Sonochemical Synthesis of a Zinc Oxide Core—Shell Nanorod Radial p–n Homojunction Ultraviolet Photodetector

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ABSTRACT: We report for the first time on the growth of a homogeneous radial p–n junction in the ZnO core–shell configuration with a p-doped ZnO nanoshell structure grown around a high-quality unintentionally n-doped ZnO nanorod using sonochemistry. The simultaneous decomposition of phosphorous (P), zinc (Zn), and oxygen (O) from their respective precursors during sonication allows for the successful incorporation of P atoms into the ZnO lattice. The as-formed p–n junction shows a rectifying current–voltage characteristic that is consistent with a p–n junction with a threshold voltage of 1.3 V and an ideality factor of 33. The concentration of doping was estimated to be $N_A = 6.7 \times 10^{17} \text{cm}^{-3}$ on the p side from the capacitance–voltage measurements. The fabricated radial p–n junction demonstrated a record optical responsivity of 9.64 A/W and a noise equivalent power of 0.573 pW/√Hz under ultraviolet illumination, which is the highest for ZnO p–n junction devices.

KEYWORDS: p:ZnO, core–shell nanorods, doping, sonochemistry, photodetector, radial p–n junction

INTRODUCTION

The role of oxide-based functional materials has rapidly increased over the past few decades as the focus of research widened beyond their use as mere dielectrics. Today, metal oxides find applications in catalysts, transparent electrodes, magnetic materials, biosensors, piezoelectric materials, photonics, and many more. Among these oxide materials, zinc oxide (ZnO), a wide band gap (3.37 eV) semiconductor material with a high exciton binding energy (60 meV) at room temperature, has emerged to be a promising material for the fabrication of many optoelectronic devices such as light-emitting diodes (LEDs), laser diodes, and photodetectors (PDs). With a potential to replace other wide band gap materials such as GaN and SiC, ZnO has received substantial attention owing to its diverse morphologies, low toxicity, biocompatibility, radiation hardness, and amenability to wet chemical etching, which makes it appealing to commercialization and industrial applications. One-dimensional ZnO nanostructures such as nanorods (NRs), nanowires, and nanotubes have extensively been studied for the fabrication of optoelectronic devices because of their single crystalline nature and high surface-to-volume ratio. However, despite its many advantages, the progress of ZnO in nanoscale optoelectronic devices is hindered by the lack of stable and reproducible p-type doping. The difficulty in attaining p-type doping in ZnO has been attributed to various factors such as the self-compensating effect of the inherent intrinsic donor defects, hydrogen impurities, and the low solubility of p-type dopants. Apart from the above bottlenecks, the tendency of acceptors in ZnO to form deep impurity levels instead of shallow acceptor levels has made it challenging to achieve p-type doping in ZnO. This calls for the development of a synthesis technique for successful, stable, and repeatable p-type doping in ZnO by improving the surface area without the use of high processing temperatures and costs.

p-Type doping in ZnO has been reported in recent times using techniques such as chemical vapor deposition (CVD), ion implantation, pulsed laser deposition, metal-organic CVD, molecular beam epitaxy (MBE), and hybrid beam deposition, which most commonly use nitrogen and phosphorous as dopant materials. Aqueous solution methods have also been reported, which use both group I(A) elements, such as K, and group V(A) elements, such as N and P, but to the best of our knowledge, there was no report on the sonochemical method till date. In this article, we report for the first time on the synthesis of p-type ZnO nanoshell (p:ZnO nanoshell) around ZnO NR by varying only the molar ratio of precursors and the addition of ammonium dihydrogen phosphate (ADP) as the source of phosphorous (P) using the sonochemical method. In comparison with the more conventional approaches such as hydrothermal method, the sonochemical method is significantly faster owing to the fast hydrolysis rate caused by cavitation. Apart from that, the sonochemical method is inexpensive, environmentally benign,

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P atoms were verified to form Zn$_3$(PO$_4$)$_2$ following the reaction (0.18 eV) far less than the theoretical calculations. The cause of promising dopant material, with measured ionization energies experimental results indicate phosphorous (P) to be an equally electronic devices and also improves the response time of the device. The radial p–n homojunction also increases the light absorption, which helps in improving the responsivity of the detector.

