Defect-Assisted Broad-Band Photosensitivity with High Responsivity in Au/Self-Seeded TiO$_2$ NR/Au-Based Back-to-Back Schottky Junctions

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ABSTRACT: TiO$_2$ nanorods (NRs) have generated much interest for both fundamental understanding of defect formation and technological applications in energy harvesting, optoelectronics, and catalysis. Herein, we have grown TiO$_2$ NR films on glass substrates using a self-seeded approach and annealed them in H$_2$ ambient to modify their surface defects. It has been shown that broad-band photosensing properties of Au/self-seeded TiO$_2$ NR/Au-based two back-to-back Schottky junctions (SJs) for a broad wavelength of light are much superior as compared to those of the pristine and the control samples. Photosensitivity values for the H$_2$-annealed sample are 0.42, 0.71, 0.07, and 0.08 A/W for detecting, respectively, 350, 400, 470, and 570 nm lights. Very low dark current and high photocurrent lead to a gain value as high as $1.85 \times 10^4$ for 400 nm light. Unprecedentedly modified NR-based SJs show excellent photosensitivity for detecting as low as 25, 36, 48, and 28 $\mu$W/cm$^2$ power densities of 350, 400, 470, and 570 nm lights, respectively. It is found that Ti$^{3+}$ defects play a key role in an efficient photoelectron transfer from TiO$_2$ to Au. Our work, for the first time, highlights the simplicity and reveals the rationale behind the excellent properties of Au/self-seeded TiO$_2$ NR film/Au back-to-back SJs.

INTRODUCTION

Capability for detecting both ultraviolet (UV) and visible (vis) lights can be used in applications such as display monitors, optical communication, target identification, and remote controlling. However, because a semiconductor can only absorb or detect a light with energy corresponding to its band gap, for both UV and vis photodetection, one needs to combine two or more separate detection devices utilizing two different semiconductors. Therefore, photodiodes (PDs) that can provide a substantial dual-detectable operation for wider wavelengths covering from UV to visible regions with the help of just one photon-detection device instead of two individual devices are not only conceptually ideal but also technologically indispensable because such a single PD can eliminate the difficulties of fabrication and assembling several detectors with individual cooling assemblies. Furthermore, dual-detectable PDs are very alluring for advanced application areas such as medicare, general illumination, weather monitoring, and in military. Till date, many studies on high-performance p–n junction PDs have been carried out. For example, wide-bandgap GaN-based PDs are only suitable for detecting UV and Si-based PDs show a good performance in a specified wavelength region ranging from visible to infrared (IR). A few recent reports on ZnO-composite-based PDs show that they are able to detect both UV and visible lights, though these suffer from a complicated device fabrication step because of its composite structure. On the contrary, simple Schottky junctions (SJs), which are the simplest form of PDs, can satisfy the dual-detection characteristics that have never been demonstrated till date to the best of our knowledge.

