Supporting Information

ALD-Developed Plasmonic Two-Dimensional Au-WO_3-TiO_2 Heterojunction Architectonics For Design Of Photovoltaic Devices

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S 1. ALD details of TiO_2

A single cycle of a typical deposition process consisted of: TDMAT plasma / pumping / O_2 plasma / pumping / TDMAT exposure / pumping. The deposition chamber was continuously evacuated by a turbo molecular pump to a base pressure of approx. 4×10^{-6} mbar. Precursor vapors and gases were admitted through computer-controlled pneumatic valves. The flows of TDMAT and O_2 were adjusted to reach a pressure of 5×10^{-3} mbar in the deposition chamber. Initially the reaction chamber was pre-heated to 150°C, whereas TDMAT precursor was kept at 45°C. The precursor delivery facilities included ALD valves and automatic pressure control valves (APC) were kept at 150°C. On top of the chamber, a gate valve leads to a fused quartz column wrapped by a copper coil. The coil was connected to a 13.56 MHz RF generator (ENI GHW-12Z) and a matching network in order to generate an inductively coupled plasma in the column. The remote plasma was generated by feeding vapor or gas from the chamber to the plasma column through the gate valve and pulsing the RF generator. The plasma power was set to 200 W for the TMP plasma and 300Wfor the O_2 plasma, and the impedance matching was tuned to minimize the reflected power on both. All precursors were introduced into the chamber while it was continuously pumped, reaching a partial pressure of 5×10^{-3} mbar in the deposition chamber. The precursor and plasma pulse durations were set to be 1 s and 2 s, respectively. Argon was employed as a precursor carrier gas. The purge time for ALD gas products was setup to be 20 s to bring residual pressures to below 4×10^{-5} mbar, thereby avoiding CVD side reactions. Figure S1 and Table S1 respectively show the schematic drawing of plasma enhanced atomic layer deposition system (PE-ALD) and ALD recipe of 2D TiO_2 films.

