based on TP2 and TP3, similar self-powered characteristics are observed, as revealed by the I–V curves in Figure 5c,d. Both exhibit similarly large current increases under 350 and 320 nm light irradiation, and the asymmetric curves at the negative and positive biases also suggest that the as-fabricated inorganic–organic heterojunction PDs should also be p–n junction contacts. Interestingly, much smaller values of $V_{oc}$ under 320 nm light illumination are found of device TP2 ($V_{oc} = 0.01$ V, inset in Figure 5c) and device TP3 ($V_{oc} = 0.0075$ V Figure 5d), suggesting a relatively weaker self-powered behaviors with an increasing loading amount of PANI. For the further exploration of the signal-to-noise of device TP1, the linear dynamic range (LDR, typically quoted in dB) is a figure-of-merit for a PD and can be expressed as the equation:}

$$\text{LDR (dB)} = 20 \log \left( \frac{I_{ph}}{I_d} \right)$$

(1)

Considering that the dark current should be zero for an ideal PD, a very small bias of 0.05 V is adopted to evaluate the signal-to-noise ratio. The LDR is calculated to be ∼101 dB at 320 nm, much larger than those of InGaAs PDs (66 dB), which indicates a relatively large ratio of photocurrent to dark current and a high signal-to-noise ratio.

The spectral responsivity ($R_{λ}$) is a critical parameter with which to determine the sensitivity of optoelectronic devices, which is defined as the number of carriers circulating through a detector per absorbed photon. A larger $R_{λ}$ represents a higher sensitivity and is expressed as the following equation:

$$R_{λ} = \frac{(I_{ph} - I_d)}{(P)}$$

(2)

where $I_{ph}$ is the photocurrent, $I_d$ is the dark current, $P$ is the excitation wavelength, and $S$ and $P$ are the light power density and the effective irradiated area, respectively. The calculated $R_{λ}$ is as high as 3.6 mA·W⁻¹ under light illumination of 320 nm (light intensity of 0.87 mW·cm⁻²) at 0 V bias, as shown in Figure 6a. The self-powered device TP1 is intrinsically “visible-light-blind”, with a cut off wavelength of about 400 nm. Note that the sharp cutoff edge and the relatively high UV–visible rejection ratio ($R_{290 \text{ nm}} / R_{200 \text{ nm}} \approx 34$) at zero bias indicate that our device is a high-performance intrinsic visible-light-blind self-powered UV PD. Accordingly, the spectral responsivity spectra for the other two devices are revealed in Figure 6b,c. Devices TP2 and TP3 exhibit the same spectral responsivity profiles with maximal values of 785 and 70 μA·W⁻¹ at zero bias, respectively. Both show a cutoff wavelength of ∼400 nm and the highest responsivity located at 290 nm at 0 V bias, indicating good wavelength selectivity. For comparison, the responsivities under 320 nm light illumination ($R_{320 \text{ nm}}$) for the
three devices are listed in Table 1, and they follow the order TP1 > TP2 > TP3.

Moreover, by assuming the shot noise from the dark current is the major contributor, the detectivity (D*) can be calculated as:

\[ D^* = \frac{R}{(2eI_S)^{1/2}} \]  

which reflects the ability to detect weak signal from the noise environment. Owing to the suppressed dark current and enhanced responsivity, the D* is as high as \(3.9 \times 10^{12}\) Jones at the wavelength of 320 nm under a small bias of 0.05 V.

