1 Experimental Details

PEI was dissolved in deionized (DI) water to 0.1 wt%. Detailed processes of preparing TiO_2-sol have been described in our previous paper.[22] TiO_2-sol was spin coated on quartz substrates at 3000 rpm. After annealing at 650 °C for 2 h, anatase TiO_2 films were formed.[22] Then the TiO_2 films were separated into three groups labeled as samples A, B, and C. Sample B had been immersed into the ethylene glycol (EG) solution of potassium hydroxide (KOH) for 24 h. Sample C was UV/ozone-treated for 20 min. Subsequently, PEI was spun onto both samples B and C at 4500 rpm, and air dried at 80 °C. The thickness of PEI film is about 2-10 nm, which is demonstrated to be the best action thickness for interfacial dipoles and thin enough for carriers transporting from semiconductor to Au electrode via "quantum tunneling" effect.[20, 21] The interdigital electrodes structure was fabricated as follows: the positive photoresist (BP212) was firstly spin-coated onto the top of the samples A, B, and C. Then the photoresist was baked for 15 min at 90 °C. The photolithography process started with putting a mask onto the photoresist, followed by being exposed under UV radiation. The photoresist pattern was formed by being immersed in developer (KMP PD 238-II) for 40-50 s. After being baked at 120 °C for 15 min, the Au film was deposited by a radio frequency magnetron. To lift off the photoresist and useless metal, the samples were ultrasonic in acetone for 90 s. Finally, the planar interdigital electrodes were obtained. The width of both the finger and spacing were 20 μm, and the total active area was 0.38 mm^2.

Current–voltage (I–V) characteristics of UVPDs were measured with a Keithley 2601 Source Meter. A 500 W xenon lamp and a monochromator were used to provide monochromatic light. The responsivity of the device was measured by a UV power meter (FZ-A, Photoelectric Instrument Factory of Beijing Normal University) together with a Keithley 2601 Source Meter. The absorption spectra were measured by means of ultraviolet/visible spectrometer (UV 3600, Shimadzu). The surface analysis and the barrier height changes of the devices were investigated using XPS and UPS measurements. An oscilloscope and a 500 W xenon lamp are used to record the response time. The capacitances of the devices were measured by a Precision Impedance Analyzer 6500B Serious of Wayne Kerr Electronics.

2 EQE spectrums of the devices

The spectra response (R_λ) is defined as the photocurrent generated per unit power of incident light on the effective area of the device, and the external quantum efficiency (EQE) is defined as the number of electrons detected per incident photon. R_λ and EQE can be calculated by the following equations:

$$R_\lambda = \Delta I / PS,$$

$$EQE = R_\lambda \cdot (h\nu / e\lambda),$$

where ΔI is the difference between the photo-excited current and dark current, P is the light power density irradiated on the device, S is the effective area of the device, λ is the exciting wavelength, h is Planck's constant, c is the velocity of the light, and e is the electronic charge. The EQE spectrum calculated from the equation is shown in Fig. S1.

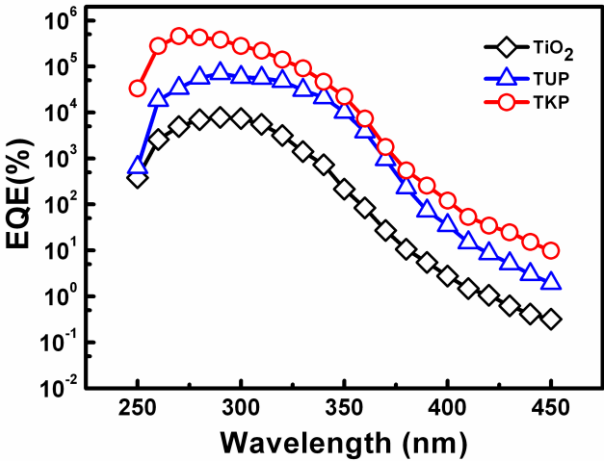

Fig. S1 The EQE spectrum of the devices at 6 V bias.