In this article, we present for the first time fabrication of a ZnO core–shell NR radial p–n homojunction (p:ZnO/n-ZnO) using a sonochemical method, which is not only fast, inexpensive, and can perform under ambient conditions but also highly stable and reproducible with improved surface area. The radial p–n homojunction offers a wide range of advantages over conventional planar p–n junctions. Foremost, the p–n junction area increases by many folds in the radial p–n junction than in the planar p–n junction, thus increasing the electron–hole collection efficiency. The distance that the electron–hole pairs need to travel before they are effectively collected is very small when compared to that in the planar p–n junction, which reduces the recombination losses encountered in optoelectronic devices and also improves the response time of the device. The radial p–n homojunction configuration also increases the light absorption, which helps in improving the responsivity of the detector.

Using the sonochemical method, we have successfully doped ZnO nanoshells with phosphorous atoms and formed a radial p–n junction. The successful formation of p–n junction and the incorporation of P atoms were verified by X-ray diffraction (XRD), Raman spectrum, and current–voltage (I–V) measurements, which show rectification, characteristic of a p–n junction with a threshold voltage ($V_T$) of 1.3 V and a reverse bias leakage current of 62.1 μA at −2 V. The capacitance–voltage measurements ($C$–$V$) were used to extract the doping concentration. The spectral response of the as-formed p–n junction was studied under a wide spectral range (350–1100 nm).

**RESULTS AND DISCUSSION**

The ZnO NRs were synthesized using the sonochemical method described in detail in the Supporting Information.\(^\text{40,41}\) ZnO nanoshells were grown around vertically oriented ZnO NRs by varying the molar ratios of zinc nitrate hexahydrate (ZNH) and hexamethylene tetramine (HMT) rather than using any other surfactant. HMT is known to play a crucial role in promoting the directional growth along the “c” axis as it binds to the nonpolar facets of ZnO, cutting off the supply of Zn$^2+$ ions to these facets, thereby promoting the growth in the (0001) plane along the “c” direction.\(^\text{42}\) Hence, in this study, by changing the molar ratios of ZNH and HMT to 4:1 (1:1 is the preferred ratio for the growth of ZnO NRs), we were able to promote the growth of ZnO along the nonpolar facets of ZnO NRs along with the growth in the “c” direction. This resulted in the growth of a nanoshell structure enclosing the whole NR including top basal plane with increased junction area when compared to conventional core–shell nanostructures, where the shell is grown only around the nonpolar facets of ZnO NR.

This method is advantageous over the more common ones, which use surfactants such as citrate ions to achieve directional growth, as no impurities were added in this method while forming a more continuous and defect-free junction as observed from the transmission electron microscope (TEM) image.\(^\text{43–45}\) A continuous and defect-free junction is desired in designing optoelectronic devices to minimize the recombination losses at the junction.

The step-by-step synthesis of p-doped ZnO nanoshells around ZnO NRs to form a homogeneous radial p–n junction is shown in Figure 1. In step 1, the ZnO NRs were grown on a gold-coated Si/SiO$_2$ substrate using the process described earlier. The as-synthesized NRs are 1 μm in length and 50 nm in diameter. In step 2, a portion of ZnO NRs was etched away to expose Ti/Au, which would act as an Ohmic contact to n-ZnO NRs. In step 3, a 1 μm thick poly(methyl methacrylate) (PMMA) was deposited by spin coating followed by a hard-bake at 180 °C for 3 min. PMMA is later carefully etched...
halfway through, using reactive ion etching (RIE) in oxygen (O$_2$) plasma. This step exposes 600−800 nm of ZnO NRs for further synthesis of p-doped ZnO nanoshells, whereas the remaining PMMA shields the n-type ZnO NRs at their base. This inhibits the growth of ZnO nanoshells around the core at the base, which ensures no electrical junction is formed between the nanoshells and the bottom seed layer. By controlling the thickness of the PMMA layer in our fabrication, we can control the overlapping aspect ratio of the junction surface area between the n-type and the p-type regions, which is desirable in fabricating high-performance LEDs to achieve the controlled p−n junction performance. In step 4, p:ZnO nanoshells were grown around the previously prepared ZnO NRs by sonicating a solution of (ADP + ZNH + HMT) in deionized (DI) water at 50% amplitude for 20 min. The concentration of ADP varied from 1 to 2 mM in steps of 0.2 mM. The scanning electron microscope (SEM) analysis presented in Figure 2a,c has shown that after the growth of nanoshells, the effective diameter of the NRs increases from 50 to 100 nm, which indicates the successful growth of nanoshells. In step 5, another layer of PMMA was deposited over the synthesized core−shell structures and etched in RIE to expose the tips of the nanoshells for depositing metal contacts for electrical measurements. However, owing to a slight angular growth of some NRs, not all nanoshells were exposed equally during this process, and some of the nanoshells remained covered by PMMA as shown in Figure 2e. Further etching of PMMA was not performed to avoid the risk of exposing the ZnO core, which would result in the top metal contact making direct connection with the n-ZnO core. In step 6, physical masks were used to deposit Ni/Au on the p:ZnO nanoshells using e-beam evaporation. The I−V measurements at different annealing temperatures were taken, which show a successful p-type doping at 1.6 mM ADP and 500 °C annealing temperature.

