

# Ultrahigh quantum efficiency photodetector and ultrafast reversible surface wettability transition of square $\text{In}_2\text{O}_3$ nanowires

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## ABSTRACT

Due to a large surface-to-volume ratio, the optoelectronic performance of low-dimensional semiconductor nanostructure-based photodetectors depends in principle on chemisorption/photodesorption at the exposed surface, but practical examples that show such an effect are still unavailable. Some theoretical calculations have predicted that the {001} facets of  $\text{In}_2\text{O}_3$  can effectively accumulate photogenerated holes under irradiation, providing a model material to examine whether the facet cutting of nanowires (NWs) can boost their optoelectronic performance. Herein, we present the design and construction of a novel nanowire-based photodetector using square  $\text{In}_2\text{O}_3$  NWs with four exposed {001} crystal facets. The photodetector delivers excellent optoelectronic performance with excellent repeatability, fast response speed, high spectral responsivity ( $R_\lambda$ ), and high external quantum efficiency (EQE). The  $R_\lambda$  and EQE values are as high as  $4.8 \times 10^6$  A/W and  $1.46 \times 10^9\%$ , respectively, which are larger than those of other popular semiconductor photodetectors. In addition, the square  $\text{In}_2\text{O}_3$  NWs show hydrophobic wettability as manifested by a contact angle of  $118^\circ$  and a fast photoinduced reversible switching behavior is observed.

## 1 Introduction

Low-dimensional semiconductor nanostructures have

attracted considerable attention since they provide possibilities for revolutionary advances in nanodevices such as photodetectors, photovoltaics, and lasers [1–4].

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In particular, nanostructured photodetectors have promising applications in light-wave communication, optical imaging, optoelectronic integrated circuits, and so on [5–8]. As such, considerable effort has been put into designing and fabricating photodetectors using different kinds of nanostructures [9–15]. Nevertheless, owing to the large surface-to-volume ratio and abundant surface states, photogenerated carriers can be lost due to surface recombination, thereby shortening the carrier lifetime and compromising the performance of the nanophotodetector [16, 17]. To solve this problem, several strategies have been proposed, for instance, surface modification (such as surface passivation, metal deposition) and fabrication of heterostructures [16, 18, 19]. Despite recent advances, the performance of photodetectors still cannot meet practical demand and a novel approach to suppress surface recombination of photogenerated carriers is imperative. It has recently been shown that photogenerated electrons and holes can be driven to different crystal facets by the difference in the energy levels between the facets to promote separation of the photogenerated carriers [20–23]. This phenomenon may be exploited to enhance the optoelectronic properties of nanostructures by controlling the exposed facets.

Indium oxide ( $\text{In}_2\text{O}_3$ ), an important n-type semiconductor with excellent electrical and optical properties, is a prospective building block for next-generation electronic and optoelectronic devices [24–28]. Theoretical calculation has predicted that the polar {001} facets of  $\text{In}_2\text{O}_3$  can accumulate photogenerated holes [29–31], implying that the optoelectronic performance can be boosted by chemisorption/photodesorption of oxygen. Hence, a photodetector composed of a single  $\text{In}_2\text{O}_3$  nanowire (NW) with only the exposed {001} facet may deliver enhanced optoelectronic performance. The operating principle of a single  $\text{In}_2\text{O}_3$  NW-based photodetector is displayed in Figs. 1(a) and 1(b). Under dark conditions, oxygen molecules tend to chemisorb onto the n-type  $\text{In}_2\text{O}_3$  NW {001} facets by trapping free electrons from the conduction band and becoming negative ions  $\text{O}_2^-$ , which reduces the free electron density,  $\text{O}_2(\text{g}) + \text{e}^- \rightarrow \text{O}_2(\text{ad})$ . This process forms a depletion layer and upward surface band bending (SBB) near the {001} facets leading to low conductivity. When illuminated with light energy above the bandgap

of  $\text{In}_2\text{O}_3$ , electron–hole pairs are created in the bulk. Owing to the presence of new valence subbands, the photogenerated holes will migrate from the bulk towards the top exposed {001} facets and these accumulated holes can react with the negatively charged adsorbed oxygen ions, resulting in oxygen desorption and concomitant release of the captured free electron  $\text{h}^+ + \text{O}_2(\text{ad}) \rightarrow \text{O}_2(\text{g})$ . Oxygen desorption can reduce the SBB and decrease the width of the depletion layer, so that the square  $\text{In}_2\text{O}_3$  NW delivers better optoelectronic performance than other nanostructures. Furthermore, it is found that the square  $\text{In}_2\text{O}_3$  NWs also show a faster transition of the photoinduced surface wettability between hydrophobicity and hydrophilicity as a result of the unique surface electronic band structure.

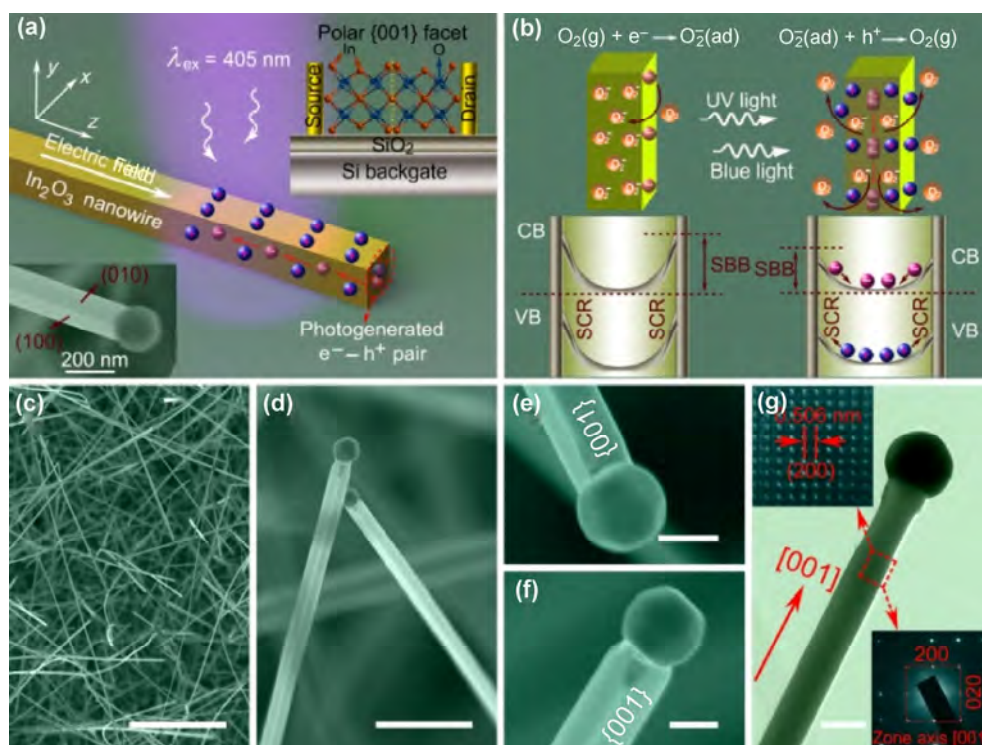
## 2 Experimental

### 2.1 Sample preparation

$\text{In}_2\text{O}_3$  NWs were fabricated by chemical vapor deposition (CVD) [31]. A mixture of high-purity  $\text{In}_2\text{O}_3$  (0.2 g, 99.99%) and active carbon (0.3 g) was used as the source and loaded onto an alumina boat which was inserted into a quartz tube at the front end of a furnace. A Si wafer (0.5 mm thick, and 1 cm × 1 cm in size) coated with a 5 nm thick gold film was placed downstream in the quartz tube to collect the products. Prior to heating, the furnace was evacuated to 20 mTorr to remove residual oxygen from the system. The furnace was heated to 1,100 °C in 20 min and kept at this temperature for 2.5 h. During sample fabrication, a mixture of Ar (98%) and  $\text{O}_2$  (2%) was bled at a flow rate of 100 sccm and the pressure inside the furnace was 1 atm. After the system was cooled to room temperature, a light grey layer was deposited on the silicon substrate.

