Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Ultrathin TiO_2 Nanosheets Synthesized by a High-Pressure Solvothermal Method and Enhanced Photoresponse Performance of $CH_3NH_3PbI_3$-TiO_2 Composite Films

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Experiment Section

Synthesis of the nanomaterials

The synthesis of anatase TiO_2 nanocrystals was accomplished via a constant-pressure solvothermal route modified from Jaroniec's method[1]. In a typical process, different amount of HF (40%) was added into 25 ml tetrabutyl titanate (TBOT) and stirred for 0.5 h to prepare the precursor solution. Afterwards, the resultant solution was sealed into a 15 ml Teflon tube with 100% filling, which was placed into a hot-press autoclave (Fig. S1). After ethylene glycol was added into this autoclave to a filling ratio of 100%, the autoclave was sealed and applied a pressure of 200 MPa, then heated at 200 ºC for 12 h. Finally, the product was successively washed with ethanol and deionized water for several times, and dried at 80 ºC for 12h. In order to investigate the ratio of exposed (101) and (001) facets of anatase TiO_2 nanocrystals on the performance of $CH_3NH_3PbI_3$-TiO_2 composite photodetectors, a series amounts of HF (1 ml, 2 ml, 4 ml and 8 ml, the corresponding samples were denoted as HF-1, HF-2, HF-4 and HF-8, respectively) were added into the above precursor solutions. For comparison, TiO_2 nanocrystals were also synthesized by the conventional solvothermal method with the same starting reagents ratio of sample HF-4, and $CH_3NH_3PbI_3$-TiO_2 composite photodetector was fabricated by using these TiO_2 nanocrystals.

Process of fabricating thin film photodetector

The fabrication processes of both pure perovskite and $CH_3NH_3PbI_3$-TiO_2 composite thin film gas sensors are presented in Fig. S9. In the process of fabricating pure perovskite thin film sensor, the precursor solution was firstly prepared by thoroughly mixing equal molar of CH_3NH_3I and PbI_2 in DMF, then 100 μl of the as-prepared solution precursor solution was drop-casted on the surface of Al_2O_3 substrate at rotation speed of 1000 rpm. Afterwards, the rotation speed was increased to 1500 rpm and maintained for 10s, thus perovskite thin film was obtained (the optimized rotation speed, Table S1). Finally, cross-finger shaped interdigital Au electrodes were sputter-coated on the surface of the film, and a perovskite thin film gas sensor was fabricated. When preparing $CH_3NH_3PbI_3$-TiO_2 composite thin film gas sensor, the experimental

process was the same as mentioned above, except that 50 mg anstase TiO_2 nanocrystals was mixed with the precursor solution before drop-casting process. The device fabricated with TiO_2 that synthesized using different amount of HF solution was denoted as sample (HF-x), in which the x is the actual amount of HF that was used. I-V and dynamic response curves of the sensors were monitored by a Keithley 4200 semiconductor parameter analyzer.

Experimental process of high-pressure thermal treatment of the samples

During the high-pressure thermal treatment process of the $CH_3NH_3PbI_3$-TiO_2 composite film, the as prepared composite film was firstly enclosed into a Teflon membrane, and then placed in the high-pressure hot-press autoclave (Fig. S10). Afterwards, the autoclave was full-filled with simethicone and sealed. After applying a constant pressure of 50 MPa (the optimized pressure, Table S2), the autoclave was heated to 100℃ at a rate of 0.3 ℃/min and maintained constant for 6 h. Thirdly, the hot-press autoclave was cooled to room temperature at the same rate (i.e., 0.3 ℃/min), and the pressure was released. Finally, the thermal treated composite film was sputter-coated interdigital gold electrodes for further characterization.

Computational simulation details

Molecular dynamics simulation was conducted using FORCITE package in the Materials Studio. The COMPASS[2,3] force-field was used to describe the interaction between perovskite and the surface atoms of anatase TiO_2.

