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Supplementary Information

High-performance self-powered ultraviolet photodetectors based on mixed-dimensional heterostructure arrays formed from NiO nanosheets and TiO_2 nanorods

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Experimental

Preparation of TiO_2 NRs: TiO_2 NRs were grown on FTO substrates by hydrothermal method. After cleaned by deionized water, acetone, isopropanol and absolute ethanol, FTO surface is treated by UV/ozone to remove the organic matter. FTO was put into the autoclave with the conductive surface facing down in the transparent precursor solution for TiO_2 NRs including 15 ml H_2O, 15 ml HCl and 0.5 ml $C_{16}H_{36}O_4Ti$. After the growth at 170 °C for 3 h, TiO_2 NRs film was rinsed with deionized water followed by the annealing process in ambient air at 450 °C for 2 h.

Preparation of mixed dimensional 2D/1D heterojunctions: NiO nanosheets were deposited on TiO_2 NRs films by hydrothermal method. This process consists of the following three parts: (i) 1 mmol $NiSO_4{\cdot}6H_2O$, 2 mmol NH_4F and 5 mmol $CO(NH_2)_2$ were dissolved in 100 ml high purity water under stirring for 20 minutes. The homogeneous transparent solution was transferred into the autoclave with the TiO_2 NRs facing down. NiO nanosheets were grown at 105 °C for 3 h, 5 h and 7 h. After rinsed with deionized water, NiO nanosheets were annealed in ambient at 350 °C for 2 h. (ii) NiO nanosheets with different precursor concentrations were grown for 3 h. The molar ratio of $NiSO_4.6H_2O$: NH_4F: $CO(NH_2)_2$ were kept 1:2:5. The molar amount of $NiSO_4.6H_2O$ is 0.6 and 0.2 mmol. (iii) The thick NiO nanosheet layers with the film thickness (~1.8 μm) was obtained using 1 mmol $NiCl{\cdot}6H_2O$, 2 mmol NH_4F and 5 mmol $CO(NH_2)_2$ grown for 3 h. The thin NiO nanosheet layers with the same film thickness were obtained using $NiSO_4.6H_2O$ grown for 7 h. The NiO nanosheets were grown on the FTO substrates under the above experimental conditions.

Preparation of the device: Au metal with a thickness of about 40 nm was sputted on NiO nanosheets/TiO_2 NRs. The working area is approximately 0.04 cm^2. The preparation process of devices is shown in Fig. S1.

Characterization Methods: The morphologies of the samples were characterized by a field-emitting scanning electron microscopy (FESEM, Hitachi S-8010). X-ray diffraction (XRD, Rigaku, 2500 V/PC) patterns and Raman spectra (RENISHAO in Via Raman Microscope) investigated the crystal structure. X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB-250) was used to analyze the chemical state of the element and Fermi level. Absorption spectra of samples were obtained using a UV-vis spectrometer (Hitachi UV 4100). The electrochemical impedance spectroscopy (EIS) and Mott-Schottky (M-S) analysis were performed via the electrochemical workstation (CHI660D, Shanghai, China).

Measurement methods: A Keithley 2450 Source Meter was used to measure steady-state and transient photocurrent. LED-365 nm lamp and Hitachi F-4500 provide the monochromatic light. Transient photocurrent (TPC) was measured using a Tektronix MSO 2012B Mixed Signal Oscilloscope to determine the response (rise and decay) time of the self-powered UV PDs.