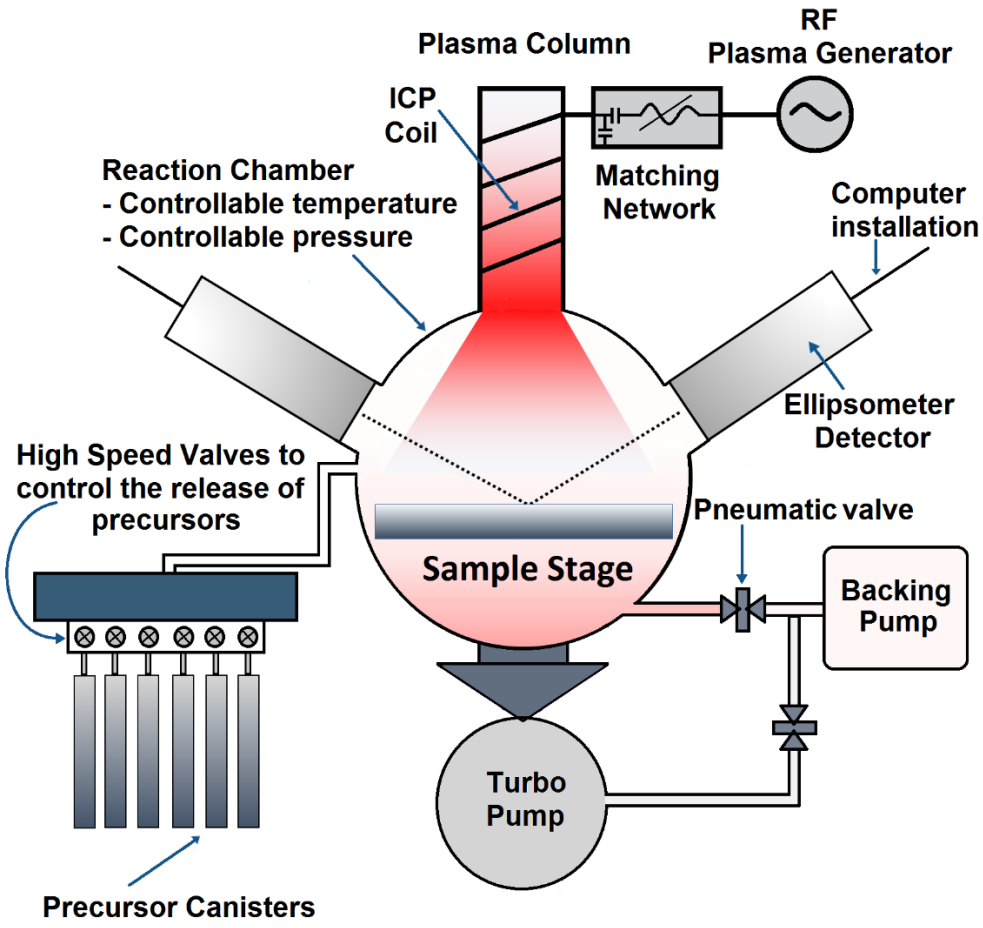

Figure S1. The schematic drawing of plasma enhanced atomic layer deposition system (PE-ALD).

Table S1. The recipe of PE-ALD process of TiO_2 film.

Block	**Delay (S)**	**Cycle**	**Total**
Pretreatment	0	1	1
Valve to plasma Open/On	5	-	-
Plasma Pulse	0	3	3
Gas A to Plasma Open/On	2	-	-
RF trigger Open/On	10	-	-
RF trigger Closed/Off	0	-	-
Gas A to Plasma Closed/Off	5	-	-
Valve to plasma Closed/Off	5	-	-
ALD Cycle	0	10	100
TDMAT Open/On	1	-	-
Ar to precursors, Open/On	10	-	-
Ar to precursors, Closed/Off	0	-	-
TDMAT Closed/Off	20	-	-
Valve To Plasma Open/On	2	-	-
Gas A to plasma open/On	1	-	-
RF trigger Open/On	10	-	-
RF trigger Closed/Off	0	-	-
Gas A to Plasma Closed/Off	5	-	-
Valve to Plasma Closed/Off	10	-	

S 2. ALD details of WO_3

In ALD process of WO_3 the utilization of glove-box with Ar gas allowed to minimize the exposure of deposited nanostructured films to moisture when unloading them from the reactor.

Table S2. The recipe of PE-ALD process of WO_3 monolayer film.

Block	**Details**	**Cycle**	**Total**
Residual flow	10 sccm	0	-
Trap temperature	150°C	6	-
Exhaust line temperature	150°C	7	-
ALD valves temperature	150°C	10	-
Chamber temperature	280°C	8	-
Chamber temperature	280°C	9	-
Temperature of tungsten precursor	80°C	12	-
Stabilize heater	46 sec	-	-
Manifold process flow	20 sccm	0	-
Wait for substrate to reach temperature	2400 sec	-	-
Start H_2O exposure step, cycle start	-	-	-
Reduce flow	10 sccm	0	-
H_2O pulse	0.015 sec	-	-
H_2O exposure step	5 sec	-	-
End H_2O exposure step	-	-	-
Increase flow	20 sccm	0	-
Purge H_2O	12 sec	-	-
Start Tungsten exposure step	-	-	-
Reduce flow	10 sccm	0	-
Tungsten Pulse	1 sec	2	-
End Tungsten exposure step	-	-	-
Increase flow	20 sccm	0	-
Purge Tungsten	14 sec	-	-
End of cycle	-	-	-