As for the situation in which the HF solution interact with anatase TiO_2, the (001) surface were created by periodically replication of an elementary cell in x and y directions, where periodical condition was applied. The thickness of the vacuum slab was set to be 15 Å in order to avoid unnecessary interactions between adjacent layers. NPT ensemble with simulation time of 1000 ps was used to run the test, and the step was set to 1 fs. During the simulation, two different pressures were used to represent the conditional solvothermal (10 MPa) and the high-pressure situation (200 MPa). The initial configuration of the structure was shown in Fig. S11(a)

As for the situation in which the anatase TiO_2 interact with the perovskite surface, the (001) surfaces of anatase TiO_2 and perovskite were created by periodically replication of an elementary cell in x and y directions, where periodical condition was applied. The thickness of the vacuum slab was set to be 15 Å in order to avoid unnecessary interactions between adjacent layers. NVT ensemble with simulation time of 1000 ps was used to run the test, and the step was set to1 fs. The initial configuration of the structure was shown in Figure. S11(b).

Characterization

X-ray powder diffraction (XRD) pattern of the sample was recorded on a Rigaku D/Max-γA X-ray diffractometer with Ni filtered Cu Kα radiation (V = 50 kV, I = 100 mA), and the scanning speed was 4 °C min^{-1}. The morphology was observed with transmission electron microscope (TEM, JEOL H-7000), high resolution transmission electron microscope (HRTEM, JEOL JEM-2100) and scanning electron microscope (SEM, Hitachi S-4800).

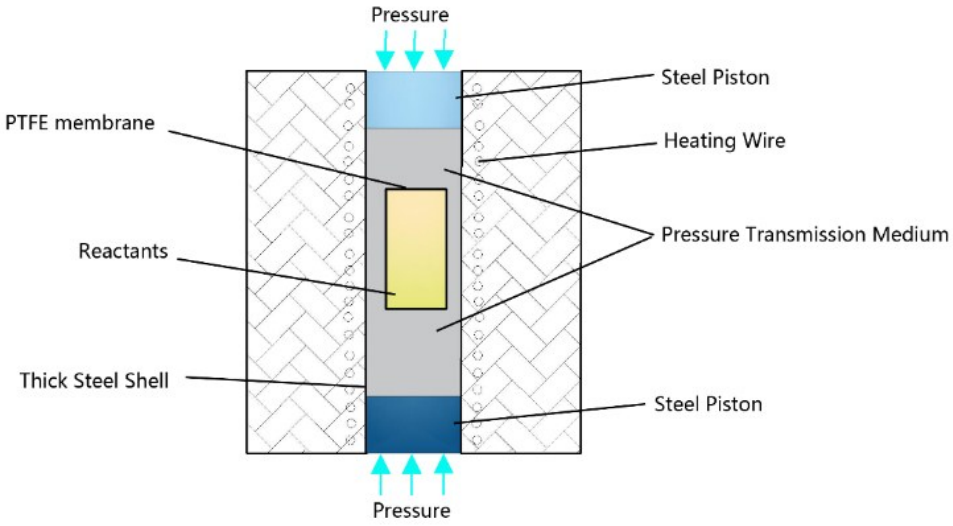

Fig. S1 Schematic structure of the constant-pressure solvothermal autoclave.