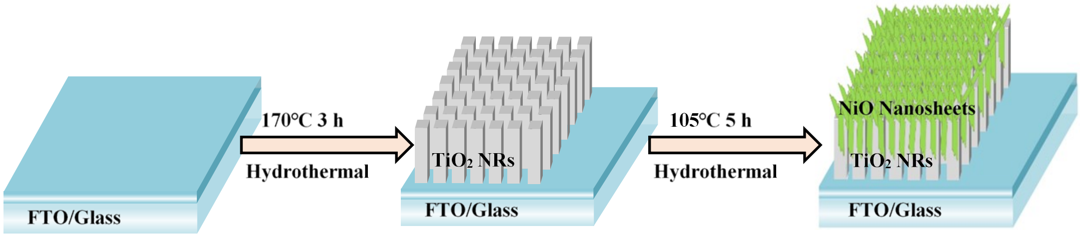

Fig. S1 Preparation process of mixed-dimensional heterostructure arrays formed from 2D NiO nanosheets and 1D TiO_2 nanorods.

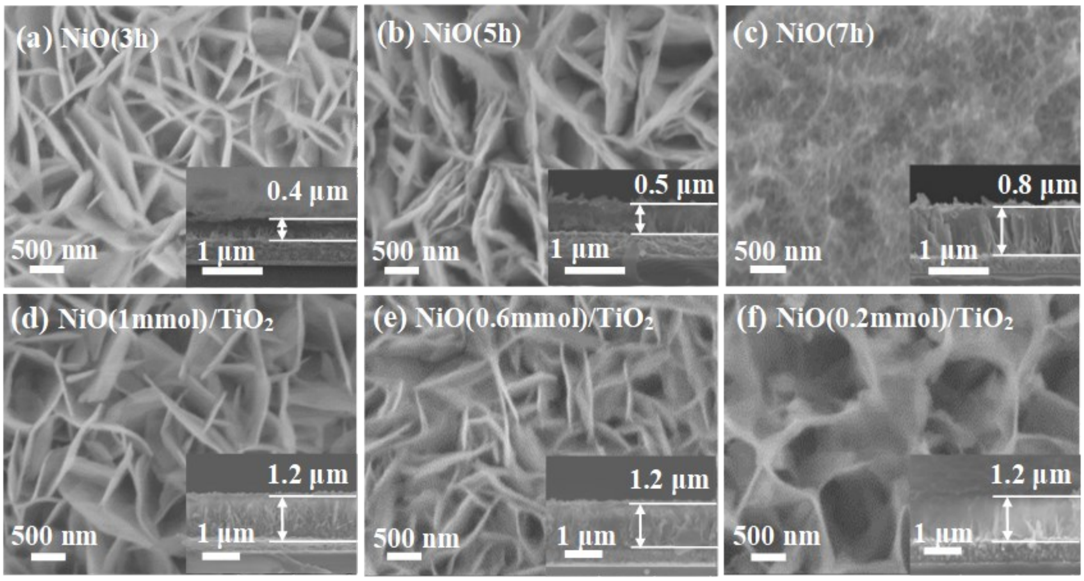

Fig. S2 (a)-(c) SEM images of NiO nanosheets grown for different time. (d)-(f) SEM images of NiO/TiO_2 heterojunctions with NiO nanosheets grown in different concentrations solution.