S. 3. The graphical scheme of fabricated ALD 2D films

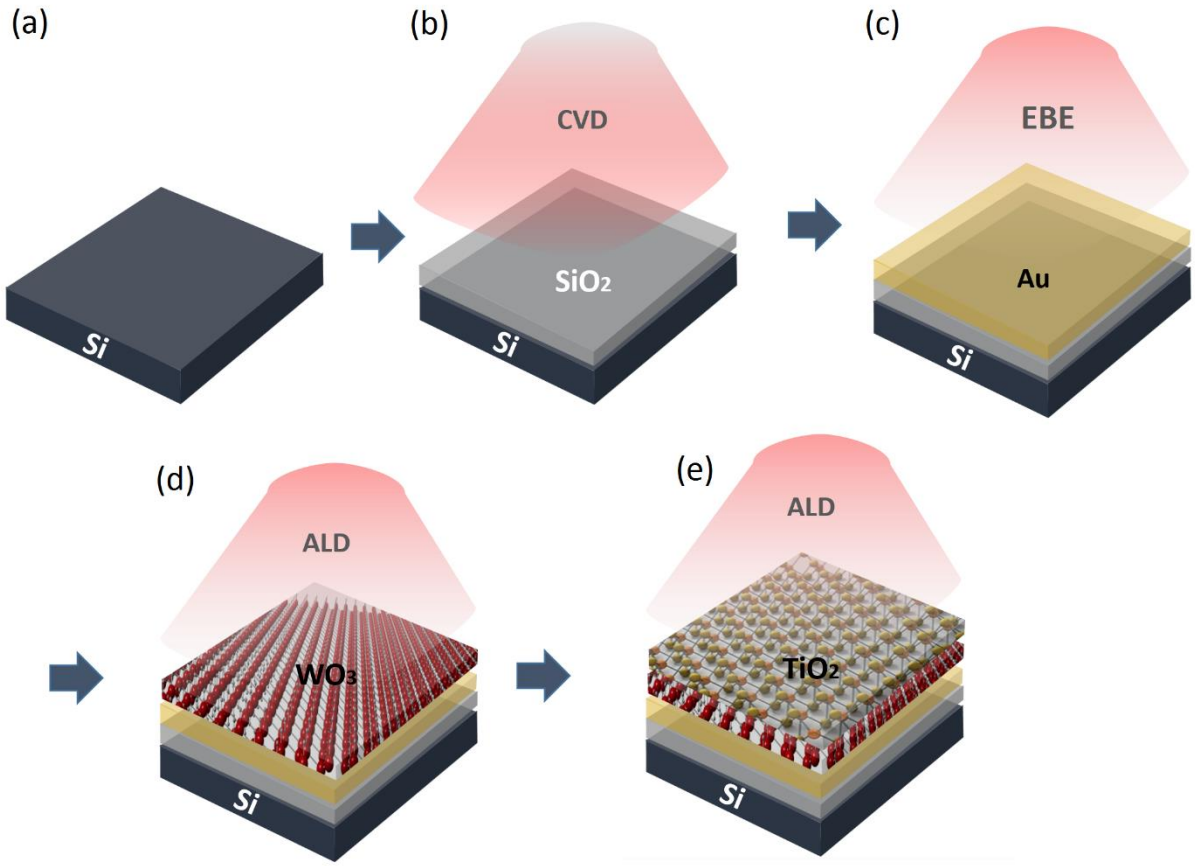

Figure S2. The graphical scheme of developed heterojunction samples, (a) bare Si substrate, (b) CVD of SiO_2 on Si substrate, (c) EB deposition of Au film on SiO_2 film, (d) ALD of WO_3 on Au film, (e) ALD of TiO_2 on WO_3 film.

S. 4. XRD pattern of Au substrate

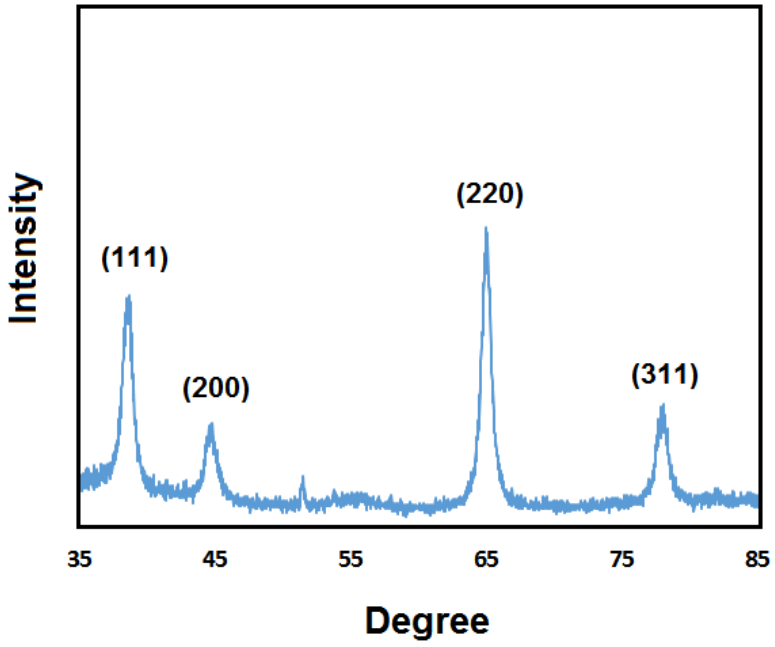

Figure S3. The X-ray diffraction pattern of non-coated EBE developed Au substrate.