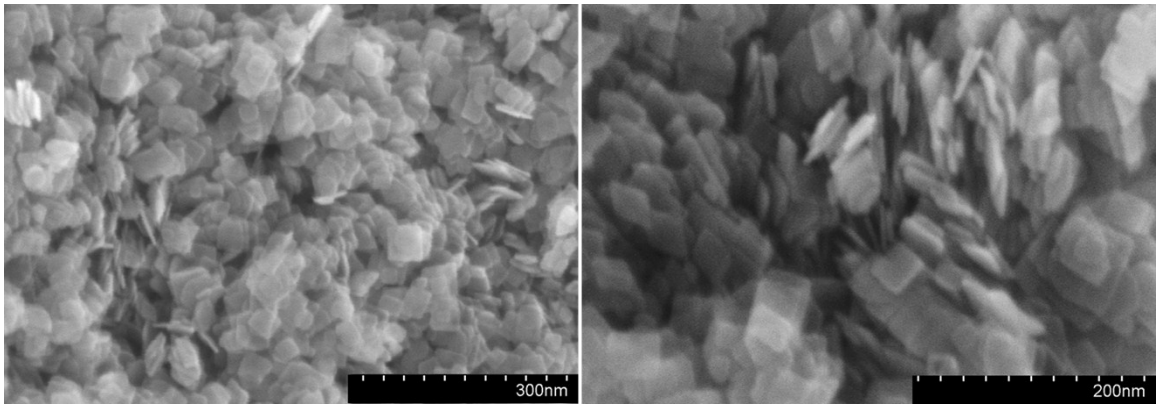

Fig. S2 SEM images of the ultrathin anatase TiO_2 nanosheets synthesized with 4 ml HF.

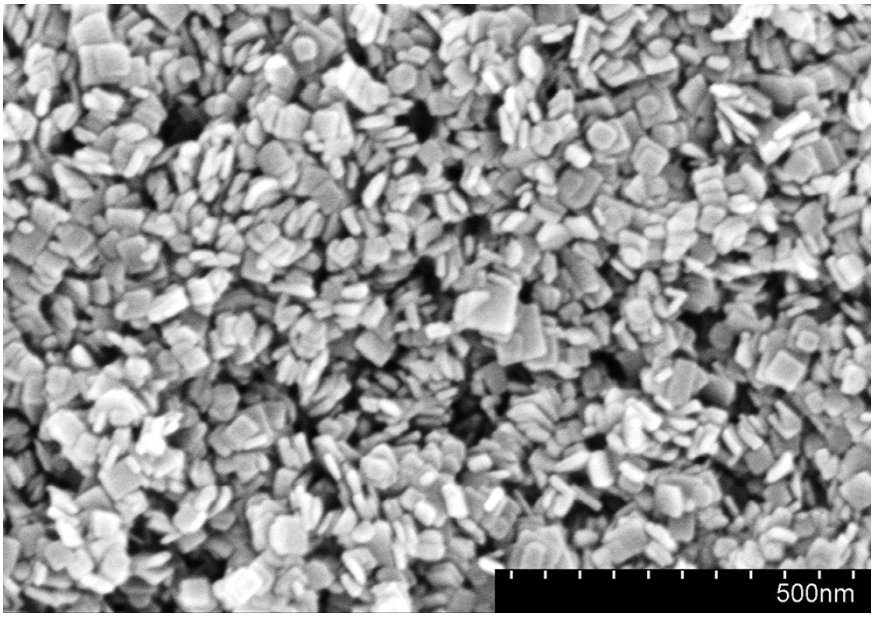

Fig. S3 SEM image of TiO_2 nanosheets synthesized with 2 ml HF. The thickness of them is 6-10 nm.