Nanostructures of wide-band-gap semiconductor TiO$_2$ remain very important over the last few decades because of their applications in solar cells, photocatalysis, electrochemistry, water splitting, hydrogen production, drug delivery, space research, photodetectors, etc., due to their easy preparation and good chemical stability. The electronic band gaps of 3.0–3.4 eV limit their optical absorption in the UV region of the solar spectrum with a low gain. It is well known that one-dimensional (1D) nanostructures show enhanced surface-related properties. Especially, interaction of TiO$_2$ surfaces with H$_2$ has been studied for a long time. Reduction occurs when a TiO$_2$ surface is annealed in a H$_2$ atmosphere under high vacuum conditions. It has been observed that thermal treatment in H$_2$ ambient produces colored TiO$_2$, changing its optical and electronic properties toward superior performance, which has been originated mostly from the change in the structural disorders/defects. However, TiO$_2$ nanorod (NR) films are reported to be grown successfully only on FTO substrates because of lattice matching (almost 98%). FTO, being a costly substrate, again the FTO/TiO$_2$ structure becomes costly. Therefore, in this article, we have grown self-seeded NR films of TiO$_2$ on...
ordinary glass substrates using a pulsed-laser-deposited (PLD) thin seed layer of TiO2. This technique can be addressed as the first attempt till date to grow TiO2 NR films on glass substrates to the best of our knowledge. Furthermore, we have modified the surface of TiO2 NR films by annealing them in H2 ambient under high vacuum to modify the surface defects and investigated photosensing properties of two back-to-back SJs. It has been shown that the photodetection properties of Au/self-seeded TiO2 NR film-based SJs are much superior to those of pristine and only-vacuum-annealed TiO2 NR films (control samples). The photoresponsivity values for H2-annealed NR film-based SJs are 0.42, 0.71, 0.07, and 0.08 A/W for detecting lights of 350, 400, 470, and 570 nm wavelengths, respectively, which are excellent as broad-band light detection. Here, the contrast between the low value of the dark current and the high value of the photocurrent makes this particular SJ a very attractive one with a high gain value of $1.85 \times 10^4$, the highest among the other reported ones. Not only this, the H2-annealed NR films show excellent photoreponsivity values for detecting as low as 25, 36, 48, and 28 $\mu$W/cm² power densities of broadband lights of 350, 400, 470, and 570 nm wavelengths, respectively, which has not been reported for TiO2 NR-based photodetectors till date to the best of our knowledge. Therefore, this work presents two-fold novelty, a simple self-seeded growth strategy of TiO2 NR films over a glass substrate and excellent broad-band photosensitivity with high responsivity values of Au/self-seeded TiO2 NR film/Au back-to-back SJs.

### RESULTS AND DISCUSSION

**Structural, Elemental, and Spectroscopic Characteristics.** The X-ray diffraction (XRD) pattern of the PLD seed layer grown on a glass substrate (S0) is shown in Figure 1a with the diffraction peaks corresponding to the (110), (200), (210), (211), and (220) peaks of the rutile phase, whereas a single peak at $\sim 37.5^\circ$ corresponds to the (004) peak of the anatase phase of TiO2. Therefore, the seed layer contains a mixed phase but is dominated by the rutile phase, which was observed earlier by Kitazawa et al.\(^3^2\) Figure 1b shows similar XRD peaks for the rutile phase, whereas the intensity of the (004) peak assigned to the anatase phase is decreased for as-grown NR films (S1) grown over the seed layer, indicating more dominance of the rutile phase for the hydrothermally grown NR films. After annealing in vacuum (S2) and in H2 ambient (S3), the patterns remain almost similar, whereas the intensity of the peaks for the rutile phase increases with a complete absence of the anatase phase for the S3 sample. This is similar to the results of Soo et al.\(^3^3\) who had also found the dominance of the rutile phase over the anatase phase after annealing in a H2 atmosphere at a temperature above 300 °C.

The full width at half-maximum value for S1 is 0.48, whereas for S2 and S3, the values are 0.35 and 0.36, respectively, which indicates a better crystallinity of S2 and S3 samples over S1 because of annealing.

The UV–vis absorbance spectra of NR films (S1, S2, and S3) plotted in Figure 1c show a gradual increase in the absorption value from 600 nm, whereas the UV–vis absorbance spectrum of S0 shown in Figure 1d shows a sharp rise in the absorption value below 370 nm because of band edge absorption of TiO2. In Figure 1c, S3 shows a significant enhancement in the absorption value in the UV region as compared with S1 and S2 and also shows an increased visible light absorption in the wavelength region of 500–400 nm, which is shown in the inset of Figure 1c. An increased absorption both in the UV and vis light regions after hydrogenation as compared to that in pristine ones was also observed by He et al.\(^2^7\) and Wang et al.\(^3^4\) This increase in absorbance is considered to be a result of the presence of some
disordered states, which may create some mid-gap states and narrow the band gap. The FESEM image of the TiO₂ NR array film shown in Figure 1e shows a quasi-vertical nature of the NR array film. From the magnified image of the NR films (Figure 1f), the average diameter of the NRs is found to be ∼50–60 nm and are not vertical but interconnected.