S. 5. Spectroscopic analysis and AFM measurements of Si/SiO_2-TiO_2

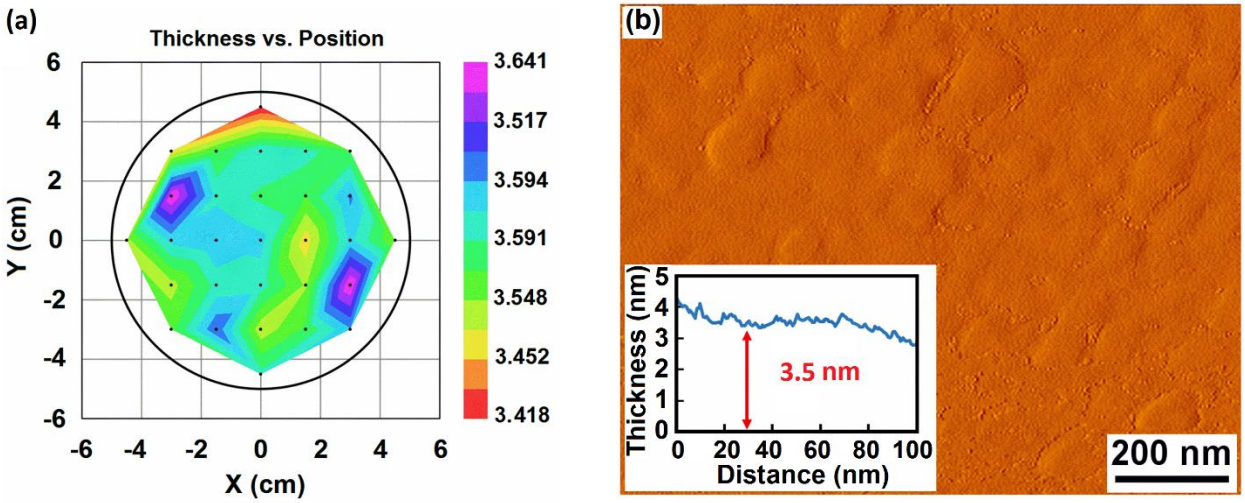

Figure S4. (a) The spectroscopic map of 3.5 nm thick 2D TiO_2 film deposited on Si/SiO_2 substrate, and its (b) AFM image and thickness measurement.