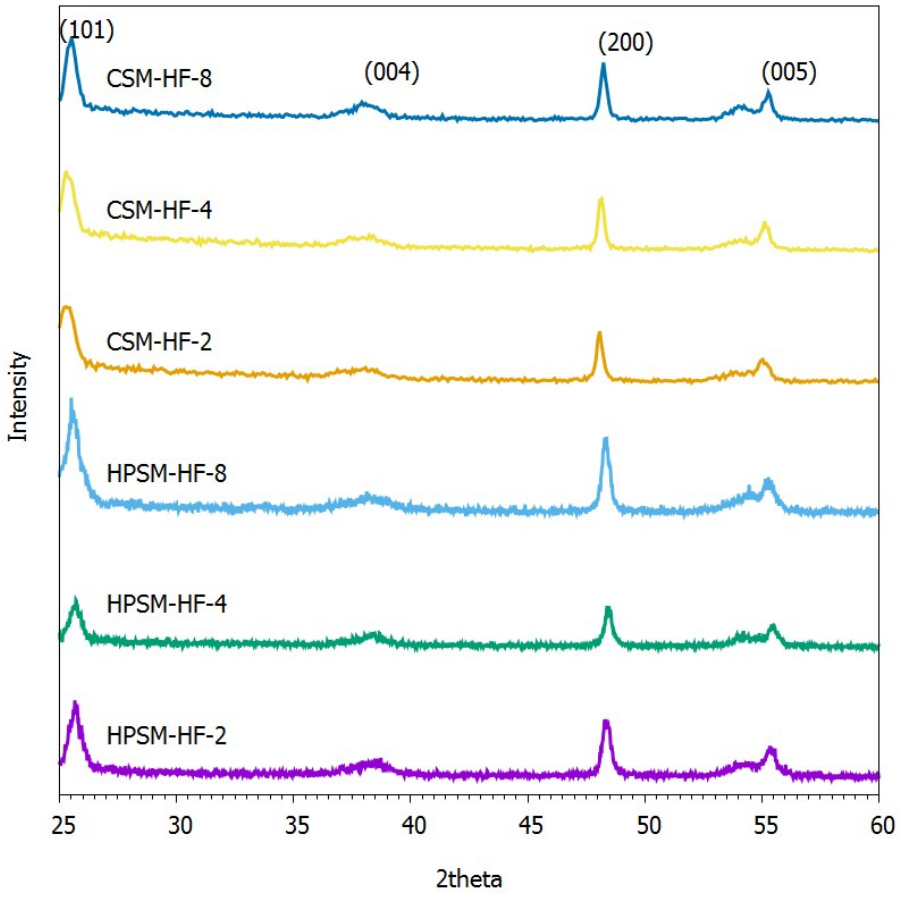

Fig. S4 XRD patterns of the anatase TiO_2 samples synthesized via the high-pressure solvothermal method (HPSM) and the conventional solvothermal method (CSM) with different amount of HF**.**

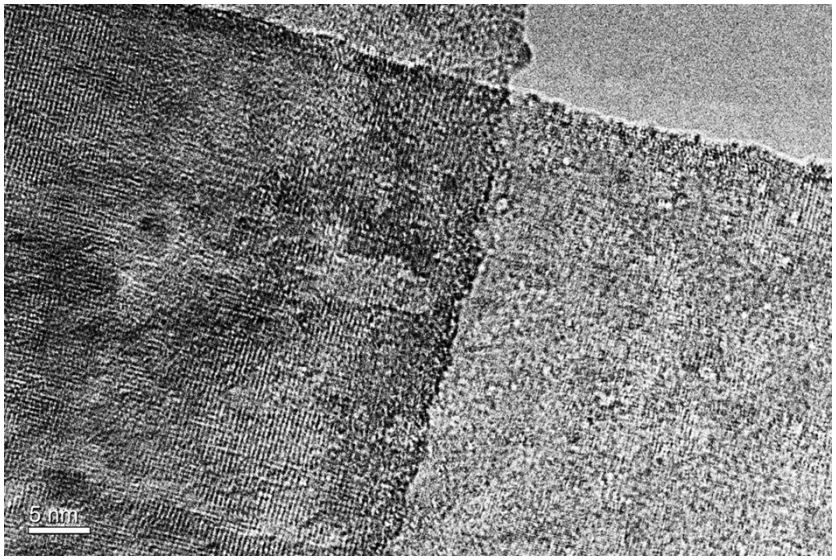

Fig. S5 HRTEM image of TiO_2 nanosheets synthesized with 8 ml HF. There are much etched sites on the (001) planes of nanosheets.

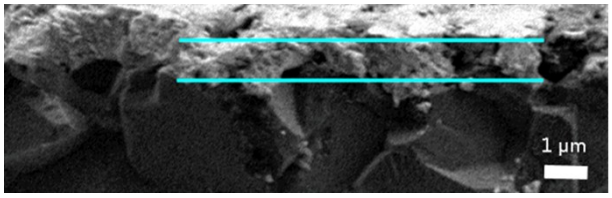

Fig. S6 Cross section image of the photodetector fabricated with high-pressure thermal treatment.

