Supporting information

$$\alpha h\nu = A\,(h\nu - Eg)^n \quad (1)$$

$$E_{FE} = h\nu - E_{cutoff} \quad (2)$$

$$E_{VB} = E_{FE} + E_{onset} - E_e \quad (3)$$

$$E_{CB} = E_{VB} - E_g \quad (4)$$

where α, ν and Eg are the absorption coefficient, incident light frequency and band gap, respectively, and h and A are constants. Typically, the value of n is 2 for indirect bandgap semiconductors and 1/2 for direct bandgap semiconductors. Here, n = 2. hv is the radiant energy (hv=21.22eV), Ee is the energy of free electrons on the hydrogen scale (Ee = 4.5 eV).

$$E_{RHE} = E_{Ag/AgCl} + 0.0591PH + 0.1976\,V \quad (5)$$

$$ABPE = (J_{light} - J_{dark}) \times \left(\frac{1.23 - V_{RHE}}{P_{light}}\right) \quad (6)$$

Here, J_{light} and J_{dark} is the photocurrent density under light and dark conditions. V_{RHE} represents the relationship between applied potential and RHE, and P_{light} is the intensity of incident light (100 mW/cm^2, AM 1.5 G).

$$\mathrm{IPCE} = \frac{1240J}{\lambda Plight} \quad (7)$$

$$1/c^2 = \frac{2(\mathrm{V} - V_{fb} - \frac{K_B T}{\mathrm{e}})}{\varepsilon\varepsilon_0 e A^2 N_d} \quad (8)$$

$$\mathrm{N}_d = \frac{2}{\varepsilon\varepsilon_0 e}\left[\frac{d(\frac{1}{c^2})}{d_V}\right]^{-1} \quad (9)$$

$$J_{H_2O} = J_{abs} \times \eta_{bulk} \times \eta_{surface} \quad (10)$$

$$J_{Na_2SO_3} = J_{abs} \times \eta_{bulk} \quad (11)$$

$$\eta_{bulk} = J_{Na_2SO_3}/J_{abs} \quad (12)$$

$$\eta_{surface} = J_{H_2O}/J_{Na_2SO_3} \quad (13)$$

J_{H_2O} stands for photocurrent density, and J_{abs} refers to photon absorption represented by current density (100 % photocurrent of APCE is assumed).*c* represents the space charge capacitance, K_B means Boltzmann constant (1.38 × 10^{-23} J/K), *T* indicates Kelvin temperature, ε and ε_0 are the relative permittivity and the permittivity of vacuum of CdS, *e* represents elementary charge and *A* is coated electrode area, the bias voltage applied to the electrodes is expressed by V.

$$FE_{O_2} = \frac{4nF}{I \times t} \times 100\% \tag{14}$$

Where n is the actual number of moles of the product (mol), F is Faraday's constant (96485.34C/mol), I is the photocurrent produced (A) and t is the reaction time (s).

Table S1 Flat band potential (V_{fb}) and donor density (N_d) of electrodes deduced from Mott-Schottky

Condition / Sample	Light		Light+△T	
	V_{fb} (V vs RHE)	N_d (cm^{-3})	V_{fb} (V vs RHE)	N_d (cm^{-3})
CdS	-0.21	1.25×10^{19}	-0.20	2.02×10^{19}
CdS/In_2S_3-H	-0.36	2.12×10^{19}	-0.37	2.31×10^{19}
CdS/In_2S_3-HC	-0.41	2.26×10^{19}	-0.43	2.49×10^{19}