A representative comparison of the X-ray photoelectron spectroscopy (XPS) spectra of S3 and S1 samples in Figure 2a shows peaks due to the Ti 2p (2p₃/2 and 2p₁/2) state and in Figure 2c shows peaks due to the O 1s (1s) state. S1 shows the presence of two symmetrical peaks due to the Ti⁴⁺–O bond in the Ti 2p spectrum at ∼458.6 eV for Ti 2p₃/2 and at ∼464 eV for Ti 2p₁/2.³⁵ In contrast to S1, the S3 sample distinctly shows two asymmetric peaks with two distinct shoulders toward lower binding energies. In Figure 2b, the Ti 2p₃/2 peak signal for S3 is nicely fitted with three peaks. Two peaks at ∼457.2 and 455.8 eV are due to Ti³⁺ and Ti⁵⁺, respectively, apart from the peak at 458.6 eV due to Ti⁴⁺. Therefore, our XPS results clearly indicate that, after reduction, both Ti³⁺ and Ti⁵⁺ appear, which has also been reported earlier by Singh et al.²⁶ and Lu et al.³⁶ Appearance of the defect states after hydrogenation has also been indicated in the previous studies.³⁷–³⁹ Furthermore, there is a change in the O 1s peak shape of S1 and S3. The O 1s peaks in Figure 2d,e are deconvoluted into two peaks, one (P₁) at ∼530 eV due to lattice O₂⁻ (Ti–O–Ti bond) and another (P₂) at ∼531 eV due to surface hydroxyl (Ti-OH). The ratios of peak areas of P₂ to P₁ values for both S1 and S3 samples are similar. This indicates further that there is no change in the surface-adsorbed OH groups due to H₂ annealing. Chen et al.⁴⁰ have also reported no change in the Ti-OH signal in the XPS spectra after H₂ annealing.