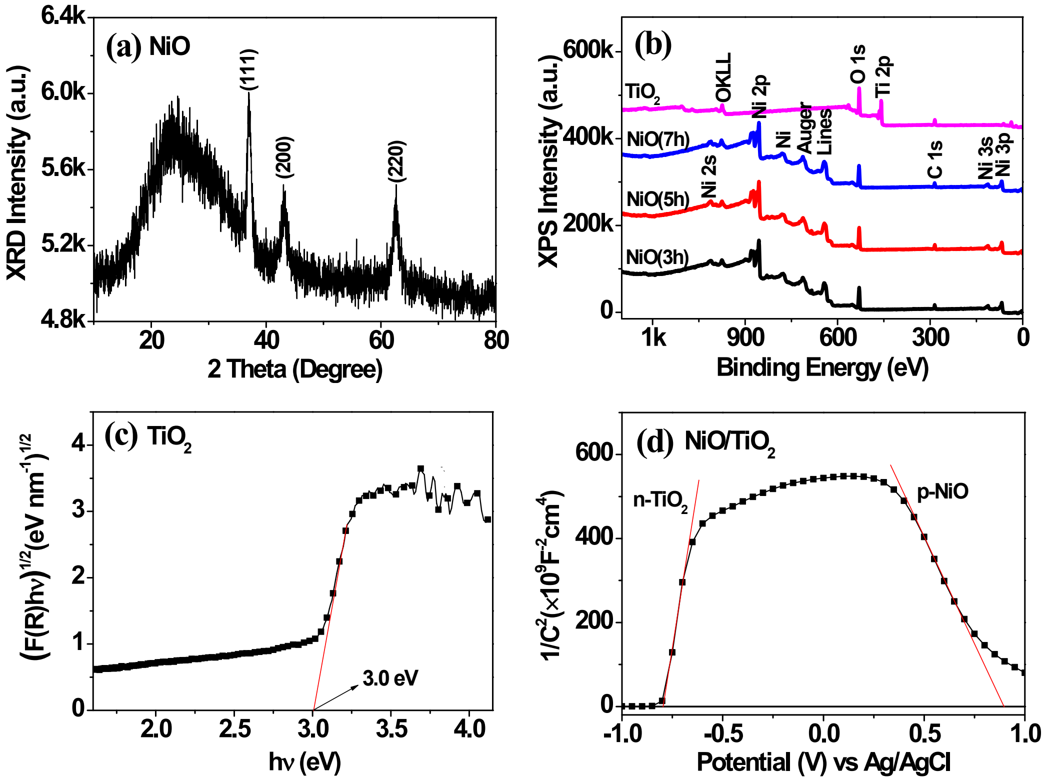

Fig. S3 (a) XRD patterns of NiO nanosheets grown on glass substrate. (b) The full XPS spectra for NiO nanosheets and TiO_2 nanorods. (c) TiO_2 band-gap estimated from absorption spectrum. (d) M-S curve for NiO/TiO_2 heterojunction film.