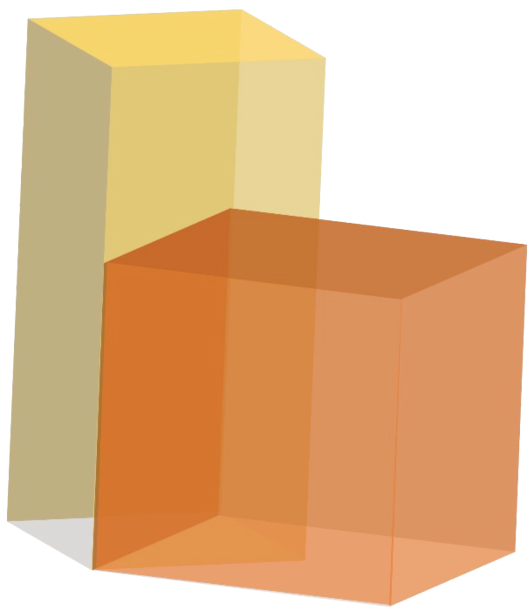

Fig. S1 Diagram of the crystal transition mechanism

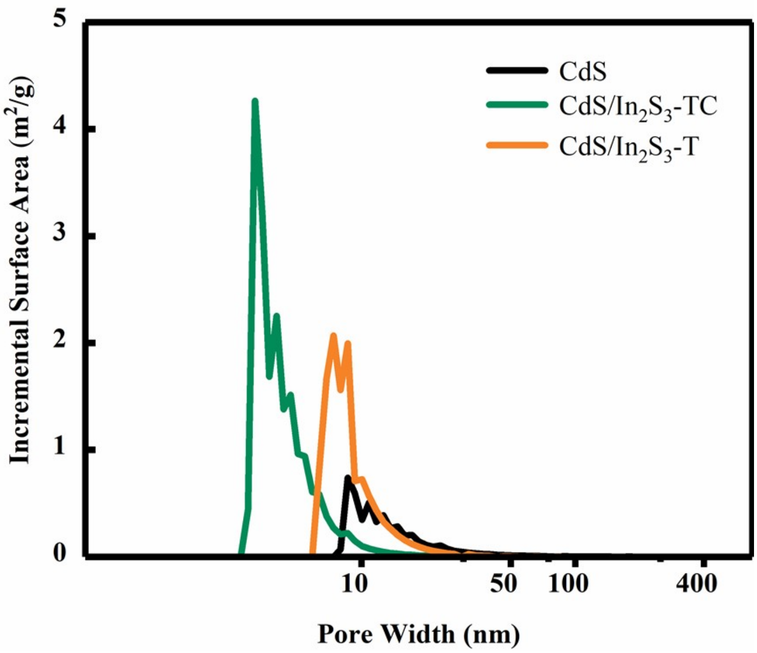

Fig. S2 The pore distribution for the CdS, CdS/In_2S_3-T and CdS/In_2S_3-TC

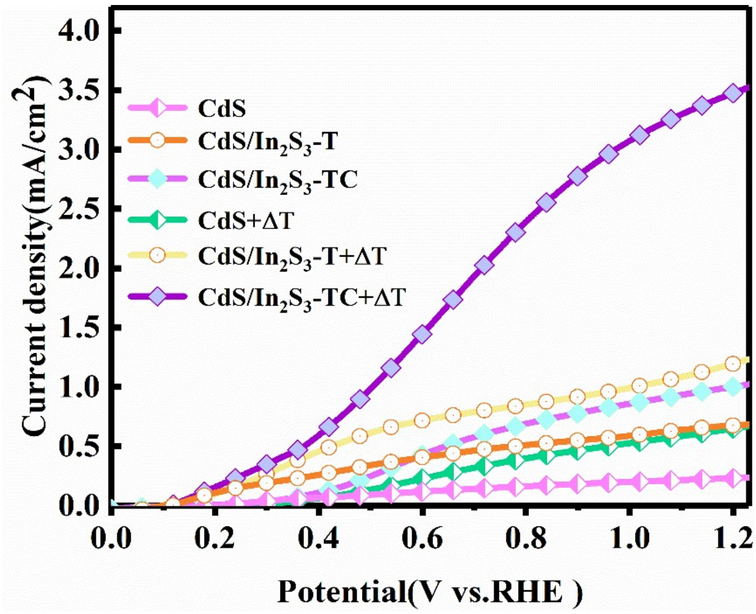

Fig. S3 The LSV curves of different samples under photoelectrocatalytic and pyro-photoelectrocatalytic conditions