**Dark Current Density (Jₜ)–Voltage (V) Characteristics.** Two lateral Au contacts on top of TiO₂ NR films consist of an Au/TiO₂ junction connected in series, resulting in back-to-back two junctions. Ideally, both the junctions should form Schottky contacts and hence the nonlinear J–V
curves should be obtained for the fabricated Au/TiO2/Au back-to-back SJs. The nonlinearity is expected to stem from the Au/TiO2 junction, which has been reported earlier by Chakrabarty et al.41 and Karaagac et al.42 However, Figure 3a shows that S0 (seed layer) exhibits almost symmetric and linear \( J - V \) characteristics, indicating an almost zero junction barrier height. The linear and symmetric behavior observed in the \( J - V \) characteristics around \( V = 0 \) originates from the trap-populated TiO2 surface layer adjacent to the interface, as observed by others. 43 It has been shown previously that a high VO concentration can break the interface barrier in M/TiO2 junctions. 44 Our results indicate that the PLD seed layer contains abundant surface trap states (probably V O) because of a deposition condition of high vacuum (i.e., nonavailability of O2) in the growth chamber. Therefore, the zero barrier height is attributed to the electron leakage through the traps in the carrier-depleted region of the TiO2 layer adjacent to the junction and thus the current becomes independent of the barrier height established at the junction. 45 This is because, in complex junctions, charge carriers choose the lowest barrier/resistance path and, hence, the \( J - V \) characteristic of the junction is expected to approximately indicate the minimum barrier height built up at the junction. Thermal annealing in air compensates the VO defects and increases the O2 concentration at the interface, which causes a barrier setup. In fact, we could not measure the \( J - V \) curve for an air-annealed sample because of its very low current value (less than pA). Figure 3b shows the \( J_d - V \) curves of S1, S2, and S3, where the curve for S2 is multiplied by a factor 50 for better clarity. The \( J_d - V \) curve for S1 is distinctly asymmetric and rectifying on both sides of \( V = 0 \), indicating the formation of junction interface barriers, as indicated by the asymmetric \( J - V \) even though two symmetric contacts (Au) have been used. 46 In the forward bias condition, the barrier height is much higher than that expected from the difference in the electronegativity value of anatase and/or rutile TiO2 and the work function of Au. This result is consistent with the reported independence of the height of the junction barrier formed on TiO2 by various metals. 45 For Au/TiO2, however, these numerical values lead to a barrier height approximately around 0.4 eV. 46 A much higher barrier value in our case indicates a complex junction nature. In the reverse bias condition, the barrier height is even higher because of slow release of carriers from the interface trap states. 46,47 It appears that higher levels of O2 coverage occur on the Au surface at the junction. For annealed samples S2 and S3, the barrier height gradually becomes lower as compared to that of S1. To better understand the difference in the interfacial barrier, we also have to bear in mind that intermediate thin oxide layers of a few nanometers may be formed at Au/TiO2 interfaces, 48 especially on samples exposed to environmental conditions. 49 Further to this, some induction of VO, acting as equivalent to doping, is also expected. 50 These processes result in the formation of an effective barrier with a height that deviates from the expected theoretical predictions. Therefore, in present junction cases, the observed Schottky barriers cannot be described on the basis of the commonly used concept that the junction barrier height is equivalent to the difference between the metal work function and semiconductor electron affinity. From the \( J_d - V \) curves, it is evident that S1 shows the lowest \( J_d \), whereas the value increases slightly as the sample is annealed in vacuum condition (S2) and the enhancement is ~6 times at ~4 V when the sample is annealed in H2 ambient (S3). Therefore, the difference between S1 and S2 is probably due to vacuum-generated vacancies and the difference between S1 and S3 is due to Ti3+ at the surface of the TiO2 layer during the annealing process. 37,50 Ti3+ forms a band below the conduction band minima. 51 In wide-band-gap materials, the conductivity is also determined by the properties of the gap states through mechanisms such as hopping and Poole–Frenkel effects. Nevertheless, a thorough investigation of the conduction mechanism through the NR films is not our main focus in this work.

**Wavelength-Dependent Photoresponse.** To investigate the wavelength-dependent optoelectric behavior, the photocurrent spectrum of the samples has been recorded by varying the wavelengths of the illumination from 800 to 300 nm at a fixed bias voltage of ~4 V, as shown in Figure 4a. S1 and S2 show a rise in the photocurrent only below 430 nm with the highest \( J_{ph} \) observed at ~400 nm illumination. However, S3 shows a considerable photoresponse in the wavelength region of 400–700 nm with two maxima at ~470 and ~570 nm wavelengths apart from a sharp peak at ~400 nm, indicating a broad-band photoresponse. The wavelength-dependent responsivity (R) and detectivity (D) have been calculated using the standard formulas

\[
R = (J_{ph} - J_d)/P
\]  

(1)

\[
D = \frac{R}{\sqrt{2qJ_d}}
\]

(2)

where \( J_{ph} \) is the photocurrent density, \( P \) is the power density of illumination, and \( q \) is the charge of an electron. The inset in
Figure 4a shows the detectivity values of \( \sim 3 \times 10^9 \), \( 7 \times 10^9 \), and \( 68 \times 10^9 \) Jones for 400 nm illumination for S1, S2, and S3, respectively. For S3, visible illumination detectivity values at 470 and 570 nm wavelengths are \( \sim 6 \times 10^9 \) and \( 8 \times 10^9 \) Jones, respectively, which are higher than the highest detectivity values achieved by S1 and S2. In Figure 4b, the wavelength-dependent responsivity curve shows a clear hump in a region of 500−700 nm with a maximum centered at 570 nm for the S3 sample. Figure 4b also indicates that S3 has much higher photoresponsivity values in the entire 350−800 nm region as compared with S1 and S2.