### 2.2 Fabrication of field-effect transistors (FETs) and photodetectors

To fabricate the single-NW-based devices, the  $\text{In}_2\text{O}_3$  NW was carefully detached from the Si substrate by ultrasonic treatment to produce a suspension in ethanol with a density ensuring successful preparation of a single NW device. The NWs were dispersed in low



**Figure 1** (a) Operating principle of the photodetector comprising a single In<sub>2</sub>O<sub>3</sub> NW. (b) Corresponding schematic showing SBB caused by oxygen chemisorption/photodesorption with and without light illumination. (c) and (d) Low- and high-magnification FE-SEM images of the In<sub>2</sub>O<sub>3</sub> NWs. (e) and (f) High-magnification FE-SEM images acquired from different directions of a NW showing the square cross section. (g) Low-magnification image of a single In<sub>2</sub>O<sub>3</sub> NW. The top left and bottom right insets depict the HR-TEM image and SAED pattern of the area marked by the red dashed box. Scale bars: (c) 10 and (d) 1  $\mu$ m, and (e)–(g) 100 nm.

densities onto 300 nm SiO<sub>2</sub>/Si substrates by spin casting. The SiO<sub>2</sub>/Si substrates were first subject to a 30 min UV/ozone treatment, followed by spinning at 1,000 rpm. Standard photolithography was employed to pattern the electrodes of In<sub>2</sub>O<sub>3</sub> back-gated FETs onto the 300 nm SiO<sub>2</sub>/Si substrates. Ti/Au (10/100 nm) source and drain electrodes were deposited on top of the NWs by electron-beam deposition, followed by lift-off. All devices were annealed at 300 °C in Ar to improve contacts.

### 2.3 Characterization

The In<sub>2</sub>O<sub>3</sub> NWs were characterized by X-ray powder diffraction (XRD, Philips, Xpert), field-emission scanning electron microscopy (FE-SEM, Hitachi S4800), high-resolution transmission electron microscopy (HR-TEM, JEOL-2100), X-ray photoelectron spectroscopy (XPS, PHI5000 VersaProbe), and a VARIAN Cary 5000 spectrophotometer. The electronic and optoelectronic measurements were conducted on the Keithley 4200

semiconductor characterization system in a Cascade Summit 12000 probe station. In the photoresponse determination, 350, 405, 470, 505 and 625 nm laser diodes were employed. All the measurements were all performed in air and at room temperature unless mentioned otherwise. The surface wettability was evaluated by measuring the water contact angle (CA) using an OCA200 contact angle system (Dataphysics, Germany).

## 3 Results and discussion

### 3.1 Structural characterization

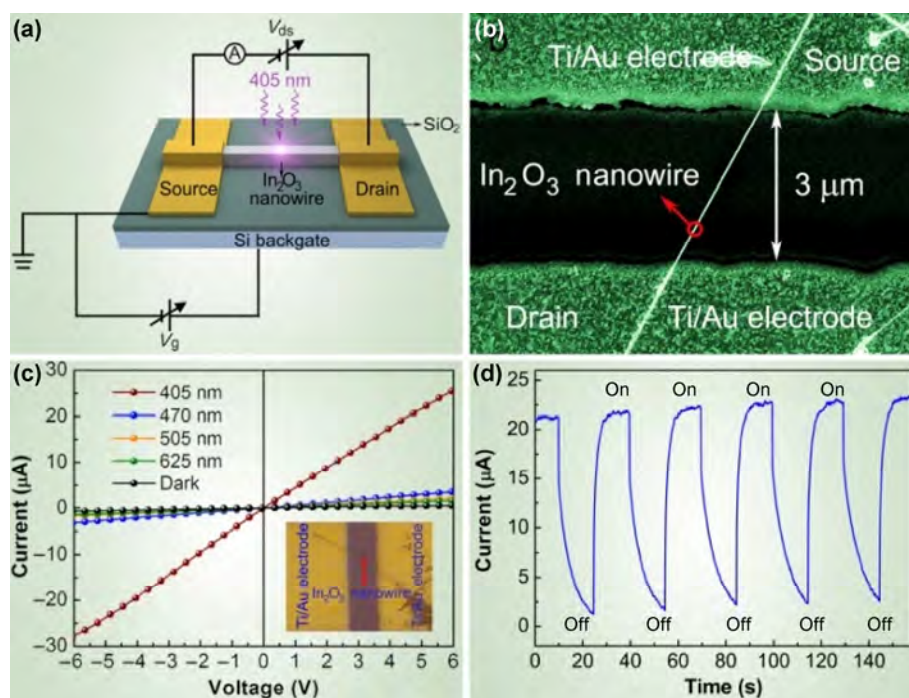
The XRD results in Fig. S1 in the Electronic Supplementary Material (ESM) show strong, sharp reflection peaks that can be indexed to the body-centered cubic (bcc) structure of In<sub>2</sub>O<sub>3</sub> (JCPDS card No. 06-0416), suggesting that the In<sub>2</sub>O<sub>3</sub> NWs have high crystallinity. No impurity peaks are observed. The XPS spectra

provide evidence of the formation of pure  $\text{In}_2\text{O}_3$  with some oxygen deficiencies (Fig. S2 in the ESM). FE-SEM images show that the product consists of a large quantity of NWs with lengths ranging from several tens to hundreds of micrometers and a uniform width over their entire length (Fig. 1(c) and Figs. S3(a) and S3(b) in the ESM). Figure 1(d) and Fig. S3(c) in the ESM show that the square  $\text{In}_2\text{O}_3$  NWs have a uniform size distribution and the average width is approximately 100 nm. Hence, the square  $\text{In}_2\text{O}_3$  NWs can be used to construct a single NW-based photodetector with excellent repeatability and stability. The high-magnification FE-SEM images of an individual  $\text{In}_2\text{O}_3$  NW obtained from different directions (Figs. 1(e) and 1(f), and Fig. S4(a) in the ESM) show that the NW has typical rectangular prismatic morphology with four smooth lateral facets between adjoining edges with corresponding interfacial angles of  $90^\circ$ . This value is identical to the theoretical value for the angle between the  $\{100\}$  and  $\{010\}$  facets of the bcc structure of  $\text{In}_2\text{O}_3$  (Figs. S4(b) and S4(c) in the ESM). FE-TEM was performed to identify the crystallographic growth direction and exposed lateral facets of the