Besides sensitivity and selectivity, stability is also a very significant factor for PD devices. The time-dependent photocurrent curves (Figure 7a–c) suggests good stability and reversibility without notable photocurrent-decay for all the three devices TP1-TP3. For device TP1 in Figure 7a, when the condition changes from dark to light, the current increases quickly to a stable value around 32 nA and decays dramatically to the original value when the light is switched off. The photo-to-dark current ratio \((I_{ph} - I_d)/I_d\) is estimated to be \(1.3 \times 10^3\). The photocurrent values decrease greatly for devices TP2 and TP3 (Table 1) due to the weaker self-powered response, consistent with the I-V results in Figure 5. The response speed is a key parameter to determine the properties of a PD to react to a fast-changing optical signal. Obviously, the rise time \(\tau_r\) and decay time \(\tau_d\) of all the three devices from the I-t curves are less than 0.3 s (limitation of the measurement system) as no data points can be collected upon light switching. Thus, a 355 nm pulsed Nd:YAG laser as the optical source with an oscilloscope was used to measure the time-resolved response at 0 V and the results are shown in Figure 7d-f and Table 1. The time interval between two collected data points was 50 μs. The rise time \(\tau_r\) (defined as the time required for the peak photocurrent to increase from 10% to 90%) and decay time \(\tau_d\) (peak photocurrent to drop from 90% to 10%) are estimated to be 3.8 and 30.7 ms for device TP1, respectively, indicating ultrafast response speed consistent with the \(\tau_r\) and \(\tau_d\) of the three devices from the I-t curves (Figure 7a–c). The high sensitivity and good stability as well as fast response speed of the self-powered hybrid inorganic/organic devices are promising for large-area photodetector applications. Table 1 is a comparison among various hybrid inorganic and organic PDs related to this work. Although some devices showed higher photocurrent/responsivity, they either required higher applied voltage or exhibited slower photoresponse speed, while our devices have the advantages of ease of fabrication and zero-bias operation.

In addition, the photosensitivity of device TP1 to 320 nm UV light illumination was further examined using a range of irradiances of 0.1–0.56 mW·cm\(^{-2}\) light intensities (Figure 8a).
Note that there was a steadily increasing photocurrent response in relation to the light intensity, achieving a photocurrent of 40 nA at 0.56 mW cm$^{-2}$, which is consistent with the fact that the charge-carrier photogeneration efficiency is proportional to the absorbed photon flux. The nonlinear relationship for the variation of photocurrent against light intensity upon 320 nm light illumination (inset in Figure 8a) suggests a complex process of electron–hole generation, recombination, and trapping within the self-powered device.

A possible mechanism on the self-powered TiO$_2$–PANI hybrid photodetection device is proposed according to the energy-band structure diagram illustrated in Figure 8b. Upon UV light irradiation, the electrons in PANI are excited from the highest occupied molecular orbital (HOMO, $\pi^*$) to the lower unoccupied molecular orbital (LUMO, $\pi$) on account of UV light absorption of PANI. As the ground energy state of PANI is at the level within the band gap of TiO$_2$, it is likely that the electrons in the valence band of TiO$_2$ might be excited to the HOMO of PANI by way of $\pi-\pi^*$ transition, which subsequently transited to the conduction band of TiO$_2$. This electron transition process can restrain the electron–hole recombination in TiO$_2$ and increase the photodetection of the nanohybrids.34,57 Here, PANI in fact acts as a hopping state for electron transfer, which largely enhances the transition probability of the valence electrons in TiO$_2$ to its conduction band, resulting in an increase in photoconduction. Besides, on the basis of the above experimental results, it is found that the photocurrent and responsivity of the three TiO$_2$–PANI hybrid PDs obey the trend of TP1 > TP2 > TP3. This is explained by the decreasing electron trapping within the self-powered device.15,18,52,53

In summary, three types of inorganic–organic hybrid PDs based on an array of ordered TiO$_2$ nanowells and $p$-type conducting PANI (TP1–TP3) were successfully prepared and realized as self-powered devices with enhanced photoresponse including high responsivity, excellent wavelength selectivity, fast speed, and good stability. The thin layer of $n$-type TiO$_2$ nanowalls is used as the pathway for electron transport and light scattering, while PANI acts as a hopping state or bridge for electron transfer, which largely enhances the transition probability of the valence electrons in TiO$_2$ to its conduction band, resulting in an increase in photocurrent in a self-powered mode. Interestingly, the performances can be easily tuned by adjusting the loading amount of PANI in the nanohybrids. It is found that the photocurrent and responsivity greatly decrease with the increasing PANI amount due to the reduced effective junction area under irradiation between TiO$_2$ and PANI and the decreased active sites of TiO$_2$. The fast transient response (on the order of milliseconds) for the three devices is highly desirable for practical applications in high-frequency and high-speed devices. This work presents us with an economic strategy for developing future tunable inorganic–organic heterojunction devices in a self-powered mode.

### REFERENCES