Structural characterization was done using a 30 kV JEOL 7000 SEM and a Philips CM-200 200 kV TEM. Figure 2a−d shows the top view and the cross-sectional view of SEM images of the unannealed ZnO core and p:ZnO nanoshell/n-ZnO NR core−shell NRs. It is observed that the ZnO NRs that act as the core are 50−60 nm in diameter and are vertically oriented with a needle-like pointed tip, whereas the newly formed nanoshell around the core is hexagonal in structure with a thickness of 40−50 nm, giving an overall diameter of ≈100 nm. Figure 2f shows the cross-sectional view of p:ZnO nanoshell/n-ZnO NR with PMMA filling the voids between the rods isolating the p:ZnO nanoshells from the NRs. Figure 2e shows the exposed...
tips of the p:ZnO nanoshell/n-ZnO NR for the deposition of electrical contacts.

Figure 3a,b shows the TEM image of an unannealed single core–shell NR and the corresponding selected area electron diffraction (SAED) pattern, respectively. The ZnO core can be easily distinguished from the p:ZnO nanoshell because of an obvious difference in contrast between the core and the shell regions. From the SAED pattern, it is obvious that both the ZnO core and ZnO nanoshell that enclose the ZnO NR are single crystalline materials and form a defect-free junction. The result of the chemical composition analysis of an unannealed sample, which was performed using energy-dispersive X-ray spectroscopy (EDS), is shown in Figure 3c and shows 0.96% weight of phosphorous in the p:ZnO nanoshells. Figure 3d shows the XRD measurements of both undoped ZnO NRs and p-doped p:ZnO nanoshell/n-ZnO NR structures after annealing. In ZnO NRs, the ZnO(002) diffraction peak is the dominant peak, which indicates that the samples have a preferred orientation along the c-axis. We also observe the ZnO(101) peak that can be attributed to the tips of ZnO NRs that are sharp like needles. In the case of p-doped p:ZnO nanoshell/n-ZnO NR, the (002) peak is the only dominant peak that corresponds well with the SEM pictures showing smooth hexagonal edges on the nanoshells. We also observed
that when compared with the ZnO NR, the position of the (002) diffraction peak in the p:ZnO nanoshell/n-ZnO NR after the activation of dopants by annealing has left-shifted by 0.17 degrees, which provides strong evidence that the ZnO nanoshell has been successfully doped with phosphorus. A similar behavior was reported in the earlier reports of p-doped ZnO.34,46 In Figure 3c, Raman spectra of the undoped ZnO NR and the p-doped p:ZnO nanoshell after annealing are presented. The nonpolar E2 mode (E2h), which was observed at 436 cm\(^{-1}\) in ZnO NRs, red-shifts by 1.8 cm\(^{-1}\) (to 434.2 cm\(^{-1}\)) and broadens in the p:ZnO nanoshell. Such a shift in the nonpolar E2 mode was reported earlier in Sb-doped and N-doped ZnO.46,47 This decrease in frequency can be ascribed to the local lattice softening owing to the incorporation of "P" ions. Both XRD and Raman spectra confirm the substitution of Zn sites by P ions in the crystal lattice and the formation of P\(_{Zn}\)−2V\(_{zn}\) complex defects.