square NWs. The low-magnification FE-TEM image in Fig. 1(g) confirms the wire-like geometry and the HR-TEM image reveals  $\{200\}$  and  $\{020\}$  crystallographic facets with a lattice spacing of 0.506 nm and interfacial angle of  $90^\circ$ , implying that the preferred growth direction of the square  $\text{In}_2\text{O}_3$  NWs is along the  $\{001\}$  orientation (top left inset in Fig. 1(g) and Fig. S4(d) in the ESM). The selected area electron diffraction (SAED) pattern displays a square diffraction spot (bottom right inset in Fig. 1(g)). These results provide convincing evidence that each square  $\text{In}_2\text{O}_3$  NW is enclosed by four high-symmetry  $\{001\}$  facets. The growth mechanism has been described in our previous work [31]. Succinctly speaking, a combination of both Au catalytic vapor–liquid–solid (VLS) and vapor–solid (VS) mechanisms is responsible for formation of square  $\text{In}_2\text{O}_3$  NWs.

### 3.2 Optoelectronic performance of a single $\text{In}_2\text{O}_3$ NW

Photodetectors based on a single  $\text{In}_2\text{O}_3$  NW were fabricated and their optoelectronic properties were determined. A schematic of the single NW-based photodetector and representative FE-SEM image are



**Figure 2** (a) and (b) Schematic and FE-SEM image of a single  $\text{In}_2\text{O}_3$  NW-based photodetector structure. (c)  $I$ - $V$  curves of the NW-based photodetector with and without light illumination at different wavelengths. The inset shows a micrograph of the device. (d) Current–time response measured by periodically switching on and off 405 nm light illumination at a bias of 5 V.

presented in Fig. 2(a) and 2(b), respectively. As shown in Fig. 2(a), two Ti/Au electrodes (10 nm/100 nm) with a 3  $\mu\text{m}$  separation are deposited onto the  $\text{In}_2\text{O}_3$  NWs on the  $\text{SiO}_2/\text{Si}$  substrate, which serve as the source and drain, respectively. The NW connecting the two electrodes has a typical length of 3.7  $\mu\text{m}$  and width of 100 nm and is exposed to light as shown in Fig. 2(b) (denoted as device 1). The inset of Fig. 2(c) and Fig. S5 in the ESM show typical optical images of the device. A clear contrast is visible between the NW and Au electrode on the  $\text{SiO}_2/\text{Si}$  substrate, corroborating the FE-SEM result in Fig. 2(b) and demonstrating that there is only one NW between source and drain. The current versus voltage ( $I$ - $V$ ) curves of device 1, measured with and without light exposure at different wavelengths, are displayed in Fig. 2(c) and Fig. S6 in the ESM. The linear and symmetrical  $I$ - $V$  curves suggest good Ohmic contact between the NW and Ti/Au electrodes [32]. The electrical transport characteristics of the NW measured based on the back-gated  $\text{In}_2\text{O}_3$  NW FETs as shown in Fig. S7 in the ESM also confirm this point [24–26]. The dark current of the device is 0.45  $\mu\text{A}$ . Under illumination with light wavelengths of 470 nm (0.79  $\text{mW}/\text{cm}^2$ ), 505 nm (0.55  $\text{mW}/\text{cm}^2$ ), and 625 nm (0.46  $\text{mW}/\text{cm}^2$ ), the photocurrents slightly increase compared to the dark current. In contrast, when exposed to light energy greater than the bandgap of  $\text{In}_2\text{O}_3$  (2.8 eV, 442 nm), the photocurrents increase drastically. To demonstrate this phenomenon more clearly, the photocurrent measured at 5 V is shown in Fig. S8 in the ESM. When illuminated with 405 nm light (1.21  $\text{mW}/\text{cm}^2$ ), the photocurrent reaches 21.7  $\mu\text{A}$  which indicates a 47-fold enhancement compared to that in darkness. The results demonstrate the excellent photoresponse ability and wavelength selectivity of the square NW-based photodetector.

Generally, the repeatability and response speed are key parameters of a photodetector [33]. To evaluate these two factors, the current–time response was examined by periodically switching on and off the 405 nm light illumination in air at a bias of 5 V (Fig. 2(d) and Fig. S9(a) in the ESM). When the light is turned on, the photocurrent increases rapidly to a stable value of 21.7  $\mu\text{A}$  and then sharply reverts to the original value when the light is turned off. The reversible periodic switching between on and off

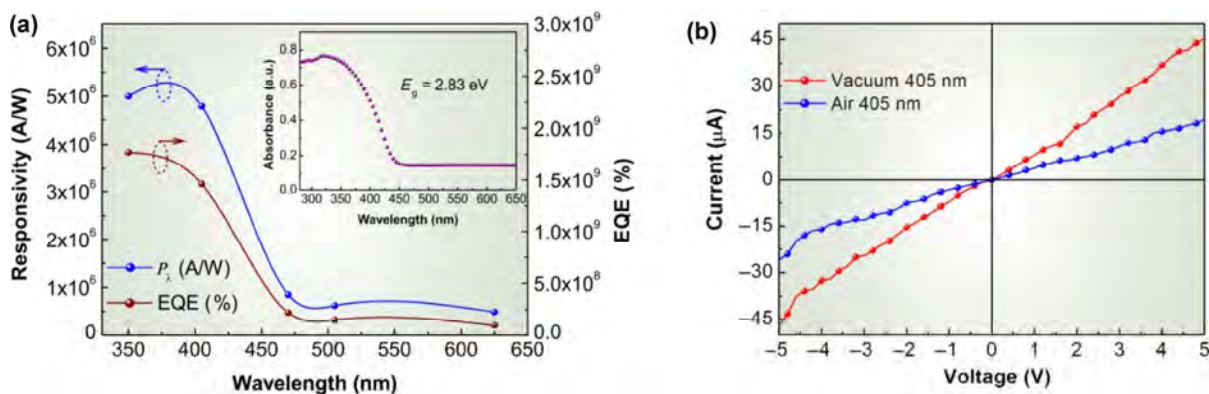
states upon turning on/off light illumination is clearly observed during the entire observation time of 10 min, which suggests excellent repeatability and stability. The rise and decay times, defined as the time needed for peak photocurrent to change from 10% to 90% of its maximum value or vice versa [9], were measured to be 3 and 13 s, respectively. In addition, they are stable after 20 switching cycles and much faster than the values previously observed from  $\text{In}_2\text{O}_3$ -based photodetectors as shown in Fig. S9(b) and Tables S1 and S2 in the ESM [27, 34].