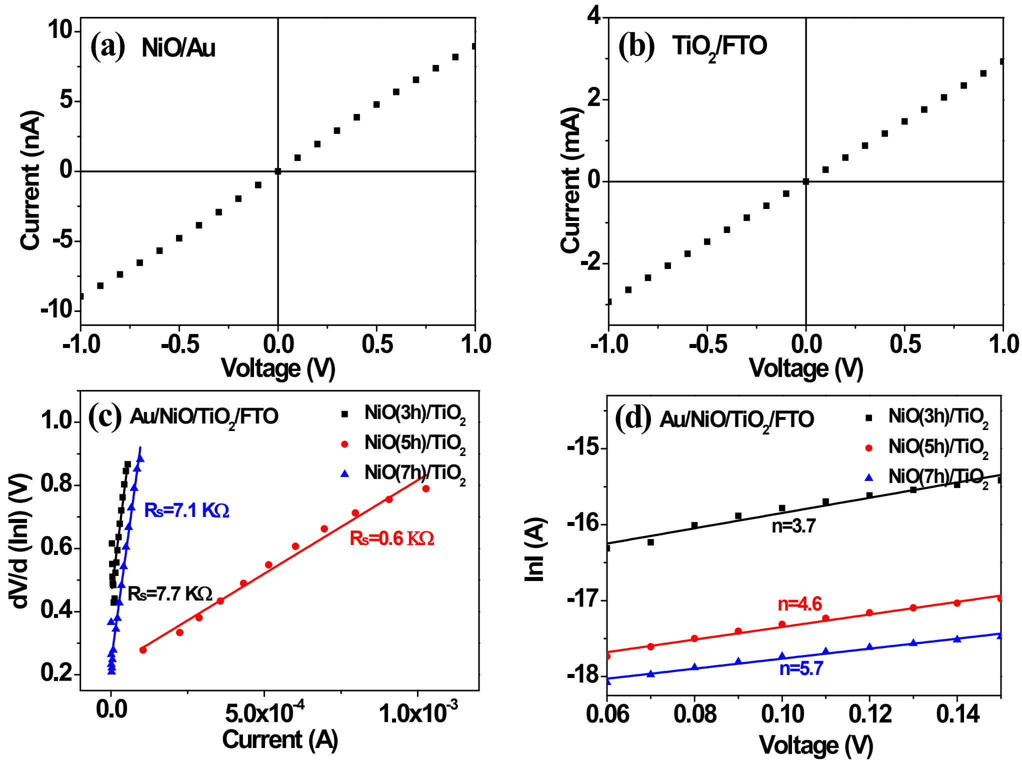

Fig. S4 I-V curves for devices of (a) NiO/Au and (b) TiO_2/FTO in the dark. (c) dV/d (lnI) -I curves of heterojunction devices. (d) lnI-V curves of heterojunction devices.

The calculation equations for series resistance (R_s) and ideality factor (n) can be transformed into the differential formula (1):[1]

$$\frac{dV}{d\ln(I)} = \frac{nkT}{q} + IR_S \quad (1)$$

From the Figure S4c, the dV/d (lnI) -I curves are straight lines. The slope of the straight line is the R_s. The calculated R_s is 7.7, 0.6 and 7.1 KΩ for the heterojunction devices with NiO nanosheets grown for 3 h, 5 h and 7 h, respectively. R_s first decreases and then increases with NiO growth time increase. The n can be obtained from the Y-axis intercept of dV/d (lnI) -I curves, which can be deduced according equation (2):[1]

$$n = \frac{q}{kT}\frac{dV}{d\ln(I)} \quad (2)$$

The lnI-V curves in Fig. S4d show the linear behavior. The n is 3.7, 4.6 and 5.7 for the heterojunction devices with NiO nanosheets grown for 3 h, 5 h and 7 h, respectively. The n increases with NiO growth time increase.

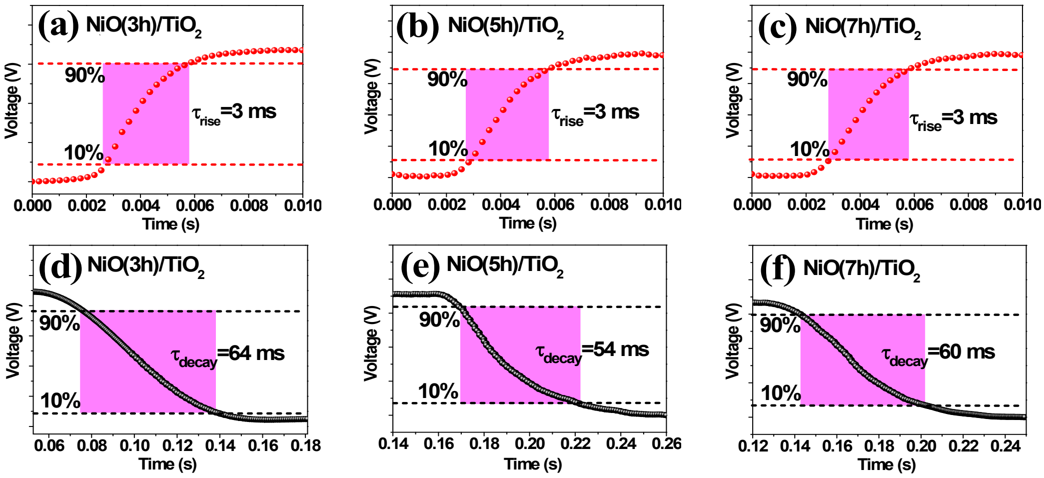

Fig. S5 Photoresponse time of NiO/TiO_2 heterojunction devices under 365 nm illumination at zero bias: (a)-(c) the photocurrent response time and (d)-(f) the photocurrent decay time for the devices with NiO nanosheets grown for 3 h, 5 h and 7 h.