3 The spectral response of the devices

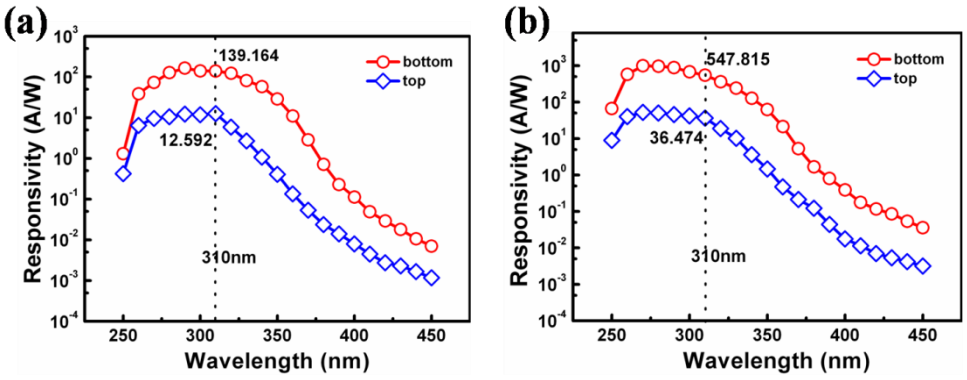

Fig. S2 The spectral response of (a) TUP and (b) TKP devices at 6V bias by applying the light from the top and the bottom.

4 The time response spectrum of the devices

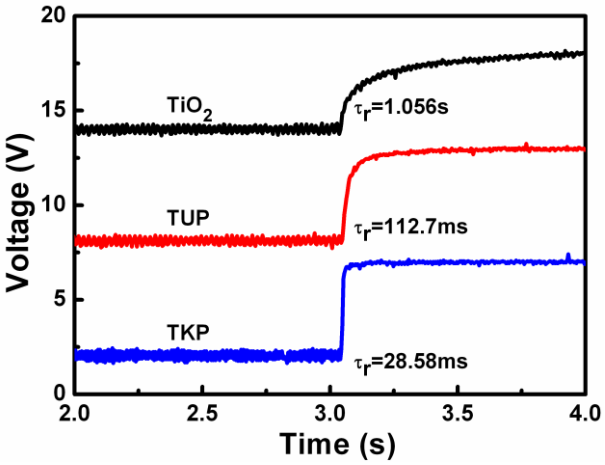

Fig. S3 The magnification image of the rise time region for the devices.

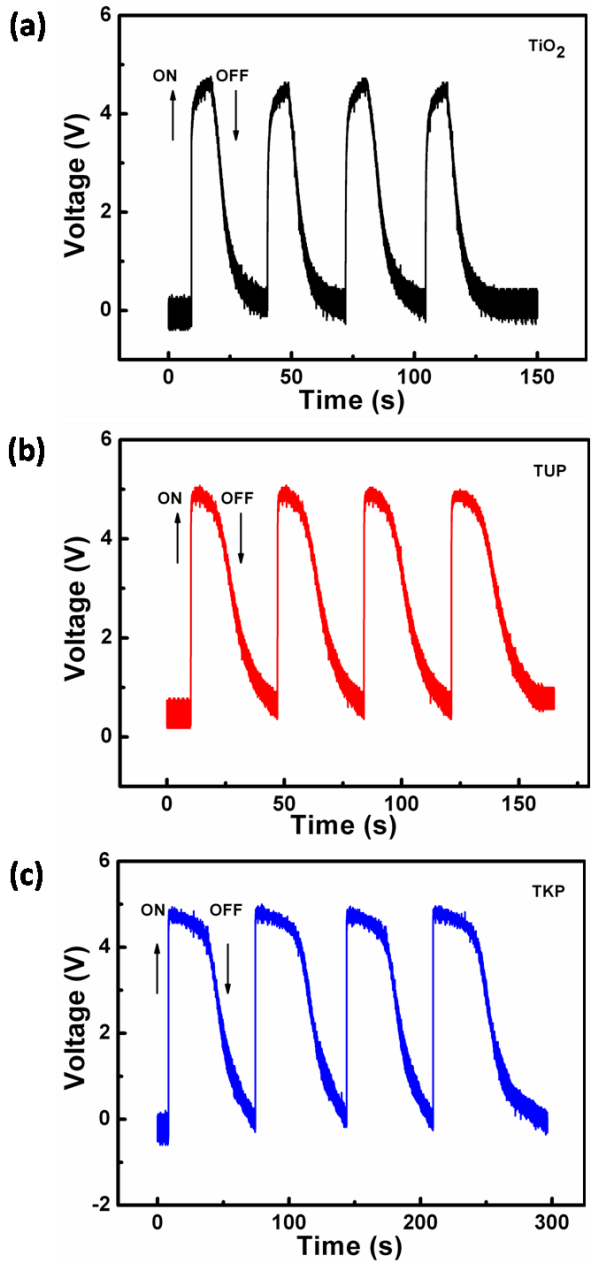

Fig. S4 The time response spectrum of the devices under periodic light pulses.