In addition to the repeatability and response rate, the spectral responsivity ( $R_\lambda$ ) and external quantum efficiency (EQE) or quantum efficiency (QE) are two important parameters for a photodetector and they impact applications [12, 35].  $R_\lambda$  can reflect the wavelength selectivity of a photodetector and is defined as the ratio of the photocurrent to the incident light intensity. EQE is related to the sensitivity and is defined as the conversion rate of photons to electron–hole pairs. They can be expressed by the following equations, respectively

$$R_\lambda = \frac{\Delta I}{PS} \quad (1)$$

$$\text{EQE} = \frac{hc}{e\lambda} R_\lambda \quad (2)$$

Where  $\Delta I$  is the difference between the photocurrent and dark current,  $P$  is the incident light power density,  $S$  is the effective illumination area of the photodetector,  $h$  is Planck's constant,  $c$  is the speed of light,  $e$  is the electronic charge, and  $\lambda$  is the wavelength of the incident light. Based on Fig. S8 in the ESM,  $R_\lambda$  and EQE of the NW-based photodetector can be calculated and the results are shown in Fig. 3(a). When irradiated with 405 nm light, the  $R_\lambda$  and EQE values are as large as  $4.8 \times 10^6$  A/W and 1.46  $\times 10^9\%$  at an applied voltage of 5 V. Both values are not only the largest among the reported  $\text{In}_2\text{O}_3$ -based photodetectors, but also larger than those of many other popular semiconductor photodetectors as shown in Table S3 in the ESM [36]. More importantly,  $R_\lambda$  and EQE values remain almost unchanged after 20 switching cycles, providing more evidence for the stability of the NW-based photodetector (Fig. S10 and Table S1 in the ESM).



**Figure 3** (a) Responsivity and EQE versus incident wavelength at a bias of 5 V. (b)  $I$ - $V$  curves of the NW-based photodetector illuminated with light of 405 nm in air and under vacuum conditions.

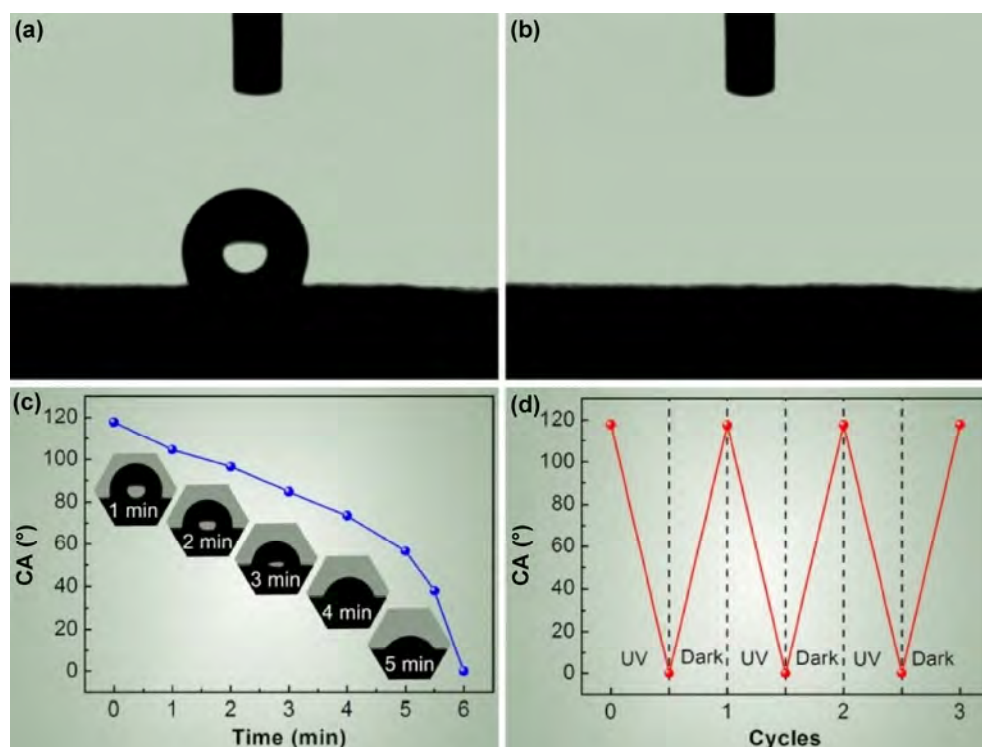
Such an ultrahigh EQE may be attributed to the exposure of {001} facets via chemisorption/photodesorption of oxygen. As mentioned above, due to the presence of new valence subbands, under illumination more photogenerated holes can accumulate on the {001} facets and discharge the negatively charged adsorbed oxygen ions, resulting in oxygen desorption and concomitant release of the captured free electron. The  $I$ - $V$  characteristics of device 1 in a vacuum and air were further investigated as shown in Fig. 3(b) and Fig. S11 in the ESM. The dark current measured under vacuum conditions is about 1.6 times larger than that in air at an applied voltage of 5 V, verifying the existence of oxygen chemisorption/photodesorption on the {001} facets [12, 13]. The photocurrent obtained under vacuum conditions is about 2.3 times larger than that in air, which reveals that the exposed {001} facets play a crucial role in the enhanced optoelectronic performance. This justifies the use of  $\text{In}_2\text{O}_3$  NWs with exposed {001} facets as the building blocks of photodetectors. Additionally, when the wavelength of the incident light was changed,  $R_\lambda$  exhibited an obvious dependence on the wavelength. It is evident that  $R_\lambda$  is very low for wavelengths longer than 470 nm and start to gradually increase when illuminated by light with energy above the bandgap of  $\text{In}_2\text{O}_3$ , confirming the wavelength selectivity. This is consistent with the stronger absorption at wavelengths below 442 nm in the UV-vis absorption spectrum (inset in Fig. 3(a)). The high spectral selectivity and large EQE suggest that the square  $\text{In}_2\text{O}_3$  NWs have

great potential for use in blue/UV-light photodetectors (below 442 nm).

To study the reproducibility of the photosensitive properties of the  $\text{In}_2\text{O}_3$  NWs, 20 photodetectors were prepared by the same procedure. The insets of Figs. S12(a) and S12(b) in the ESM depict the typical FE-SEM images of two devices (denoted as devices 2 and 3) with different channel widths between two electrodes. The corresponding  $I$ - $V$  curves obtained under the same conditions reveal that they have the same trend as the shown device above, suggesting good reproducibility. The slight difference in the photocurrent is ascribed to the difference in the effective illumination area between these two devices.

### 3.3 Reversible wettability switching behavior of square $\text{In}_2\text{O}_3$ NWs

The square  $\text{In}_2\text{O}_3$  NWs not only deliver high performance as a photodetector, but also show controllable wettability including fast conversion between hydrophobic and hydrophilic states. Smart devices such as intelligent microfluidic switches have attracted attention and functional surfaces with reversible and tunable wettability are of interest [37–40]. The surface wettability of the square  $\text{In}_2\text{O}_3$  NWs was assessed by measuring the CA and the results are shown in Fig. 4 and Fig. S13 in the ESM. The water CA on the square  $\text{In}_2\text{O}_3$  NWs was about  $118^\circ$  (Fig. 4(a)), nearly 6 times larger than that of pure  $\text{In}_2\text{O}_3$  film and comparable to those of multikinked and ultrathin  $\text{In}_2\text{O}_3$  NWs



**Figure 4** Reversible photoinduced wettability transition on the squared  $\text{In}_2\text{O}_3$  NWs tested with a water droplet: (a) before and (b) after UV illumination. (c) Water contact angles as a function of UV illumination time. The optical images display gradual decrease in the water contact angles under UV illumination. (d) Reversible wettability transition by alternating UV illumination and dark storage.