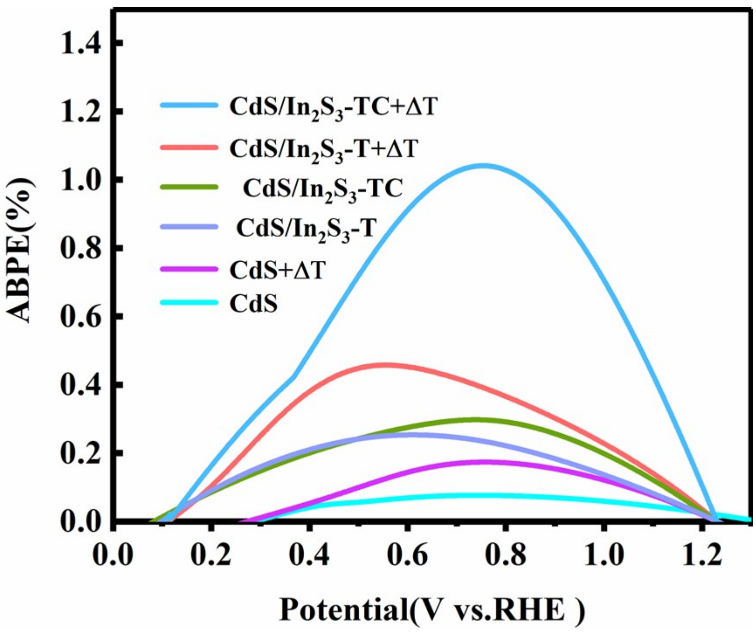

Fig. S4 The ABPE curves of different samples under photoelectrocatalysis and pyro-photoelectrocatalysis conditions

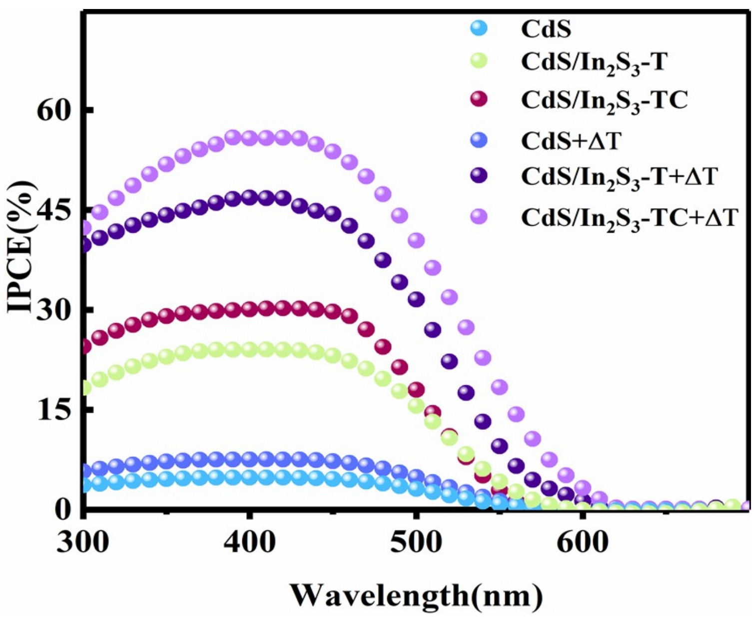

Fig. S5 The IPCE curves of different samples under photoelectrocatalysis and pyro-photoelectrocatalysis conditions