**Photocurrent Density** \( (J_{ph}−V) \) **Characteristics.** To investigate the response of the samples to a light of single wavelength chosen from the detectable wide UV to visible range, four reference wavelengths of illumination, that is, 350, 400, 470, and 570 nm, have been selected and their corresponding \( J_{ph}−V \) curves are shown in Figure 5. In Figure 5a, the \( J_{ph}−V \) curve of the S0 sample is shown, where the photocurrent values for all four wavelengths show Ohmic behavior and the values are not much different from the dark current values. In Figure 5b−d, the NR film samples (S1, S2, and S3, respectively) show photoresponse to all four chosen wavelengths as evidenced from the \( J_{ph}−V \) curves, which maintain Schottky junction behavior with a much lower barrier height of the Au/TiO2 junction. This is due to the fact that \( J_{ph} \) is dominated by the photogenerated carriers in the TiO2-depleted region under illumination, which is explained through the model in Figure 6. In each of Figure 5b−d, the highest photocurrent has been observed for 400 nm illumination.

The schematic (Figure 6) shows that the excitons are generated in the depleted region after illumination and the photoelectrons easily reach the electrode (Au) via Ti3+ defect.
states. In the above diagram, conduction band minima and valence band maxima are denoted CB and VB, where forward and reverse bias are labeled as FB and RB, respectively.

**Transient Photoresponse Characteristics.** Detailed investigation on the photoresponse properties of the samples has been carried out by recording the transient photoresponse for 10 min under illumination of all four reference wavelengths 350, 400, 470, and 570 nm (Figure 7).

After analyzing the transient curves, the values of the dark and photocurrent densities, corresponding gain (calculated as the ratio of photo-to-dark current density), responsivity, and detectivity for detecting lights of different wavelengths have been noted in Table 1.

After analyzing the transient curves, the values of the dark and photocurrent densities, corresponding gain (calculated as the ratio of photo-to-dark current density), responsivity, and detectivity for detecting lights of different wavelengths have been noted in Table 1. The values of gain, responsivity, and detectivity are the highest for detecting 400 nm light for all NR film samples. Table 1 clearly reveals that S3 has the highest values of all of the photoresponse parameters for all four detecting wavelengths among the TiO₂ NR films. The responsivity values of S3 for detecting 350, 400, and 470 nm lights increase by more than 1 order of magnitude, whereas for detecting 570 nm, it increases by more than 2 orders of magnitude as compared to that of control samples (S1 and S2), indicating wide and much superior photoresponse properties of S3 for broad-band light detection in the UV–visible region. The enhanced photocconductivity in the visible region caused by Ti³⁺ defect states situated below conduction band minima is due to an efficient electron transfer through defect sites. Paul et al.⁵² also find enhanced photoresponse in visible illumination because of enhancement of defect states in TiO₂ NRs.

**Power Dependence of Photocurrent Transients for 400 nm.** As the highest responsivity has been achieved for 400 nm for all of the samples, power-dependent photocurrent transients are measured by varying the power density of 400 nm illumination from 880 to 36 μW/cm² at a fixed bias voltage of −4 V (Figure 8). All three NR film samples (S1, S2, and S3) show an enhanced photocurrent as the power is increased gradually.

Power law fitting ($J_{ph} \propto P^\alpha$, where $P$ is the power density of illumination and $\alpha$ is the coefficient of power density) of NR film samples in 400 nm illumination is shown in Figure 8d, which reveals that the photocurrent of S1 and S2...
varies sublinearly for both lower and higher power illuminations, whereas the $\alpha$ value is more in S2 than in S1. A similar result is found by Mondal et al. after vacuum annealing of TiO$_2$ NP thin films. Interestingly, the photocurrents for S3 vary superlinearly and slightly sublinearly, respectively, for the lower and higher power illuminations, though for both cases, the values are much higher than those of S1 and S2. This result indicates that photogenerated charge separation in S3 is much efficient because of the Ti$^{3+}$ defect states as compared with the control samples.