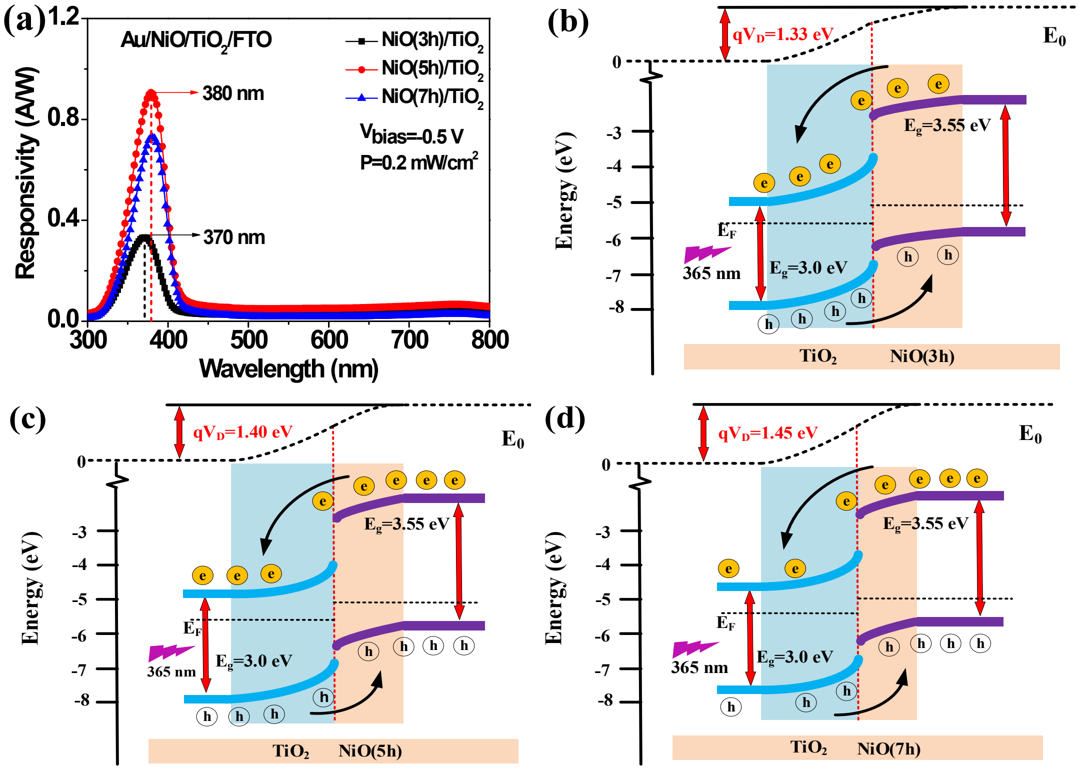

Fig. S6 (a) Responsivity as a function of wavelength in the range from 300 to 800 nm at -0.5 V reverse bias under 365 nm illumination with the power density of 0.2 mW/cm^2. (b)-(d) The band diagrams for the heterojunctions with NiO nanosheets grown for 3 h, 5 h and 7 h under -0.5 V reverse bias.