S. 6. The XPS of Au-TiO_2 films

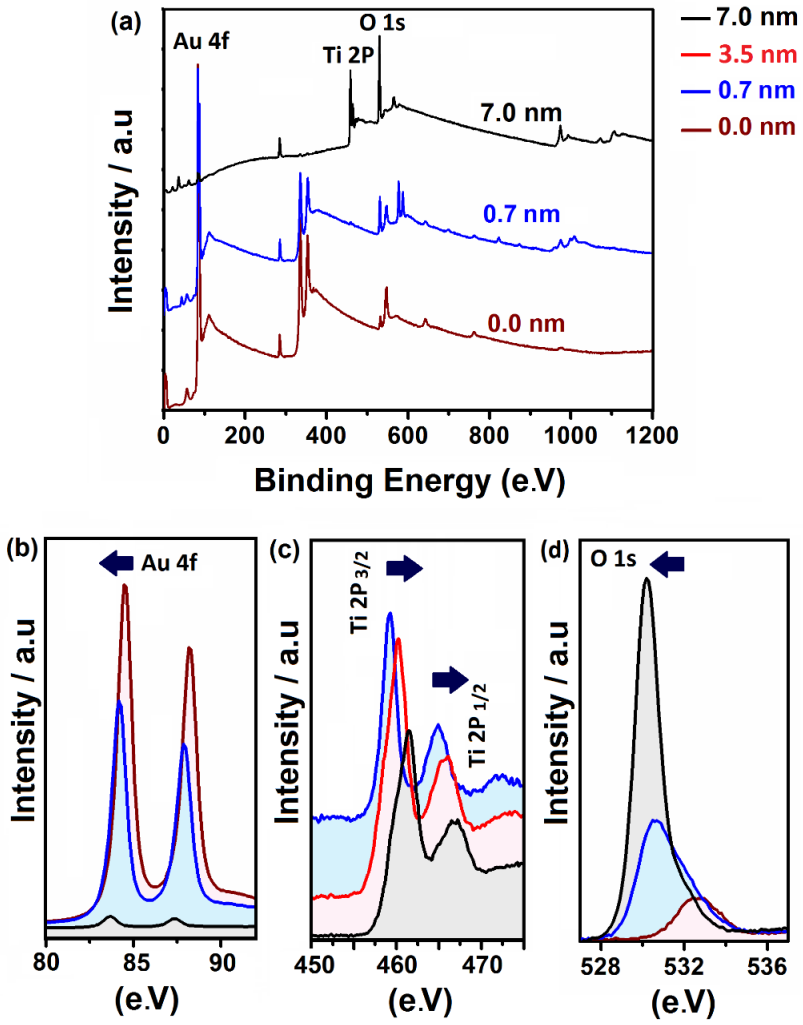

Figure S4.

Figure S5. The XPS spectra of (a) Au bare film and Au-TiO_2 samples, accompanied by the detailed core level of (b) Au 4f, (c) Ti 2p and (d) O 1s spectra.

S. 7. Raman and FTIR spectra of 2D WO_3 film

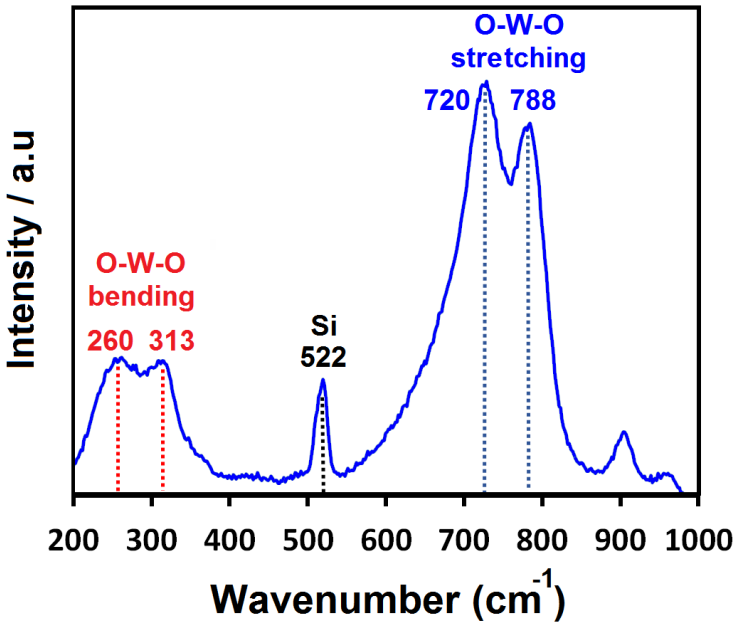

Figure S6. The Raman spectra of 2D WO_3 film, before the deposition of upper 2D TiO_2 films.