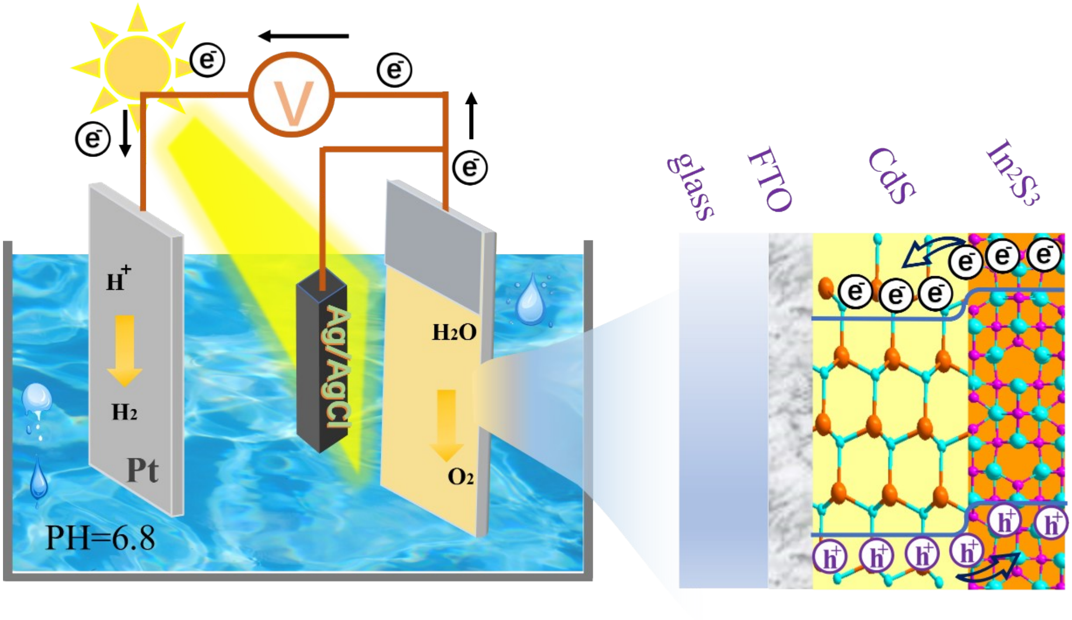

Fig. S6 Mechanism diagram of CdS/In_2S_3 heterojunctions

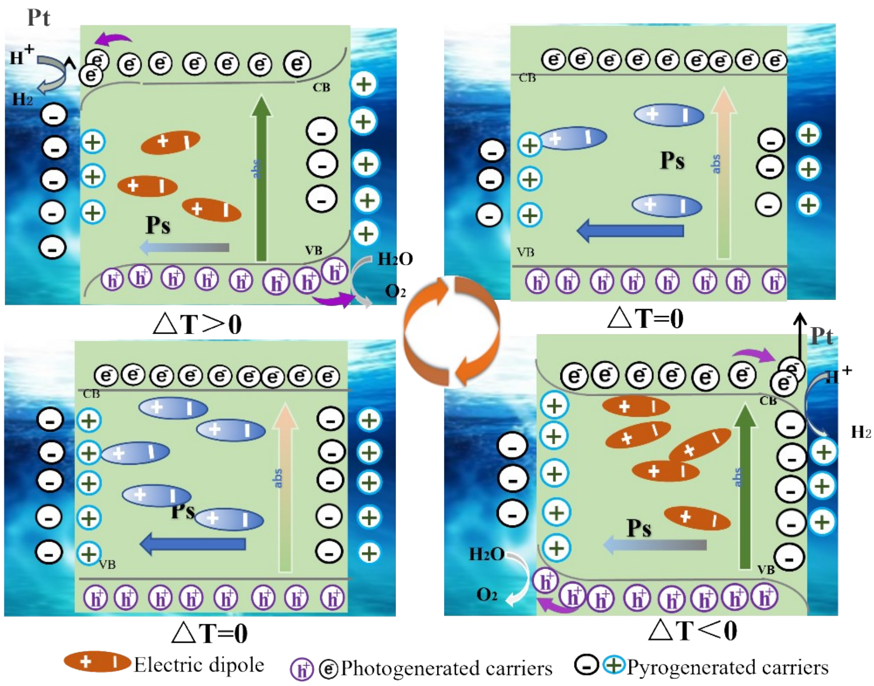

Fig. S7 Diagram of pyroelectric mechanism during temperature change

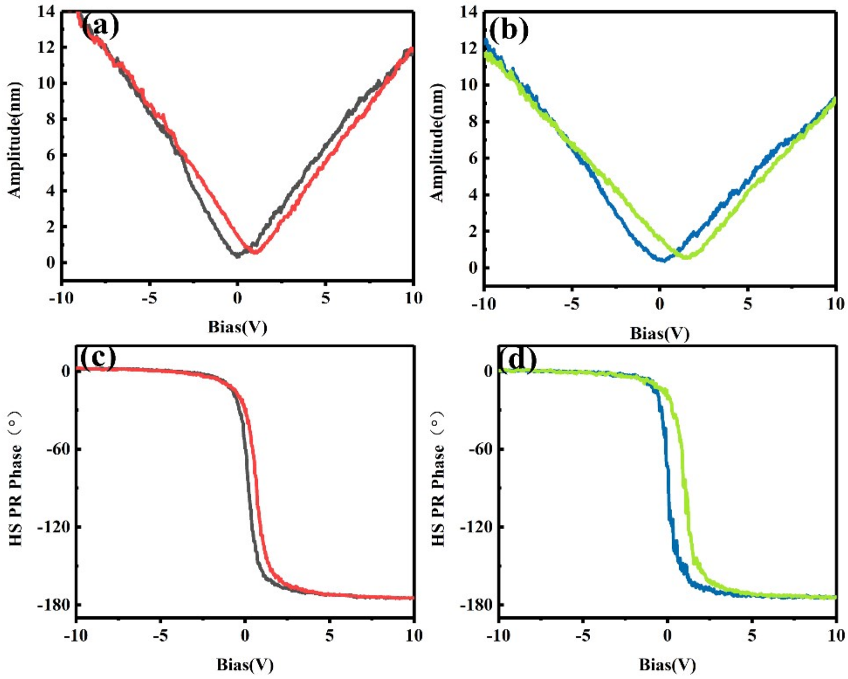

Fig. S8 Amplitude butterfly loop (a, c) and phase lag loop (b, d) of CdS/In_2S_3-T and CdS/In_2S_3-TC films