[24, 25, 41]. As reported, the air trapped in the troughs between randomly distributed  $\text{In}_2\text{O}_3$  NWs is responsible for their hydrophobic nature [42].

The evolution of the CA on the square  $\text{In}_2\text{O}_3$  NWs with UV light (30 W, 365 nm) exposure time is illustrated in Fig. 4(c). The CA gradually decreases with exposure time as shown in the inset in Fig. 4(c), in which the sequence of spreading water droplets on the surface under UV irradiation is revealed. After exposure to UV light for 6 min, the CA of the square  $\text{In}_2\text{O}_3$  NWs was about  $0^\circ$  (Fig. 4(b)), indicative of switching from the hydrophobic to hydrophilic states. Upon UV irradiation, electrons and holes are generated in the conduction band (CB) and valence band (VB) of the square  $\text{In}_2\text{O}_3$  NWs, respectively. The photogenerated holes tend to transfer to the {001} facets first and then oxidize the lattice oxygen to produce surface oxygen vacancies, that is, surface defective sites. It has been demonstrated that such defective sites can enhance  $\text{H}_2\text{O}$  dissociative adsorption on account of strong adsorption between oxygen vacancies and hydroxyl groups, thereby making the

surface of the square  $\text{In}_2\text{O}_3$  NWs hydrophilic [43, 44]. The hydrophobic/ hydrophilic transition rate of the square  $\text{In}_2\text{O}_3$  NWs was  $19.6^\circ/\text{min}$ , which is about 50 times that of the aligned  $\text{In}_2\text{O}_3$  NWs arrays ( $0.4^\circ/\text{min}$ ) and much faster than the transition rate of  $13.4^\circ/\text{min}$  observed from ultrathin  $\text{In}_2\text{O}_3$  NWs before [24]. This may be ascribed to the exposed {001} facets ability to effectively gather photogenerated holes. When irradiated with UV light, more photogenerated holes accumulate on the {001} facets leading to the formation of more oxygen vacancies on the surface. Consequently, it is not surprising that the square  $\text{In}_2\text{O}_3$  NWs exhibit a faster hydrophobicity–hydrophilicity transition rate. When the UV irradiated  $\text{In}_2\text{O}_3$  NWs are stored in darkness for 1 week, the wettability reverts to the native hydrophobic state and the process can be repeated (Fig. 4(d)). This reversible wettability is believed to arise from replacement of hydroxyl adsorption on the surface defective sites by oxygen in air and darkness because oxygen adsorption is thermodynamically more stable, thereby returning the surface of square  $\text{In}_2\text{O}_3$  NWs to their native state.

## 4 Conclusions

In summary, a novel NW-based photodetector was designed and constructed with square  $\text{In}_2\text{O}_3$  NWs with exposed four {001} facets. The photodetector delivers excellent optoelectronic performance including excellent repeatability, fast response speed, high spectral responsivity, and external quantum efficiency. The  $R_{\lambda}$  and EQE values were as high as  $4.8 \times 10^6$  A/W and 1.46 × 10%, respectively, which are larger than those of other popular semiconductor photodetectors. In addition, the square  $\text{In}_2\text{O}_3$  NWs showed hydrophobic wettability as manifested by a CA of 118° and a fast photoinduced reversible switching behavior was observed.

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**Electronic Supplementary Material:** Supplementary material (Table S1: key parameters of photodetector after 20 periodic change; Tables S2 and S3: comparison of some characteristic parameters from this work and previous reports; Figs. S1–S5: XRD pattern, XPS spectra, SEM, schematic model and optical images of square  $\text{In}_2\text{O}_3$  NWs; Figs. S6–S11:  $I$ - $V$ ,  $I$ - $t$  and  $I_{\text{ds}}$ - $V_{\text{ds}}$  curves of device 1; Fig. S12: SEM images,  $I$ - $V$  curves of devices 2 and 3; Fig. S13: contact angles measured from different  $\text{In}_2\text{O}_3$  samples) is available in the online version of this article at <https://doi.org/10.1007/s12274-017-1481-y>.

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## Electronic Supplementary Material

# Ultrahigh quantum efficiency photodetector and ultrafast reversible surface wettability transition of square In<sub>2</sub>O<sub>3</sub> nanowires

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**Table S1** Rise time, decay time, spectral responsivity ( $R_\lambda$ ), and external quantum efficiency (EQE) of the photodetector after 20 periodic change

Rsie time	Decay time	$R_\lambda$	EQE
3 s	13 s	$4.75 \times 10^6$ (A/W)	$1.45 \times 10^7$

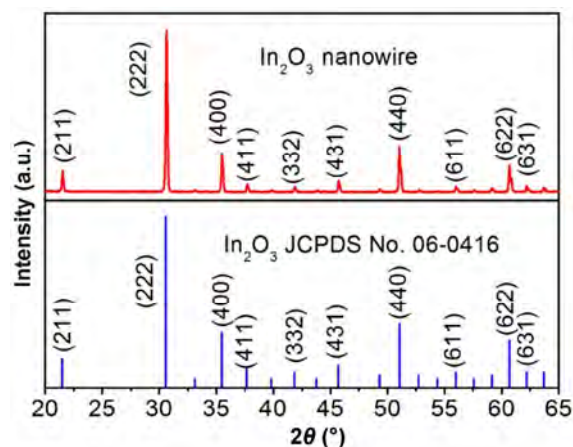
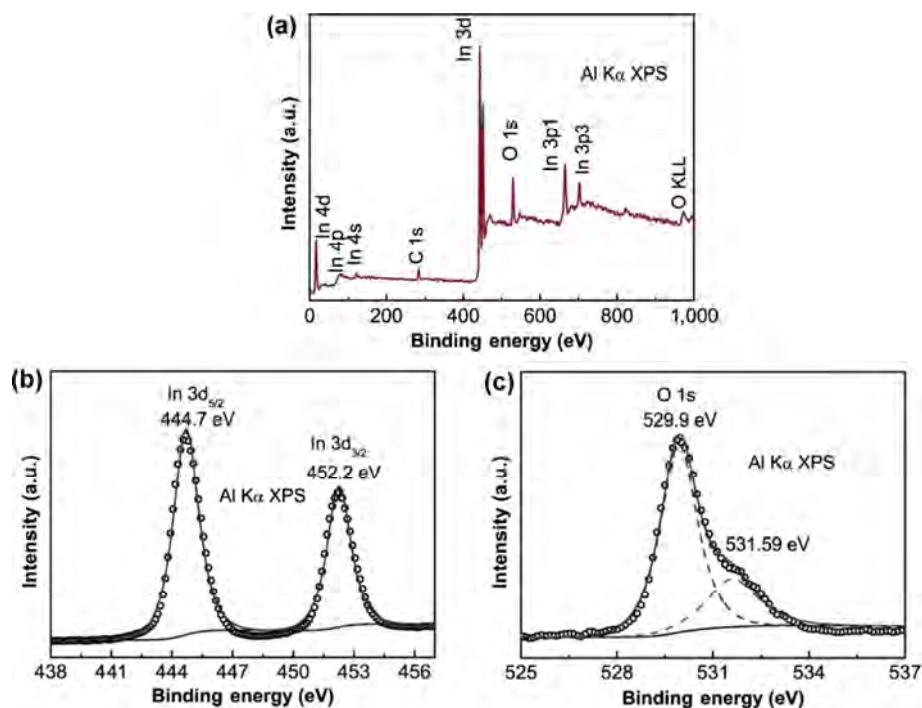
**Table S2** Comparison of the response speeds from the present In<sub>2</sub>O<sub>3</sub>-based photodetector and previously reported In<sub>2</sub>O<sub>3</sub> based photodetectors