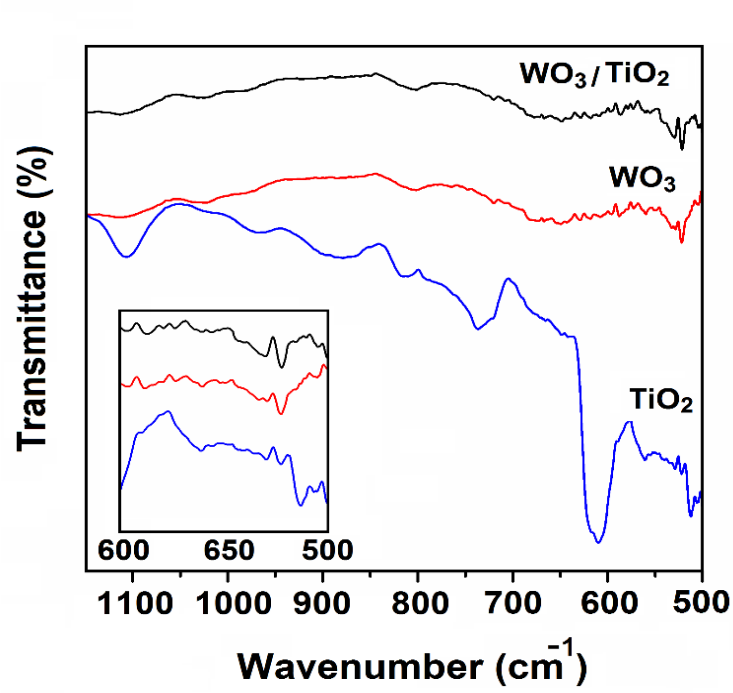

Figure S7. The FTIR spectra of 2D WO_3/TiO_2 heterojunction.

S. 8. The Nyquist plot of photodetectors

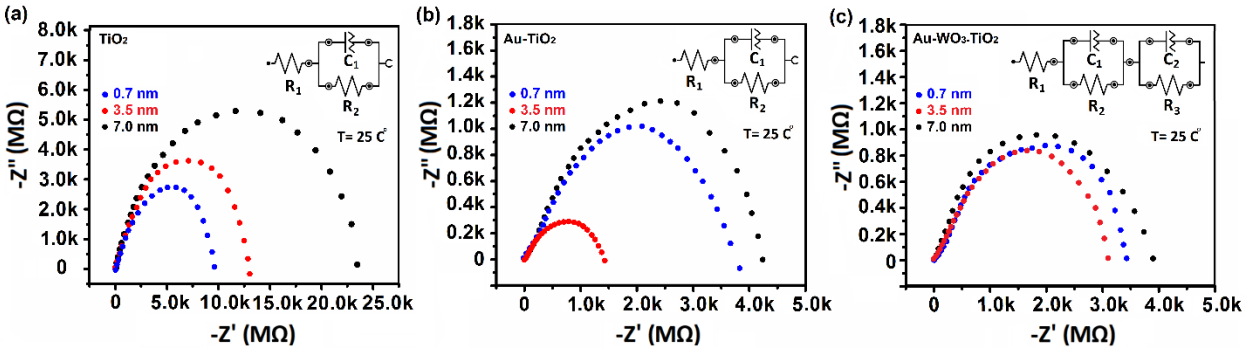

Figure S8. The Nyquist plot of (a) TiO_2, (b) Au-TiO_2 and (c) Au-WO_3-TiO_2 devices with various TiO_2 thickness, tested under λ = 785 nm laser light illumination with power density of 20 mV/cm^2.