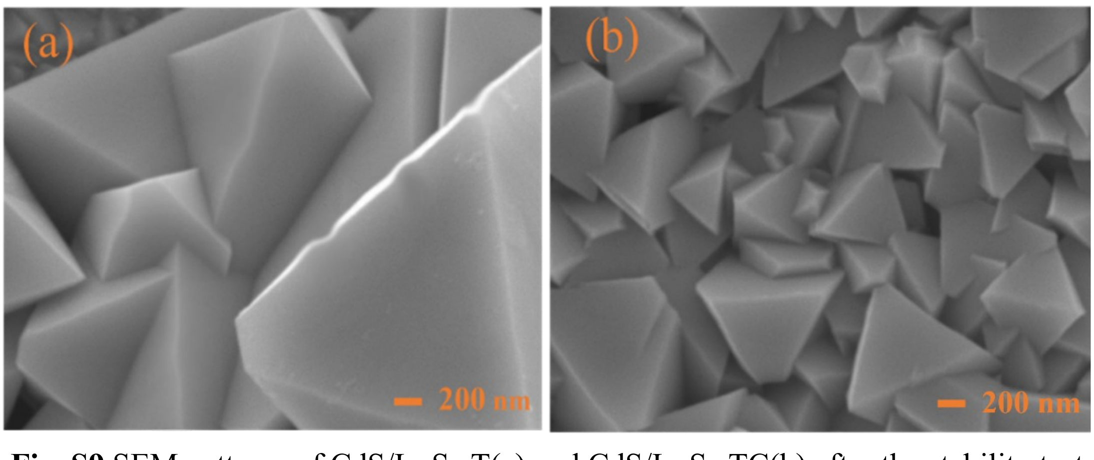

Fig. S9 SEM patterns of CdS/In_2S_3-T(a) and CdS/In_2S_3-TC(b) after the stability test

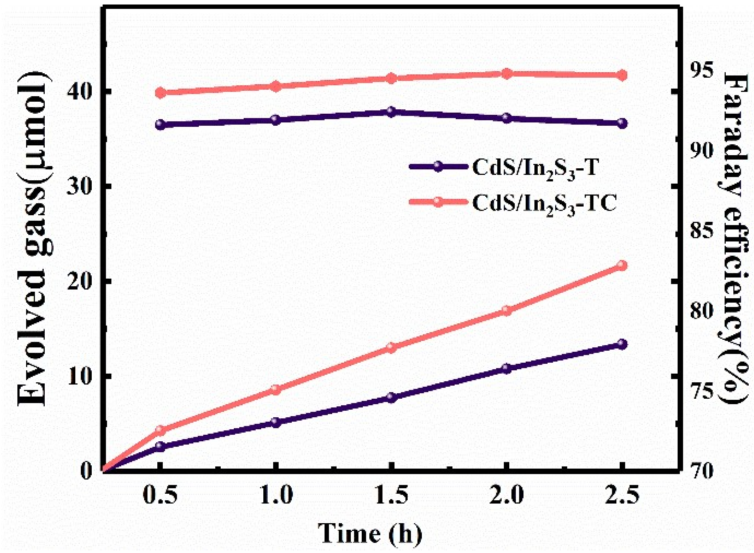

Fig. S10 The oxygen measurement data and Faraday efficiency of CdS/In_2S_3-T and CdS/In_2S_3-TC films

