Electronic Supplementary Information:

Multifunctional VI-VI Binary Heterostructure-based Self-Power pH-Sensitive

Photo-detector

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EXPERIMENTAL SECTION

Materials: Sodium tellurite (Na₂TeO₃, 99.9%), Selenium powder (Se), Poly(vinyl pyrrolidone) (PVP, K30), and poly(vinylidene fluoride) (PVDF, $Mn = 71,000 \text{ g mol}^{-1}$) were obtained from Aladdin Co. Ethanol, acetone, dimethyl formamide (DMF, 99.9%), hydrazine hydrate (N₂H₄·H₂O, 85%, w/w%), and aqueous ammonia solution (NH₃·H₂O, 10% - 35%, w/w) were purchased from Sigma-Aldrich., Inc. Deionized water (DI) was used through the whole process.

Synthesis of Te NSs: The Te NSs were prepared followed to the previous work with a light change.¹ Typically, 20 mg Na₂TeO₃ and 500 mg PVP were dissolved in 25 mL DI water. Then 1.70 mL N₂H₄·H₂O and 0.85 mL of NH₃·H₂O were added and kept stirring for 30 mins to form a homogeneous mixture. Finally, the mixture was poured into a 50 mL hydrothermal kettle and maintained at 180 °C for reacting 4 hours. The obtained product was purified with DI water, ethanol, and acetone by centrifugation at 5,000 rpm for 10 min, respectively. The Te NSs were dried in a vacuum oven at 80 °C overnight.

Synthesis of Te@Se NSs binary heterostructure: In a typical procedure, 20 mg Te NSs were dispersed in 40 mL DI water and kept stirring for 1 h. Then 40 mg Se powder were first dissolved in 500 μ L N₂H₄·H₂O and added into the mixture drop by drop. The mixture was first reacted at 40 °C for 8 h with stirring and maintained at 80 °C for 8 h without stirring. Finally, the mixture washed with DI water, ethanol, and acetone by centrifugation at 3,000 rpm for 10 min, respectively. The obtained Te@Se NSs binary

heterostructure was dried in a vacuum oven at 80 °C overnight for fabricating photodetector device and characterisation.

Preparation of Te@Se working electrode: 2 mg Te@Se was added in 1 mL PVDF/DMF (10 mg/100 mL). Then the mixture was dropped onto the indium tin oxide (ITO)-coated glass and dried in a vacuum oven at 80 °C overnight to fabricate the working electrode for PEC-type photodetection.

Characterization: The morphology of Te@Se was studied by a Semini SEM 300 and a FEI Talos 200F TEM (200KV). The UV-Vis-NIR absorption spectrum was studied by an UV-vis- NIR spectrophotometer (Hitachi S4000). The Raman spectroscopy (HORIBA Lab RAM HR800) was performed with the laser excited at 633 nm under ambient conditions, and the structure of Te@Se was performed via an XRD spectrometer at a scan rate of 20 min⁻¹ with a Cu K α (k = 1.54056 Å) radiation (Thermo Fisher Scientific, escalab EI).

Photo-response behaviors studies of Te@Se: The photo-response behaviors were studied as follows: In a PEC-type photodetection system, the Te@Se-coated ITO glass, platinum wire, and Ag/AgCl were served as the working electrode, counter electrode, and the reference electrode, respectively. The HCl, KCl, and KOH aqueous solutions with different concentrations were used as the electrolytes. The devices were illuminated with different wavelengths (350 nm, 400 nm, 475 nm, 550 nm, and 650 nm), and the light power intensities of these irradiation lights was assigned to level I, II, III, IV, and V as shown in **Table S1**. Linear sweep voltammetry (LSV) of Te@Se was studied with a scanning speed of 0.01 V s⁻¹ from -0.5 to 1.0 V. Amperometric

current–time (I–t) test was carried out with different bias potentials from o to 0.6 V. Electrochemical impedance spectra (EIS) was performed in the frequency range from 1 to 105 Hz with an amplitude of 0.005 V.

pH detection of the Te@Se-based PDs: The electrolytes with different pH were obtained through controlling the concentration of HCl, KCl, and KOH. The pH detection is performed according to the change trend of the P_{ph} measured at level IV under different conditions. The dynamic response and reversibility tests were performed through the addition of HCl and KOH into the electrolyte under stirring.

Long-term stability test: At first stage, the photo-response behaviors of the PD were tested in different electrolytes with the pH of 1 and 14. Then, the PD was immersed in electrolytes and maintained for about one month. Finally, the photo-response behaviors of the PD were tested for operating 10,000 s to evaluate its long-term stability.

DFT calculations: In the present study, the Vienna *ab initio* simulation package (VASP) code was employed to perform the density functional theory (DFT) calculations.^{2, 3} The projector augmented wave (PAW) potential method was used to describe electron–core interactions. The cut-off energy was set to 450 eV to expand the electronic wavefunctions under the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional.⁴ A vacuum space of at least 20 Å was included along the direction that is perpendicular to *ab* plane to avoid mirror interactions for each case. The structures were fully optimized until the force and maximum energy of each atom were no more than 0.01 eV/Å and 10^{-6} eV. $5 \times 5 \times 1$

and $19 \times 19 \times 1$ *k*-grid centering at the Γ point were employed for geometry optimization and electric properties calculations, respectively. Van der Waals corrections of optB88vdW functional was applied for dispersion correction in all calculations.^{5, 6}