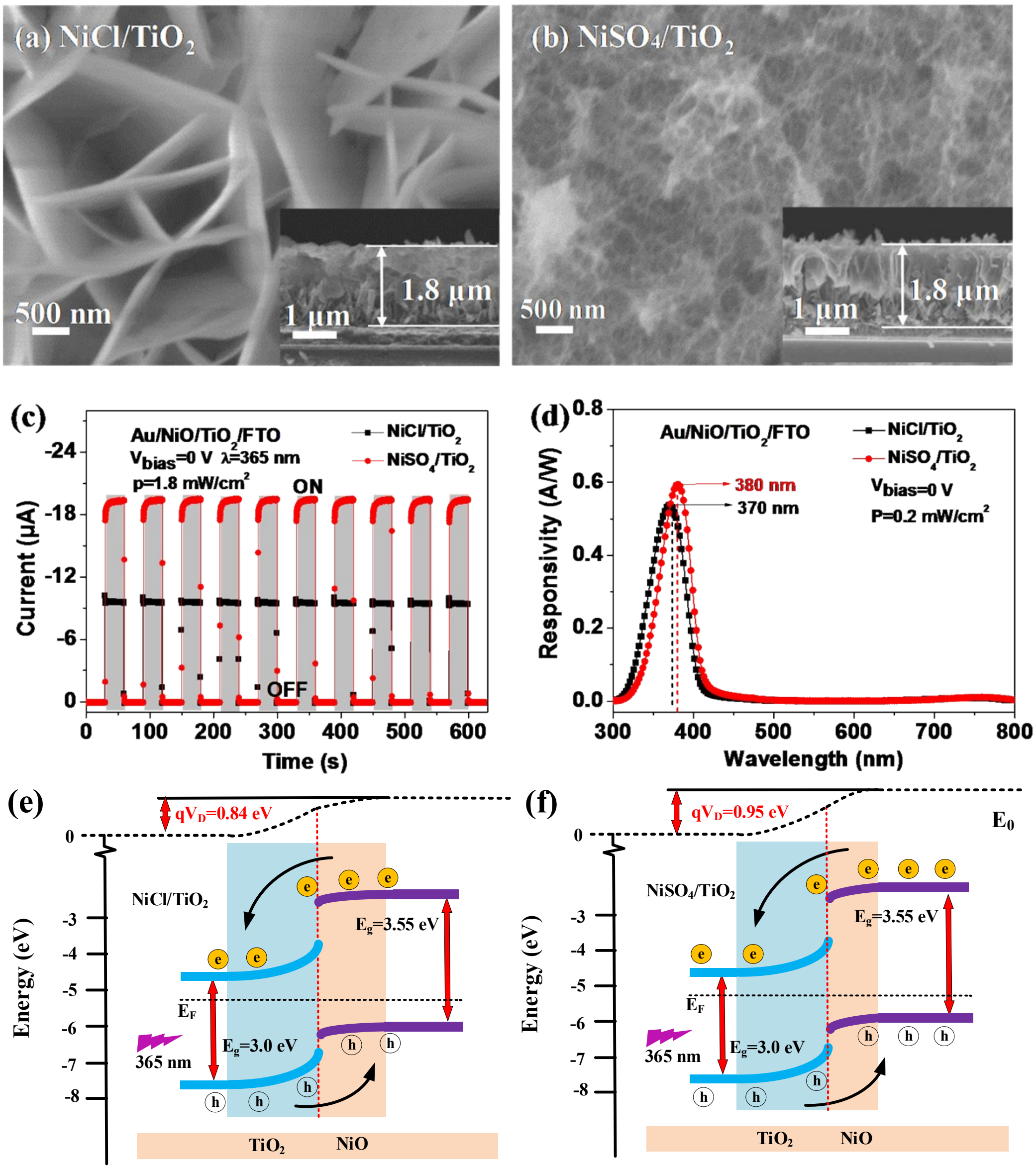

Fig. S7 SEM images of NiO/TiO_2 heterojunctions with NiO nanosheets by using (a) NiCl and (b) $NiSO_4$ nickel reactants. The thickness of the heterojunction films is 1.8 μm. (c) The transient photocurrent response of the devices with NiO nanosheets by using NiCl and $NiSO_4$ nickel reactants. (d) Responsivity as a function of wavelength in the range from 300 to 800 nm at zero bias under UV light (365 nm, 0.2 mW/cm^2) illumination. (e) and (f) Energy band diagrams of NiO/TiO_2 heterojunction devices with NiO nanosheets by using NiCl and $NiSO_4$ nickel reactants.

Reference

1 G. Turgut, E. F. Keskenler, S. Aydın, S. Dogan, S. Duman, S. Özçelik, B. Gürbulak, B. Esen, *phys. Status. Solidi. A*, 2014, **211**, 580-586.