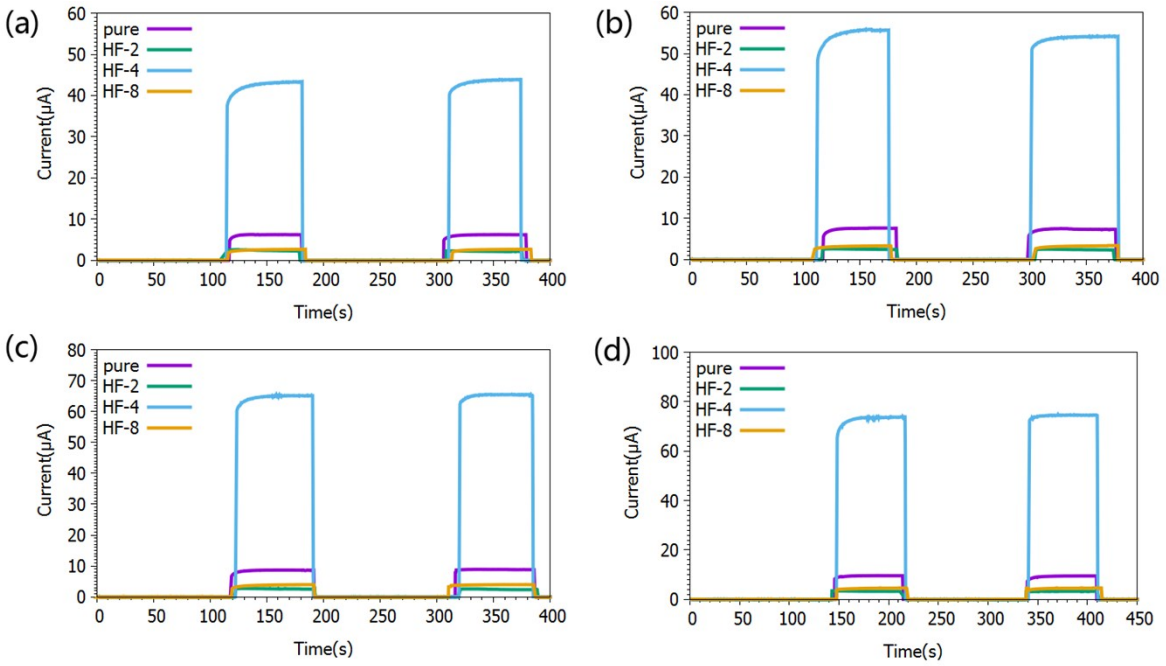

Fig. S7 Dynamic responses of the $CH_3NH_3PbI_3$-TiO_2 composite photodetectors to the illumination of 532 nm laser with different intensities. The anatase TiO_2 nanocrystals were synthesized using high-pressure solvothermal route. (a) 40 mW, (b) 60 mW, (c) 80 mW, (d) 100 mW.

For all the $CH_3NH_3PbI_3$-TiO_2 composite film photodetectors fabricated from $MAPbI_3$ and TiO_2 nanocrystals synthesized using high-pressure solvothermal route, the photocurrent increased with the increase of laser power (Fig. S7). Among them, the sample (HF-4) device exhibited the highest photoresponse, with the photocurrent much higher than that of the others.