**Power Dependence of Broad-Band Photoresponse.**

As the S3 sample shows a very high photoresponse in a broad...
wavelength region, to check its suitability as a broad-band photodetector with low power detectivity, power dependence of the photocurrent transients has been investigated for 350, 470, and 570 nm illuminations, which are plotted in Figure 9. The corresponding power law fitting is plotted in the inset of each figure. Similar to the case of 400 nm, for other detectable illuminations also, the photocurrent increases as the power of illumination increases. In 350 nm illumination, when the power density decreases from 570 to 25 μW/cm², the responsivity value also decreases from 0.42 to 0.16 A/W. However, the responsivity values are 0.07 and 0.08 A/W, respectively, for the highest power densities of 1.28 and 0.76 mW/cm² for detecting 470 and 570 nm illuminations, which are quite high. Even for the lowest illumination powers of 48 μW/cm² (470 nm) and 28 μW/cm² (570 nm), S3 shows very high responsivity values of 4.15 and 6.3 mA/W, respectively. These results indicate interesting properties of S3 for low-power as well as broad-band SJ-based photodetection. However, unless a hybrid material system is taken, it is difficult to obtain almost equal response in both the UV and the visible region using a single semiconducting material because at the expense of one (band (VB)-to-band (CB) excitation leading to UV region current) the other (defect state-to-conduction band excitation leading to visible region current) occurs. Interestingly, in comparison with the pristine sample (S1), the enhancement of responsivity of S3 in the UV illumination (400 nm) is ∼50 times and in the visible illumination (570 nm) is ∼200 times. The ratio of responsivity values in visible illumination (570 nm) to those in UV illumination (400 nm) for S3 is ∼0.11, whereas for S1, the

Table 2. Comparative Study of Operating Parameters of the Present Junction with Other Published Data

| sample | bias (V) | detectable illumination | responsivity (mA/W) | reference |
|--------|---------|-------------------------|---------------------|-----------|
| Ti/TiO₂ NW/Pt | 5 | 390 nm | 7 × 10⁻² | Tsai et al.⁵⁴ |
| FTO/TiO₂ NR/polyfluorene/Au | 5 | UV light (3.6 mW/cm²) | 3 | Han et al.⁵⁵ |
| FTO/TiO₂ NRs cloths/FTO | −1 | 365 nm (1.25 mW/cm²) | 17 | Wang et al.⁵⁶ |
| FTO/TiO₂ NR/PPH/Au | 0 | 365 nm (3.2 mW/cm²) | 14 | Han et al.⁵⁷ |
| p-Si(111)/TiO₂ NRs/platinum | 5 | 395 nm | 33 | |
| Ti sheet/hydrogenated TiO₂ NTs | 0.7 | solar light (100 mW/cm²) | 1.2 | Wei et al.⁵⁹ |
| visible light (100 mW/cm²) | 0.3 | |
| Au/TiO₂ NR/Au (S3) | −4 | 350 nm (0.57 mW/cm²) | 4.2 × 10² | this work |
| 400 nm (0.88 mW/cm²) | 7.1 × 10² |
| 470 nm (1.28 mW/cm²) | 68 |
| 570 nm (0.76 mW/cm²) | 78 |

Figure 10. Photocurrent transient on–off cycle measurements for the S3 sample for (a) 350 nm, (b) 400 nm, (c) 470 nm, and (d) 570 nm illuminations. The shaded region in the graphs denotes the illumination period.
value is \( \sim 0.03 \). It is always better to be able to detect lower-intensity lights than higher-intensity lights. In our case, lower-intensity visible lights are better detected by the S3 sample.

To evaluate the stability of the best-performed sample (S3) in the wide spectral range, transient photoresponse cycle measurements for 350, 400, 470, and 570 nm have been performed, and the results are shown in Figure 10a–d. In almost all cycles, the highest photocurrent density remains similar with only 5% change. Therefore, it is quite clear from the figures that the photodetection property of S3 is quite stable.