Supporting information

$$\alpha h\nu = A\,(h\nu - Eg)^n \tag{1}$$

$$E_{FE} = h\nu - E_{cutoff} \tag{2}$$

$$E_{VB} = E_{FE} + E_{onset} - E_e \tag{3}$$

$$E_{CB} = E_{VB} - E_g \tag{4}$$

where α, ν and Eg are the absorption coefficient, incident light frequency and band gap, respectively, and h and A are constants. Typically, the value of n is 2 for indirect bandgap semiconductors and 1/2 for direct bandgap semiconductors. Here, n = 2. hv is the radiant energy (hv=21.22eV), Ee is the energy of free electrons on the hydrogen scale (Ee = 4.5 eV).

$$E_{RHE} = E_{Ag/AgCl} + 0.0591PH + 0.1976\,V \tag{5}$$

$$ABPE = (J_{light} - J_{dark}) \times \left(\frac{1.23 - V_{RHE}}{P_{light}}\right) \tag{6}$$

Here, J_{light} and J_{dark} is the photocurrent density under light and dark conditions. V_{RHE} represents the relationship between applied potential and RHE, and P_{light} is the intensity of incident light (100 mW/cm^2, AM 1.5 G).

$$\text{IPCE} = \frac{1240J}{\lambda Plight} \tag{7}$$

$$1/c^2 = \frac{2(\text{V} - V_{fb} - \frac{K_B T}{\text{e}})}{\varepsilon\varepsilon_0 e A^2 N_d} \tag{8}$$

$$\text{N}_d = \frac{2}{\varepsilon\varepsilon_0 e}\left[\frac{d(\frac{1}{c^2})}{d_V}\right]^{-1} \tag{9}$$

$$J_{H_2O} = J_{abs} \times \eta_{bulk} \times \eta_{surface} \tag{10}$$

$$J_{Na_2SO_3} = J_{abs} \times \eta_{bulk} \tag{11}$$

$$\eta_{bulk} = J_{Na_2SO_3}/J_{abs} \tag{12}$$

$$\eta_{surface} = J_{H_2O}/J_{Na_2SO_3} \tag{13}$$

J_{H_2O} stands for photocurrent density, and J_{abs} refers to photon absorption represented by current density (100 % photocurrent of APCE is assumed).*c* represents the space charge capacitance, K_B means Boltzmann constant (1.38×10^{-23} J/K), *T* indicates Kelvin temperature, *ε* and ε_0 are the relative permittivity and the permittivity of vacuum of CdS, *e* represents elementary charge and *A* is coated electrode area, the bias voltage applied to the electrodes is expressed by V.

$$FE_{O_2} = \frac{4nF}{I \times t} \times 100\% \tag{14}$$

Where n is the actual number of moles of the product (mol), F is Faraday's constant (96485.34C/mol), I is the photocurrent produced (A) and t is the reaction time (s).

Table S1 Flat band potential (V_{fb}) and donor density (N_d) of electrodes deduced from Mott-Schottky

Sample \ Condition	Light		Light+△T	
	V_{fb} (V vs RHE)	N_d (cm^{-3})	V_{fb} (V vs RHE)	N_d (cm^{-3})
CdS	-0.21	1.25×10^{19}	-0.20	2.02×10^{19}
CdS/In_2S_3-H	-0.36	2.12×10^{19}	-0.37	2.31×10^{19}
CdS/In_2S_3-HC	-0.41	2.26×10^{19}	-0.43	2.49×10^{19}