The I–V measurement is a useful tool to verify the formation of a p–n junction and to study the evolution of doping. Here, we studied the evolution of p-type doping by measuring the electrical current between the p:ZnO nanoshell and the n-ZnO NR for various concentrations of ADP. For this purpose, the Ni/Au contact was deposited on the top of p:ZnO nanoshells prepared with different concentrations of ADP, and the Ti/Au contact deposited on ZnO NRs acts as an Ohmic contact on the n-side. Figure 4a shows the schematic of the p:ZnO nanoshell/n-ZnO NR p–n junction. Figure 4b–d, h shows the evolution of p-doping in ZnO as the concentration of ADP increases from 1 to 1.6 mM. The rectification in current is observed when the concentration of ADP is 1.6 mM, as shown in Figure 4h, which proves successful p-type doping in ZnO nanoshells. The I–V measurement between the two contacts placed on the same side is also shown in the inset of the same plot. The linear behavior confirms the formation of Ohmic contacts, and the rectification observed is entirely because of the junction between the p:ZnO nanoshell and the ZnO NR. Beyond 1.6 mM concentration of ADP, the pH of the precursor solution becomes high, making it untenable for the growth using sonochemistry. It was also observed that the temperature plays a crucial role in activating the dopants as can be seen from Figure 4e–h, where I–V measurements of samples with the same concentration of ADP annealed at temperatures 25, 300, 400, and 500 °C were presented.

We found that the dopants are activated after annealing at 500 °C for 30 min. This annealing temperature is required for Zn\(_{1-x}\)(PO\(_4\))\(_x\) induced onto the ZnO NRs during cavitation to decompose and release "P" atoms, which would diffuse into the ZnO crystal acting as acceptor dopants.34

The turn-on voltage is about 1.3 V, and the reverse bias leakage current at −2 V is 62.1 μA, which increases with increasing reverse bias voltage. This could be due to nonuniform doping in the p:ZnO nanoshell region. The ideality factor of the diode "n" can be calculated from

\[
\eta = \frac{q}{kT} \left( \frac{\partial \ln I}{\partial V} \right)^{-1}
\]  

where V is the applied voltage, k is the Boltzmann constant, and the whole value of KT/q can be expressed as 0.0258 eV at T = 300 K. In the voltage range of 1–3 V, the ideality factor "n" was calculated to be 33. Such high ideality factors in wide band gap semiconductors have been reported earlier.48 Typically, core–shell nanostructures have such high ideality factors because of the defects in the interface, imperfections in the formation of the p–n junction, parasitic rectifying junctions, deep-level-assisted tunneling, and space-charge-limited conduction owing to the low hole density and mobility.48 The C–V measurements were measured using a Keithley 4210-CVU (capacitance–voltage unit) to study the doping concentration of the as-grown p-type ZnO nanoshells. When the inverse of the square of capacitance density was plotted against the reverse bias voltage, a linear plot is obtained. The slope of this plot is related to the doping density by

\[
N_A = \frac{2}{q\epsilon_0\epsilon_r} \frac{1}{\frac{d(A/C)}{dv}}
\]  

where \(q = 1.6 \times 10^{-19}\) C is the charge of an electron, \(\epsilon_0 = 8.85 \times 10^{-14}\) F/cm is the permittivity of the free space, \(\epsilon_r\) is the relative permittivity of the medium, "A" is the area of the contact, and "C" is the measured capacitance. Figure 5 shows the capacitance versus voltage at different frequencies and (A/C)\(^2\) versus voltage of the p–n junction at 10 kHz frequency. The doping concentration \(N_A\) at 10 kHz frequency was calculated to be 6.7 \times 10^{12} cm\(^{-2}\) by measuring the slope of the C–V curve in the reverse bias, as shown in Figure 5a.