Photodetector	Rsie time	Decay time	Reference
In <sub>2</sub> O <sub>3</sub> nanowires	15 s	100 s	[S1]
In <sub>2</sub> O <sub>3</sub> nanoparticles	500 s	1,600 s	[S2]
In <sub>2</sub> O <sub>3</sub> nanowires	3 s	13 s	This work

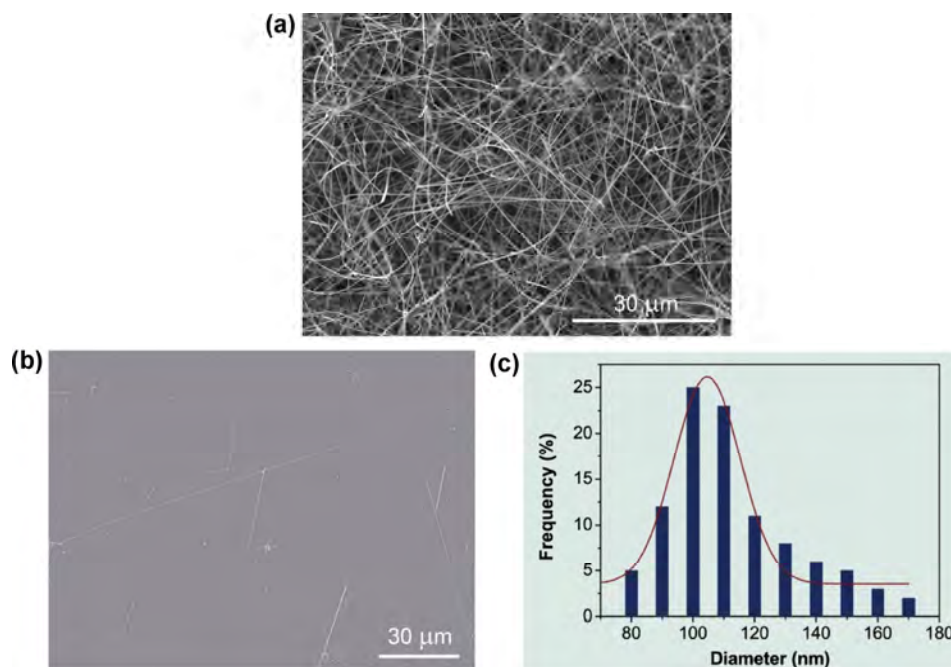
Address correspondence to hkxlwu@nju.edu.cn

**Table S3** Comparison of EQE and  $R_{\lambda}$  from this work and previous reports

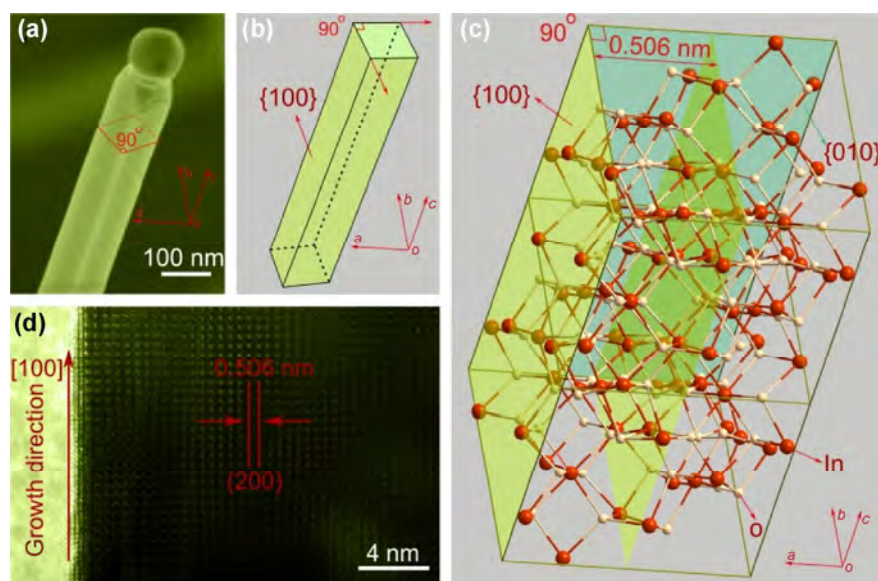
Photodetector	EQE	$R_{\lambda}$	Dark current	Photocurrent	Reference
In <sub>2</sub> O <sub>3</sub> nanoparticles	—	$2 \times 10^3$ (A/W)	—	—	[S3]
In <sub>2</sub> S <sub>3</sub> nanowire	$2.28 \times 10^5$	$7.35 \times 10^4$ (A/W)	0.12 pA (at 5 V)	293 nA (at 5 V)	[S4]
CdS nanobelt	$1.9 \times 10^5$	$7.3 \times 10^4$ (A/W)	5 $\mu$ A (at 1 V)	30 $\mu$ A (at 1 V)	[S5]
ZnS/ZnO biaxial nanobelt	$2 \times 10^6$	$5 \times 10^5$ (A/W)	0.67 $\mu$ A (at 1 V)	4.64 $\mu$ A (at 1 V)	[S6]
SnO <sub>2</sub> nanowire	$1.32 \times 10^7$	—	19.4 nA (at 1 V)	2.1 $\mu$ A (at 1 V)	[S7]
Ga <sub>2</sub> O <sub>3</sub> nanobelt	$4.2 \times 10^3$	851 (A/W)	—	—	[S8]
In <sub>2</sub> O <sub>3</sub> nanowire	$1.46 \times 10^7$	$4.8 \times 10^6$ (A/W)	0.45 $\mu$ A (at 5 V)	21.7 $\mu$ A (at 5 V)	This work

**Figure S1** XRD patterns acquired from the square In<sub>2</sub>O<sub>3</sub> NWs. All the diffraction peaks match those of the bcc structure of In<sub>2</sub>O<sub>3</sub> (JCPDS card No. 06-0416).**Figure S2** (a) Wide-scan survey XPS spectrum for In<sub>2</sub>O<sub>3</sub> NWs. (b) and (c) High-resolution XPS spectra of In 3d and O 1s obtained from the In<sub>2</sub>O<sub>3</sub> NWs, respectively.