A comparison of the performance of our Au/TiO\(_2\) NR film/Au SJs with that reported in other studies wherein TiO\(_2\) nanostructures have been used is shown in Table 2.

Table 2 reveals that our Au/TiO\(_2\) NR film-based SJ is not only operating for a broad-band range with higher responsivity values as compared with other reported values but also capable of detecting lights of low intensity, which adds an extra benchmark for the present Au/TiO\(_2\)/Au SJs. However, Zheng et al.\(^60\) have reported a very high responsivity value for a detectable wavelength of 365 nm, which is improbable.

**CONCLUSIONS**

In summary, the photosensitivity of SJs based on H\(_2\)-annealed self-seeded TiO\(_2\) NRs is reported. Due to annealing in H\(_2\) under high vacuum, Ti\(^{3+}\) surface defects below the conduction band minima of TiO\(_2\) arise, contributing not only to a high value of responsivity but also to a detection of a broad-band photo in Au/self-seeded TiO\(_2\) NR film/Au SJs. Detection of lights of UV to visible regions as well as with a very low power of <50 \( \mu \)W/cm\(^2\) with high responsivity values, which is not reported earlier, makes this SJ a probable candidate for a low-cost efficient broad-band photodetector.

**EXPERIMENTAL SECTION**

TiO\(_2\) NR films were hydrothermally grown on ordinary glass substrates. First, the glass substrates were properly cleaned for deposition of the seed layer. A TiO\(_2\) pellet (purity \( \sim 99.9\%\), Merck) was mounted in a target holder of the PLD chamber (Neocera) fitted with a KrF excimer laser (Coherent) with an emission wavelength of 248 nm. TiO\(_2\) film deposition was done on a cleaned glass substrate, maintaining the substrate temperature at 500 °C. The laser energy was 330 mJ/pulse with a repetition of 10 Hz.

To make a precursor of TiO\(_2\), a homogeneous clear mixture of distilled water and HCL (37%) in 1:1 ratio was stirred for 20 min and 50 mM titanium butoxide was then added into the mixture. Next, the seeded substrates were put into a Teflon-lined stainless steel autoclave containing the precursor solution. During growth, the autoclave was maintained at 150 °C for 12 h. After completion, the samples were taken out, cleaned by gently spraying water onto them, and put into an oven to dry at 120 °C. This as-grown sample was labeled as S1.

Next, a sample was annealed at 400 °C in vacuum for 1 h, named S2, and another sample was annealed at 400 °C for 1 h in H\(_2\) ambient (10% H\(_2\) and 90% Ar), named S3. Therefore, S1 and S2 are the control samples, whereas S3 is the sample under test. The seed layer is termed as S0.

The TiO\(_2\) NR films were characterized by various analytic and spectroscopic techniques using X-ray diffraactometry (XRD; model X’pert pro, PANalytical), UV–vis spectrophotometry (PerkinElmer model Lamda 35), X-ray photoelectron spectroscopy (XPS, Omicron, serial no.: 0571), and field
emission scanning electron microscopy (FESEM, JEOL; JSM-7500F). For photoconductivity measurement, two 70 nm thick Au (2 mm diameter) contacts were deposited through a mask on the films, wherein the illuminated area confined in between two contacts is 4 mm². The coating of Au contacts is done by a vacuum coating unit (Hind Hvac 12° vacuum coating unit; model 12A4D). Films were kept in the dark for several hours to reach an equilibrium dark current value. As an illumination source, a Xe lamp (Newport; model 66902) fitted with a monochromator was used. The power density of each illumination falling on the sample is measured by a power meter (Newport; model 1930C), exactly maintaining a similar position and other measurement conditions.

Photocurrent measurements between two contacts were performed using a Keithley source meter, model 2410, and a GPiB data transfer card. A schematic is shown in Figure 11 to show the formation and measurement of photocurrent of the Au/self-seeded TiO2 NR film/Au SJs.

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**Notes**
The authors declare no competing financial interest.

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