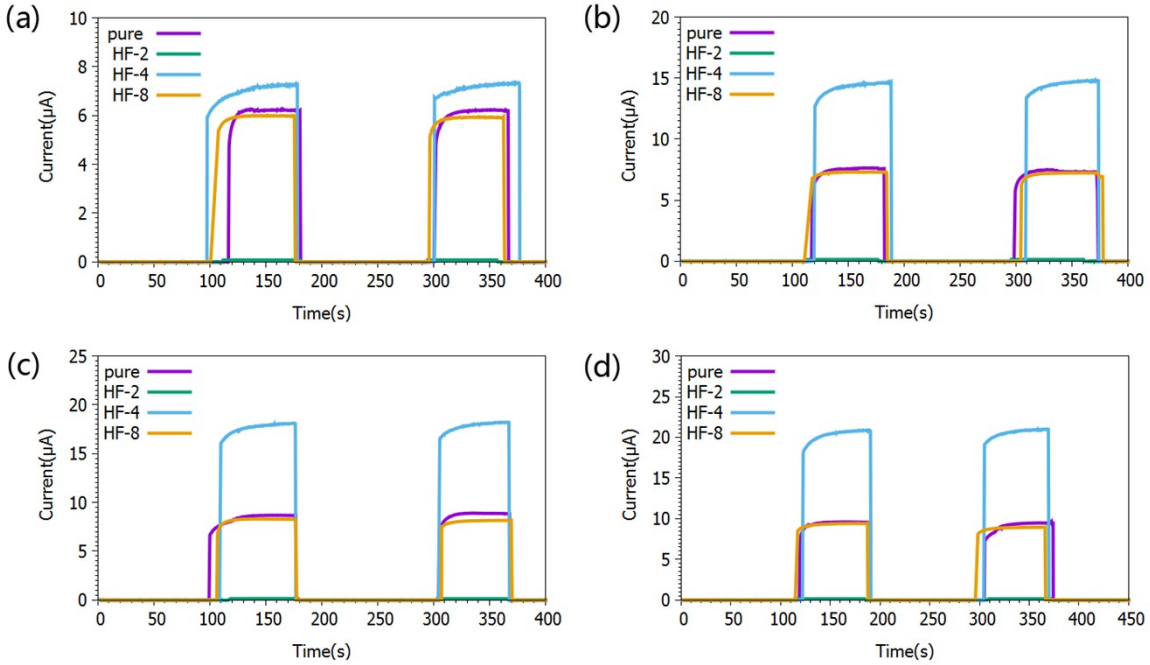

Fig. S8 Dynamic responses of the $CH_3NH_3PbI_3$-TiO_2 composite photodetectors to the illumination of 532 nm laser with different intensities. The anatase TiO_2 nanocrystals were synthesized using the conventional solvothermal route. (a) 40 mW, (b) 60 mW, (c) 80 mW, (d) 100 mW.

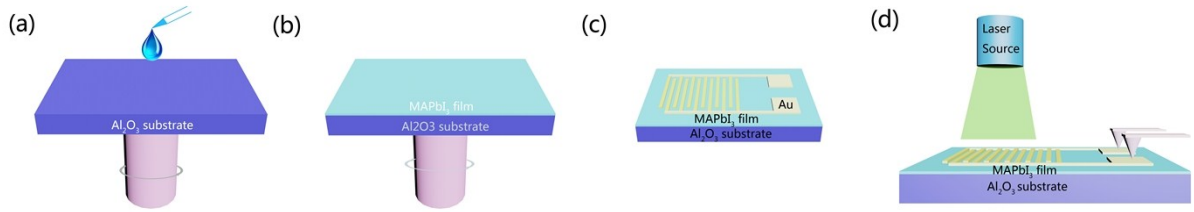

Fig. S9 Schematic illustration of the perovskite thin film photodetector fabrication process