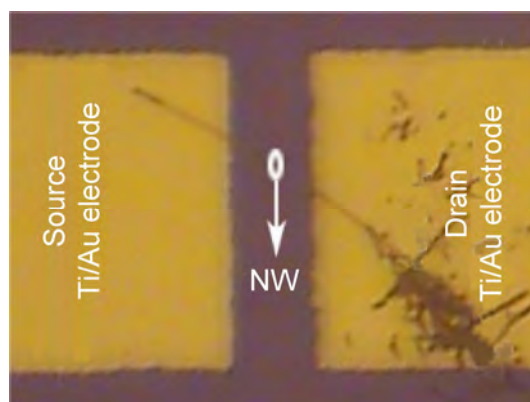
The wide-scan survey XPS spectrum shows the presence of only In, O, and C in the square  $\text{In}_2\text{O}_3$  NWs, suggesting that they have a pure  $\text{In}_2\text{O}_3$  phase (Fig. S2(a)). Figure S2(b) is the high-resolution XPS spectrum of In 3d showing characteristic peaks of 447.7 eV (In  $3d_{5/2}$ ) and 452.2 eV (In  $3d_{3/2}$ ) corresponding to chemical element state of  $\text{In}^{3+}$  ( $\text{In}_2\text{O}_3$ ). In the O 1s spectrum, the peak at 529.9 eV and shoulder at 531.6 eV are observed. The peak at 529.9 eV is ascribed to the oxygen bond of In–O–In, whereas that at 531.6 eV is attributed to surface oxygen defects. The analytical results confirm that the NWs are pure  $\text{In}_2\text{O}_3$  with some oxygen defects.



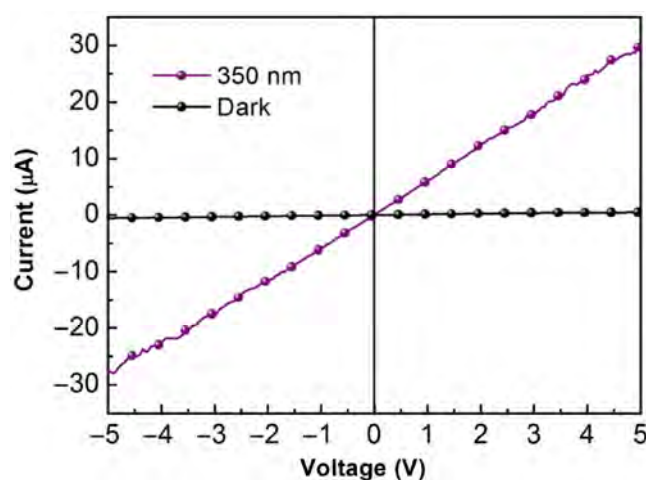
**Figure S3** (a) and (b) Low-magnification FE-SEM images of the  $\text{In}_2\text{O}_3$  NWs fabricated on an Au-coated Si substrate and a thermally oxidized Si substrate covered with a 300 nm  $\text{SiO}_2$  layer with a sparse density, respectively, revealing that the NWs are several tens to hundreds of micrometers in length. (c) NWs diameter distribution showing that the main distribution diameter of the NWs is around 100 nm.



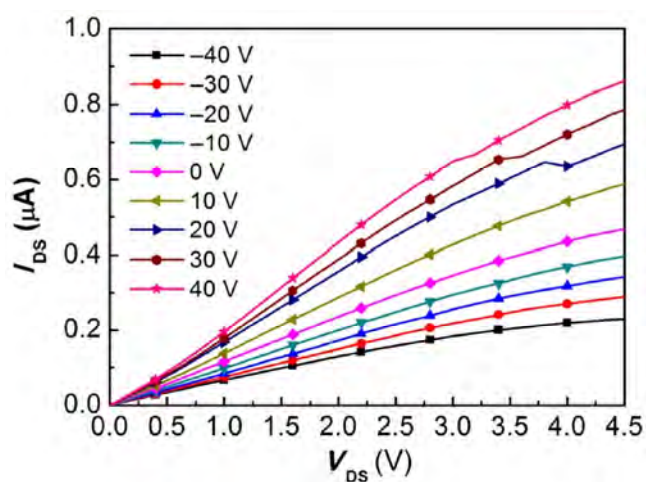
**Figure S4** (a) High-magnification FE-SEM image of an  $\text{In}_2\text{O}_3$  NW displaying the perfect square cross section. (b) Schematic diagram of an  $\text{In}_2\text{O}_3$  NW. The four side facets are {001} facets. (c) Schematic model of an ideal  $\text{In}_2\text{O}_3$  NW enclosed by the {001} facets. (d) HR-TEM image of the  $\text{In}_2\text{O}_3$  NW.



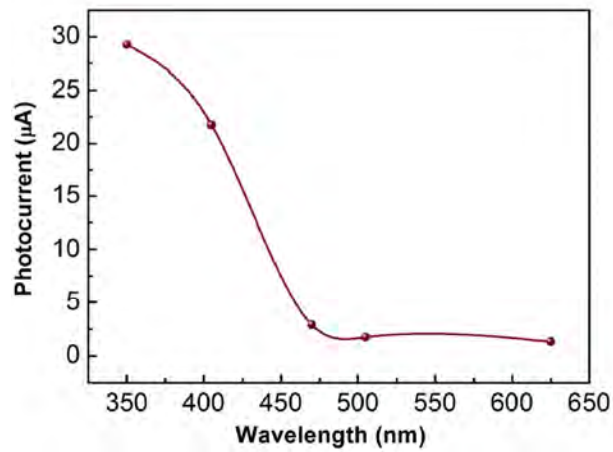
**Figure S5** Optical microscope image of the whole photodetector device clearly demonstrating that there is only one NW between source and drain.



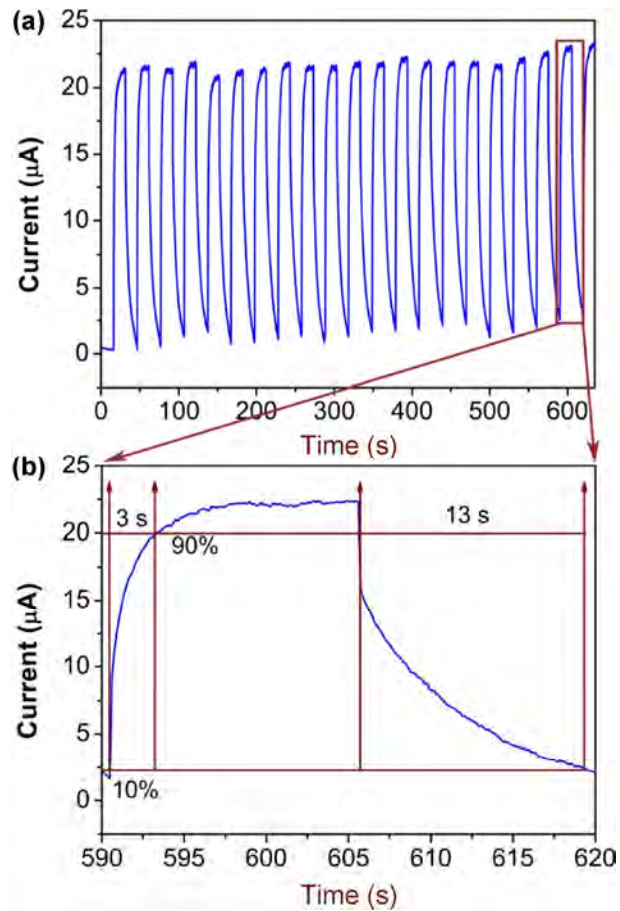
**Figure S6**  $I$ - $V$  curves of device 1 illuminated with 350 nm light ( $1.6 \text{ mW/cm}^2$ ) and under dark conditions.