Because of its wide band gap and superior stability under harsh environments, ZnO has been widely used for ultraviolet (UV) photodetection.7,49,50 In a ZnO p–n junction, an increase in the reverse current is observed under UV illumination as electron–hole pairs are generated in the depletion region by band-to-band excitation in a semiconductor when \(h\nu > E_g\). These electron–hole pairs are quickly swept away toward the electrodes because of the internal electric field. This increased reverse saturation current due to the incident light is also called the photocurrent \(I_{ph}\).48 We have fabricated a UV p–n junction photodetector by growing a p:ZnO nanoshell/n-ZnO NR p–n junction on the Au/Ti/Si/SiO\(_2\) substrate in which Ti/Au acts as the Ohmic contact to the ZnO NRs, whereas a physical mask with a window size of 0.15 cm\(^2\) was used to deposit 250 nm thick ITO by radio frequency (rf) sputtering to form contact on the p:ZnO nanoshells to allow maximum transmission of the incident light. The rf sputtering was performed at room temperature with pressure maintained steady at 11 mTorr. The rf power and time were 70 W and 100 min, respectively, to produce a deposition rate of 2.5 nm/min. The schematic of the as-prepared p–n junction is shown in Figure 6a. ZnO with a wide band gap (3.37 eV) is known to generate electron–hole pairs when exposed to UV illumination, where wavelength corresponds to the band edge excitation.
study the operation of the photodetector, the spectral response of the device in terms of the photocurrent versus the input voltage was measured from 350 to 1100 nm wavelength. Figure 6b shows the photoresponse under UV illumination at 350 nm compared with that under dark condition. At 2 V reverse bias, the reverse bias photocurrent is observed with a value of 62.1 μA. We calculated the photocurrent density, \( J_{ph} \), for a spectral range of 350–1100 nm by dividing the difference between the photocurrent and the dark current with the effective contact area of 8.83 × 10^{-3} \text{cm}^2. More details regarding the calculation of effective area are given in the Supporting Information. The photoresponsivity, \( R_{ph} \), which measures the input–output gain of the photodetector, was calculated by

\[
R_{ph} = \frac{J_{ph}}{P_o}
\]

where \( P_o \) is the input optical power density. The responsivity calculated at 2 V reverse bias is plotted in Figure 6c. We found that the responsivity shows little variation in the UV region (350–400 nm), with a maximum value of 9.64 A/W at 400 nm, and it starts to fall dramatically with the increase in wavelength after 400 nm. Responsivity data were collected over 6 months, and they showed only 5% degradation for this period, which is after 400 nm. Responsivity data were collected over 6 months, which measures the input–output gain of the photodetector, and a normalized bandwidth (time bandwidth product) of “1 Hz” at room temperature, the value of \( i_2 \) is 1.05 pA. The shot noise is given by \( i_s = \sqrt{2q(I_{ph} + I_d)B} \), where \( I_{ph} \) is the photocurrent and \( I_d \) is the dark current. The measured shot noise current at −2 V is 4.47 pA. The total noise current \( i_t = i_s + i_d = 5.52 \text{pA} \) and the NEP, which is the ratio of \( i_t \) and the responsivity, is calculated. We obtain a minimum NEP of 0.573 pW/√Hz. Table 1 compares the performance of the as-fabricated p:ZnO nanoshell-ZnO p–n junction photodiode with other UV photodetectors reported in the literature.

### Table 1. Performance Comparison of the Fabricated UV Photodetector with the Recently Reported Ones

<table>
<thead>
<tr>
<th>material/structure</th>
<th>device</th>
<th>method</th>
<th>photocurrent</th>
<th>responsivity</th>
<th>turn-on voltage (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p:ZnO/n-ZnO</td>
<td>planar p–n junction diode</td>
<td>rf sputtering</td>
<td>0.16 μA</td>
<td>0.09 A/W</td>
<td>0.9^4</td>
</tr>
<tr>
<td>graphene/n-ZnO</td>
<td>Schottky junction diode</td>
<td>MBE</td>
<td>≈60 μA</td>
<td>113 A/W</td>
<td>0.5^5</td>
</tr>
<tr>
<td>p:GaN/n-ZnO</td>
<td>planar p–n junction diode</td>
<td>sol–gel</td>
<td>170 μA</td>
<td>4 A/W</td>
<td>1.4^7</td>
</tr>
<tr>
<td>p:(Al–N)ZnO/n-ZnO</td>
<td>planar p–n junction diode</td>
<td>hydrothermal</td>
<td>70 μA</td>
<td>0.425 A/W</td>
<td>2.5^5</td>
</tr>
<tr>
<td>p:(Sb)ZnO/n-ZnO</td>
<td>radial p–n junction diode</td>
<td>CVD</td>
<td>11 μA</td>
<td>0.746 A/W</td>
<td>3.6^9</td>
</tr>
<tr>
<td>p:(Cu)ZnO/n-ZnO</td>
<td>planar homojunction</td>
<td>aqueous solution method</td>
<td>0.2 mA</td>
<td>5.75 A/W^60</td>
<td></td>
</tr>
<tr>
<td>Ga–ZnO/n-ZnO</td>
<td>M–S–M</td>
<td>sonocoagulation</td>
<td>62.1 μA</td>
<td>9.64 A/W</td>
<td>1.3 (present work)</td>
</tr>
<tr>
<td>p:ZnO/n-ZnO</td>
<td>radial p–n junction diode</td>
<td>rf sputtering</td>
<td>0.09 A/W</td>
<td>0.9^3</td>
<td></td>
</tr>
</tbody>
</table>