To evaluate the interaction between O_2 molecule and Te@Se, the adsorption energy is calculated by $E_{ads} = E_{O_2} + E_{Te/Se} - E_{Te/Se+O_2}$, where $E_{Te/Se+O_2}$ is the total energy of Te@Se with a O₂ molecule adsorption on its surface. $E_{Te/Se}$ is the energy of the isolated Te@Se, and E_{0_2} is the energy of an isolated oxygen molecule. By this definition, a positive E_{ads} corresponds to a stable adsorption, while a negative one represents that O_2 adsorption is energetically unfavorable. To analyzes the charge transfer process during adsorption. The electron density difference is also calculated by subtracting the electron density of Te@Se structure (${}^{\rho}_{Te/Se}$) and the isolated O₂ molecule (${}^{\rho}_{O_2}$) from the total $(\rho_{\text{Te/Se}+O_2})$ adsorption Te@Se system O_2 electron densitv of the $\Delta \rho = \rho_{\mathrm{Te/Se} + \mathrm{O}_2} - \rho_{\mathrm{Te/Se}} - \rho_{\mathrm{O}_2}$

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P_{λ} (mW/cm ²)	I level	II level	III level	IV level	V level
Simulated light (SL)	26.2	53.0	83.1	118	122
350 nm	0.51	1.02	1.66	2.17	2.19
400 nm	0.637	2.04	3.57	5.22	5.35
475 nm	1.91	4.33	7.01	10.1	10.6
550 nm	2.04	3.95	5.98	8.28	8.40
650 nm	2.04	4.08	6.02	8.54	8.92

 Table S1. The values of the light power density used in this work.

рН	Photocurrent (P_{ph}) $(\mu A \text{ cm}^{-2})$								
	SL		Selected Wavelength (0.6 V)						
	0 V	0.6 V	350	400	475	550	650		
1	2.15 ± 0.12	3.35 ± 0.21	0.09	0.13	0.16 ± 0.022	0.13	0.11		
2	2.30 ± 0.13	3.74 ± 0.22	0.10	0.15	0.19 ± 0.030	0.16	0.13		
3	2.63 ± 0.18	4.17 ± 0.18	0.16	0.23	0.29 ± 0.028	0.25	0.20		
4	3.16 ± 0.10	5.05 ± 0.11	0.24	0.36	0.46 ± 0.025	0.39	0.31		
5	3.65 ± 0.13	6.37 ± 0.30	0.34	0.51	0.64 ± 0.029	0.55	0.43		
6	4.71 ± 0.12	7.69 ± 0.27	0.47	0.70	0.88 ± 0.032	0.75	0.59		
7	5.71 ± 0.16	9.68 ± 0.25	0.63	0.93	1.17 ± 0.030	0.94	0.78		
8	6.91 ± 0.17	12.81 ± 0.30	0.86	1.27	1.57 ± 0.031	1.36	1.07		
9	7.91 ± 0.22	14.85 ± 0.21	1.06	1.58	1.91 ± 0.035	1.69	1.33		
10	8.73 ± 0.10	16.53 ± 0.23	1.18	1.76	2.21 ± 0.027	1.88	1.48		
11	9.24 ± 0.20	17.63 ± 0.29	1.30	1.93	2.38 ± 0.032	2.06	1.62		
12	9.69 ± 0.21	18.51 ± 0.26	1.36	2.02	2.54 ± 0.035	2.16	1.70		
13	9.95 ± 0.12	19.15 ± 0.31	1.40	2.09	2.61 ± 0.028	2.23	1.75		
14	10.15 ± 0.18	19.31 ± 0.31	1.45	2.16	2.64 ± 0.033	2.31	1.82		

Table S2. The P_{ph} values of the PDs in electrolytes with the pH ranging from 1 to 14 with different wavelengths calculated at level IV and the bias potential of 0.6V.



Figure S1. The EDS results of Te@Se. a: The spectra from Area #1. b: The elements

content of Te@Se.



Figure S2. a: The UV-Vis absorption of Te flake and bulk Se. **b:** The XRD patterns of fresh Te@Se and after 2 weeks.



Figure S3. The details of the ON/OFF signals intercepted from level IV of the PDs in different pH electrolytes at the bias potential of 0.6 V.



Figure S4. The photo-response behaviors of the PDs in different electrolytes with the pH ranging from 1 to 14 and the bias potential of 0.6 V.



Figure S5. The photo-response behaviors in different pH electrolytes ranging from 1 to 14 under 400 and 550 nm and the corresponding fitted curves.



Figure S6. a and **c**: The photo-response behaviors of the PDs in different electrolytes with the pH of 1 and 14 for operating for 10,000 s after 1 month. **b** and **d**: The details of the PDs in different electrolytes with the pH of 1 and 14.



Figure S7. Wave function squares of the VBM and CBM states in Te@Se. The electron density is drawn with an isosurface of 0.03 $e^{A^{-3}}$.



Figure S8. Band alignment between 2D Te and 2D Se by HSE06.



Figure S9. a: Structure of H⁺ terminated Te@Se. **b:** Structure, adsorption energy, and bond length around the adsorption center for O₂ molecule. **c:** Differential charge density of O₂ adsorbed Te@Se under the acidic conditions. The electron density is drawn with an isosurface of 0.006 eÅ⁻³. The yellow surface corresponds to charge accumulation, and the blue one corresponds to charge depletion. Atom color code: green, Se atom; dark yellow, Te atom; white, H atom; and red, O atom. **d-e:** The response and recovery time of Te@Se-based PDs in different pH electrolytes.