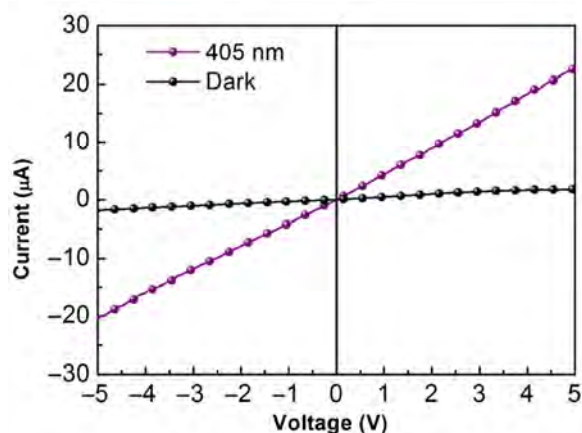
**Figure S7** Drain current vs. drain voltage ( $I_{ds}$ - $V_{ds}$ ) curves recorded from a single  $\text{In}_2\text{O}_3$  NW-based FETs with the gate voltage from 40 to  $-40 \text{ V}$ . The  $I_{ds}$ - $V_{ds}$  curve is nearly linear, suggesting good Ohmic contact between the NW and electrodes.



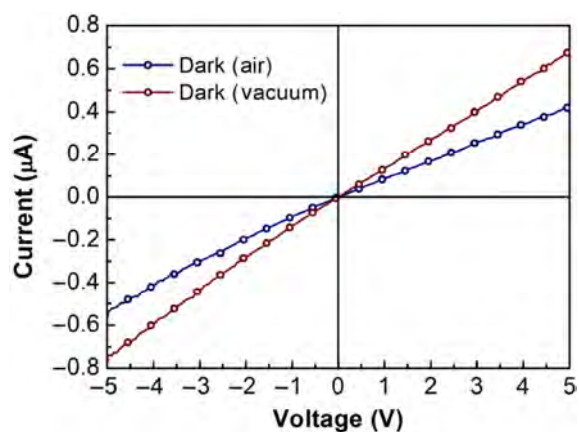
**Figure S8** Comparison of the photocurrents obtained at 5 V from device 1.



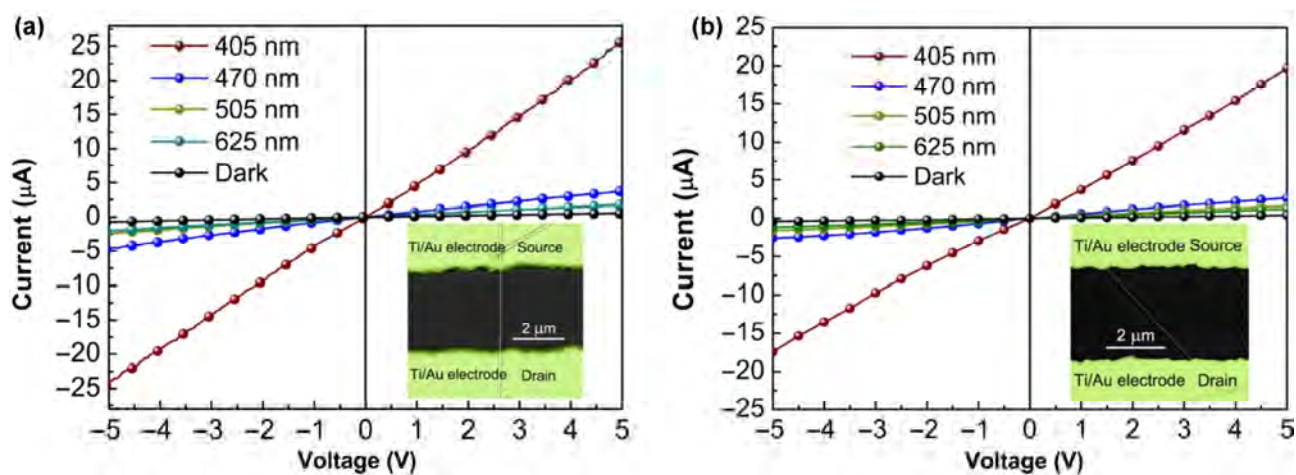
**Figure S9** (a) Current–time response measured by periodically switching on and off 405 nm light illumination at a bias of 5 V, showing the long-term stability of the  $\text{In}_2\text{O}_3$  NW-based photodetector. (b) Enlargement of the curve in the 590–620 s range outlined in (a).



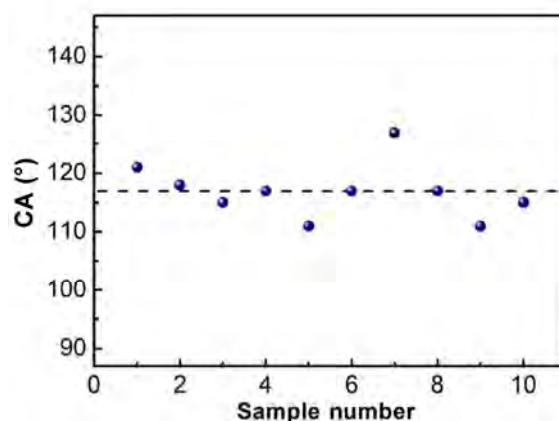
**Figure S10**  $I$ - $V$  curves of device 1 illuminated with the 405 nm light ( $1.21 \text{ mW/cm}^2$ ) and under dark conditions after 20 periodic switching. Based on this figure,  $R_\lambda$  and EQE of the NW-based photodetector can be calculated and the results are shown in Table S1.



**Figure S11**  $I$ - $V$  curves of the NW-based photodetector without illumination in air and under vacuum conditions.



**Figure S12** (a)  $I$ - $V$  curves of device 2 illuminated with the 405, 470, 505, and 625 nm light, and under dark conditions. Inset is the SEM image of device 2 with a channel width of  $3 \mu\text{m}$  between two electrodes. (b)  $I$ - $V$  curves of device 3 obtained under the same test conditions as for device 2. Inset is the SEM image of device 3 with a channel width of  $4 \mu\text{m}$  between two electrodes.



**Figure S13** Contact angles measured from different  $\text{In}_2\text{O}_3$  samples, demonstrating the hydrophobic properties of the  $\text{In}_2\text{O}_3$  NWs with average contact angle of about  $120^\circ$ .

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