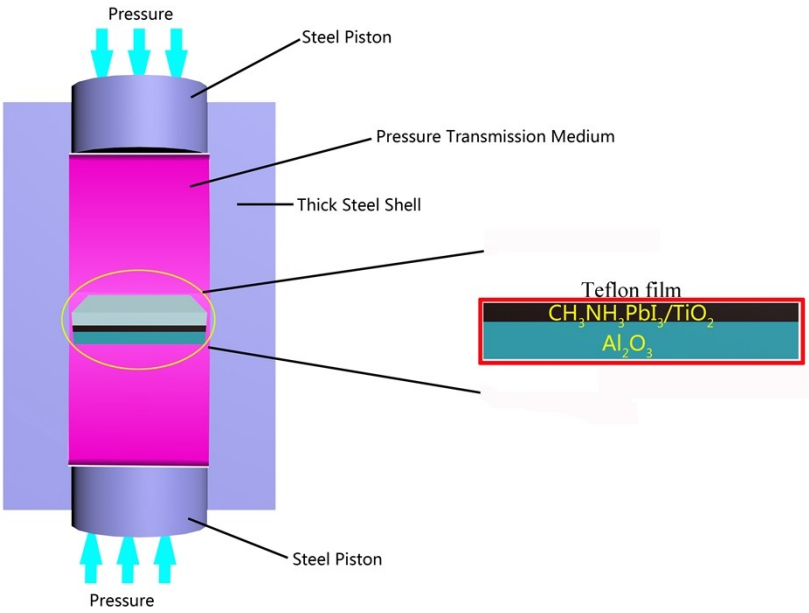

Fig. S10 Schematic diagram of the high-pressure thermal-treatment equipment.

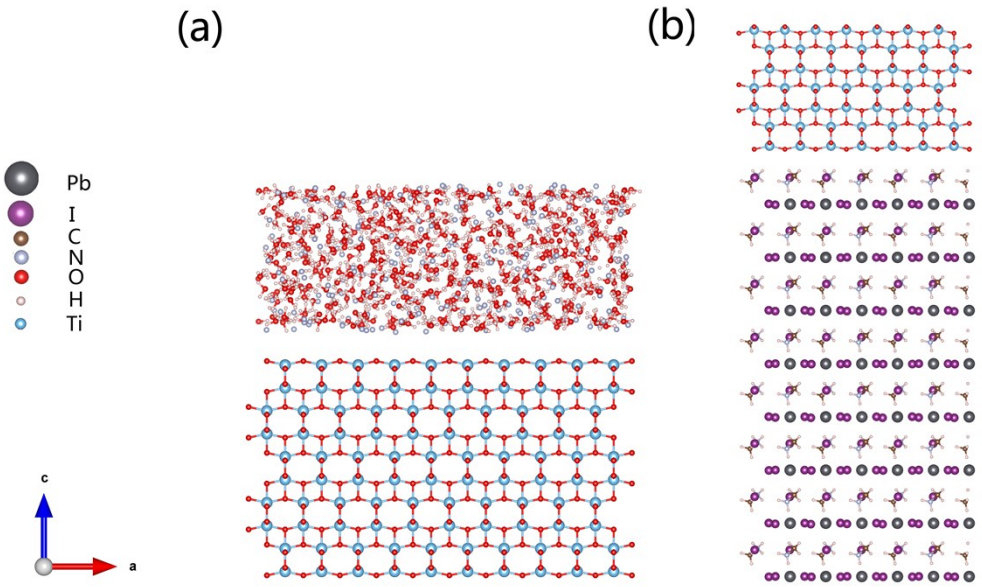

Fig. S11 Initial configuration of the simulated system. (a) HF solution on the (001) surface of anatase TiO_2. (b) anatase on the perovskite.

Table S1. The maximum photocurrent (μA) of the photodetector (pure perovskite) device fabricated under different spin-coating speed (rpm).

Spin-coating speed (rpm)	**800**	**1000**	**1200**	**1500**	**1800**	**2000**
Maximum current(μA)	1.805	2.218	3.944	4.890	4.222	2.887

Table S2. the maximum photocurrent (μA) of the device fabricated under thermal treatment with different pressure.

Pressure(MPa)	**20**	**30**	**40**	**50**	**60**	**70**
Maximum current(μA)	23.256	23.521	28.686	45.272	43.028	21.974

Notes and references

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2 H. Sun, *J. Phys. Chem.*, 1998, **5647**, 7338–7364.

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