S. 9. The photo-responsivity and EQE

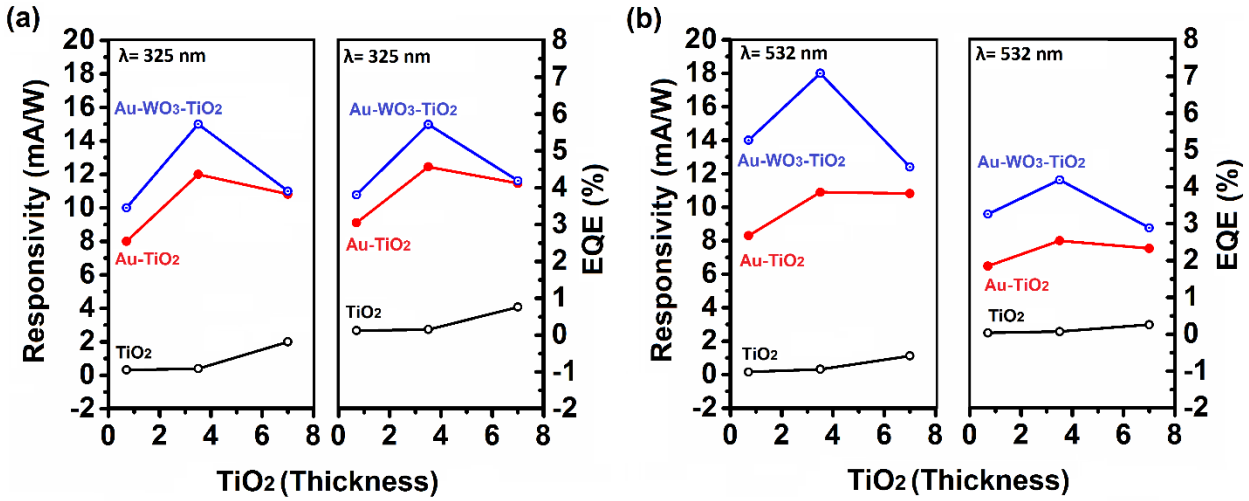

Figure S9. The photo-responsivity and EQE of 2D TiO_2, Au-TiO_2 and Au-WO_3-TiO_2 photodetectors under (a) λ = 325 nm and (b) λ = 532 nm laser light with the power density of 5 mV/cm^2.

S. 10. The response and recovery time

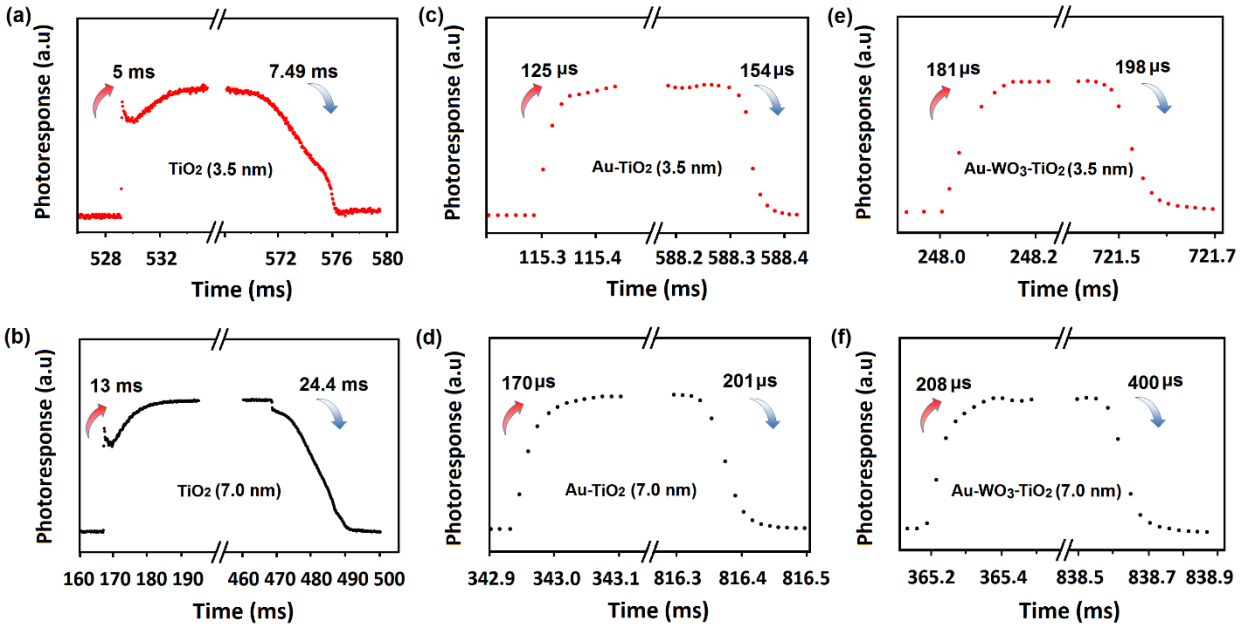

Figure S10. The response and recovery time of photoelectrode devices with different thickness of TiO_2 semiconductor film: (a) TiO_2 (3.5 nm), (b) TiO_2 (7.0 nm), (c) Au-TiO_2 (3.5 nm), (d) Au-TiO_2 (7.0 nm), (e) Au-WO_3-TiO_2 (3.5 nm), and (f) Au-WO_3-TiO_2 (7.0 nm) photodetectors tested under λ = 785 nm laser light illumination with power density of 20 mV/cm^2 at V_G = 0 V and V_{DS} = 1 V. The numbers in parentheses show the thickness of 2D TiO_2 film.