Fig. S1 Diagram of the crystal transition mechanism

Fig. S2 The pore distribution for the CdS, CdS/In_2S_3-T and CdS/In_2S_3-TC

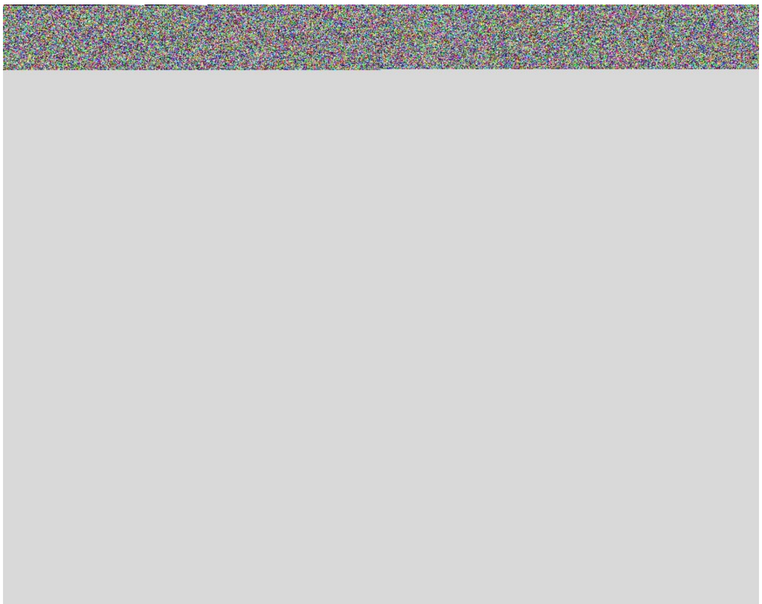

Fig. S3 The LSV curves of different samples under photoelectrocatalytic and pyro-photoelectrocatalytic conditions

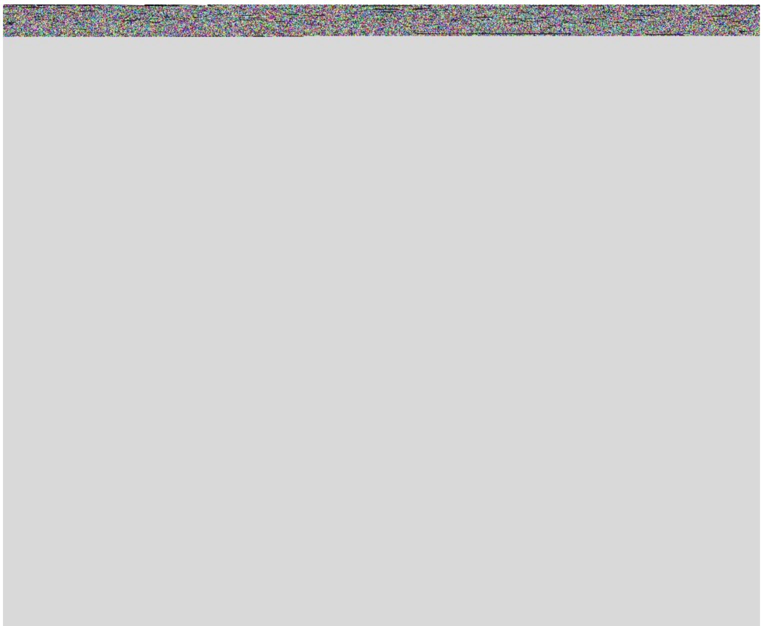

Fig. S4 The ABPE curves of different samples under photoelectrocatalysis and pyro-photoelectrocatalysis conditions

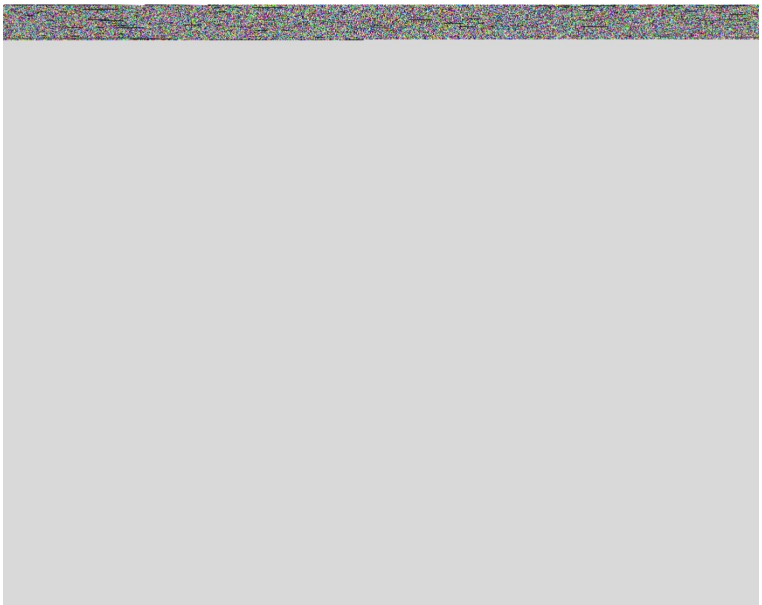

Fig. S5 The IPCE curves of different samples under photoelectrocatalysis and pyro-photoelectrocatalysis conditions