In summary, we have developed and optimized a process to successfully dope ZnO with phosphorous ions using a sonochemical method for the first time and fabricated a radial p–n junction photodiode in a core–shell geometry. The core–shell structure was synthesized without using any external surfactant but rather used only different molar ratios of precursors. A doping concentration of 6.7 × 10^{-7} cm^{-3} was achieved for the p:ZnO nanoshells. The as-fabricated homogeneous p–n junction shows a rectifying behavior with an ideality factor of 33 and a reverse saturation current of 62.1 μA at −2 V. To the best of our knowledge, the reported responsivity of 9.64 A/W under UV illumination is the highest among ZnO p–n junction UV PDs. The developed method is fast, inexpensive, and performed under ambient conditions, while resulting in stable performance in terms of responsivity over 6 months with only 5% degradation and highly repeatable performance with an observed error limit of less than 6% for both p–n junctions and PDs. This facilitates the use of flexible substrates for ZnO nanostructures, opening the door for

CONCLUSIONS
flexible and wearable electronic and photonic devices based on ZnO.

**EXPERIMENTAL SECTION**

**Growth of ZnO NRs.** The ZnO seed layer (200 nm thick) was initially deposited over an n-Si substrate by sonicating in a 100 mL solution containing 0.02 M zinc acetate dehydrate in isopropyl alcohol for four cycles of 15 min each. In the second step, the high-quality ZnO NRs were grown by sonicating a 100 mL solution of 0.02 M ZNH and 0.02 M HMT in DI water for four cycles of 30 min each. The as-grown ZnO NRs are vertically oriented with an average diameter of 50 nm and a length of 1 µm.

**Deposition of Contacts.** Electrical contacts on the ZnO NRs were deposited using e-beam evaporation. Initially, a 1 µm thick PMMA was spun-coated onto the sample and was hard-baked at 180 °C for 3 min. RIE was used to etch PMMA to expose 100 nm of ZnO NRs and p-ZnO nanoshells. Physical masks were prepared by using a laser engraver to cut windows with an area of 0.15 cm² into the ZnO NRs and p:ZnO nanoshells. Physical masks were also used to promote the growth of nanoshells and to keep the pH around 6, which is the optimum condition for the sonochemical growth. For this purpose, 1.2 gm of ZNH, 0.14 gm of HMT, and 0.0184 gm of ADP were dissolved in 100 mL of DI water and stirred for 5 min to form a homogeneous solution. The previously prepared sample with ZnO NRs was dipped into this solution and sonicated at 50% amplitude for 20 min. The thickness of the nanoshell depends on the sonication time. The thickness of the nanoshell increases with increasing sonication time. The as-prepared samples were then cleaned using DI water and allowed to dry under ambient conditions.

**Characterization.** A 30 kV JEOL 7000 FSEM was used to study the morphology of the as-grown ZnO NRs and p-ZnO nanoshells. The Philips CM-200, a 200 kV TEM, was used to study the junction and to obtain the SAED pattern for the ZnO NRs. A JEOL 6330 FSEM equipped with an X-ray detector was used to obtain the EDS spectrum to study the material composition. Raman spectroscopy (BaySpec spectrometer equipped with 532 nm laser) was used to study the incorporation of P atoms in the ZnO lattice. A Siemens 500D XRD was used to study the dominant orientation of the as-grown ZnO nanostructures. The electrical characterizations were done using a Keithley 4200-SCS semiconductor characterization system. The spectral response measurement system QEX10 from PV Measurements Inc. that houses a xenon arc lamp was used to measure the spectral response of the photodetector. The input optical power density of the xenon lamp at different wavelengths was measured using a multifunction optical meter from Newport. A plot of the optical power density of the xenon lamp with respect to wavelength is given in Figure S3. The responsivity of the photodiode was calculated by taking the ratio of photocurrent density and power density at every 10 nm between 350 and 1100 nm.

**REFERENCES**