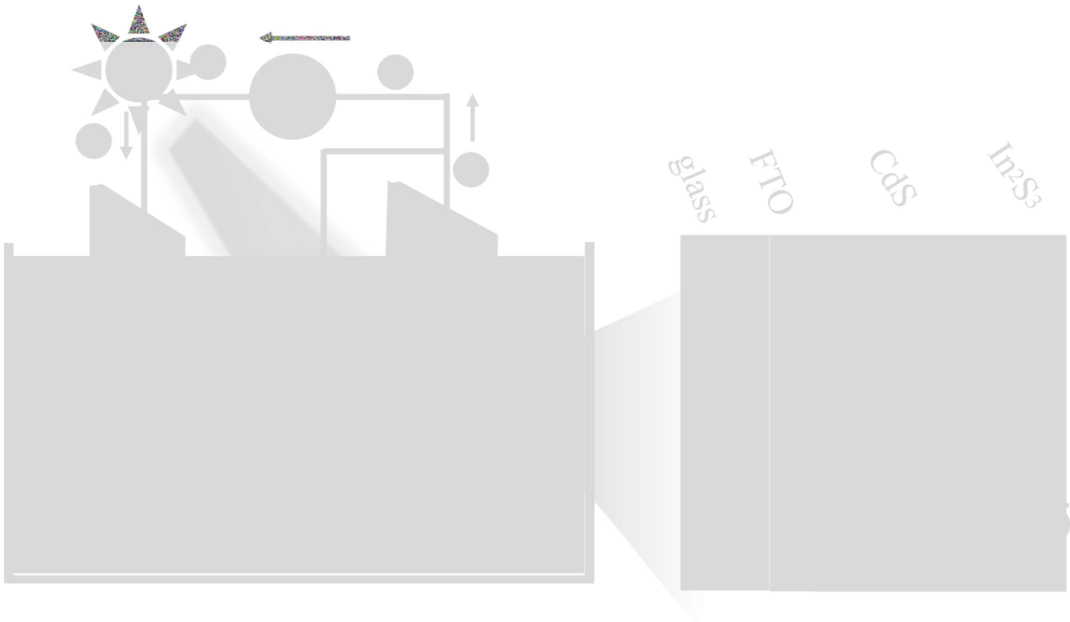

Fig. S6 Mechanism diagram of CdS/In_2S_3 heterojunctions

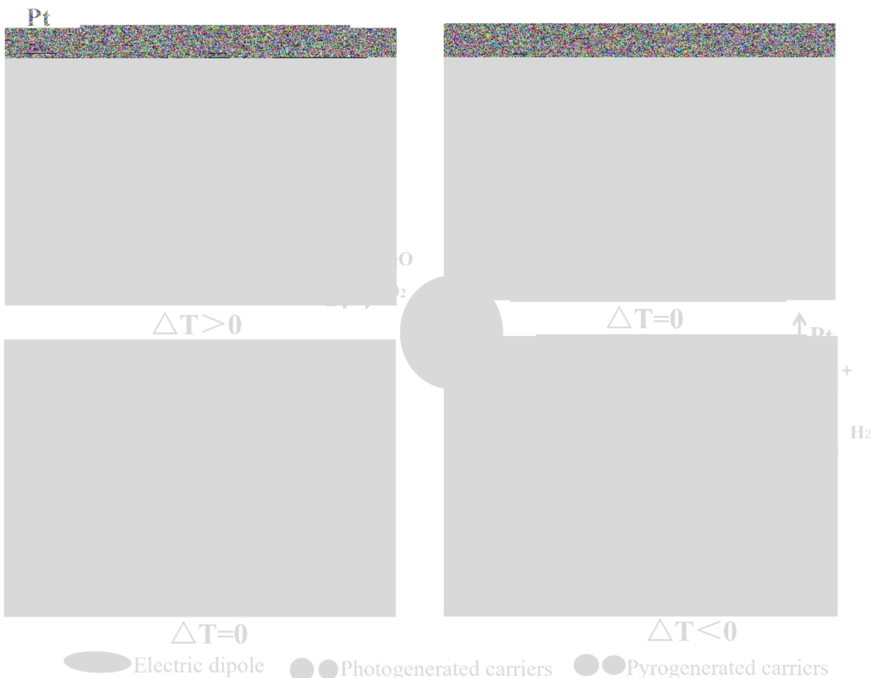

Fig. S7 Diagram of pyroelectric mechanism during temperature change

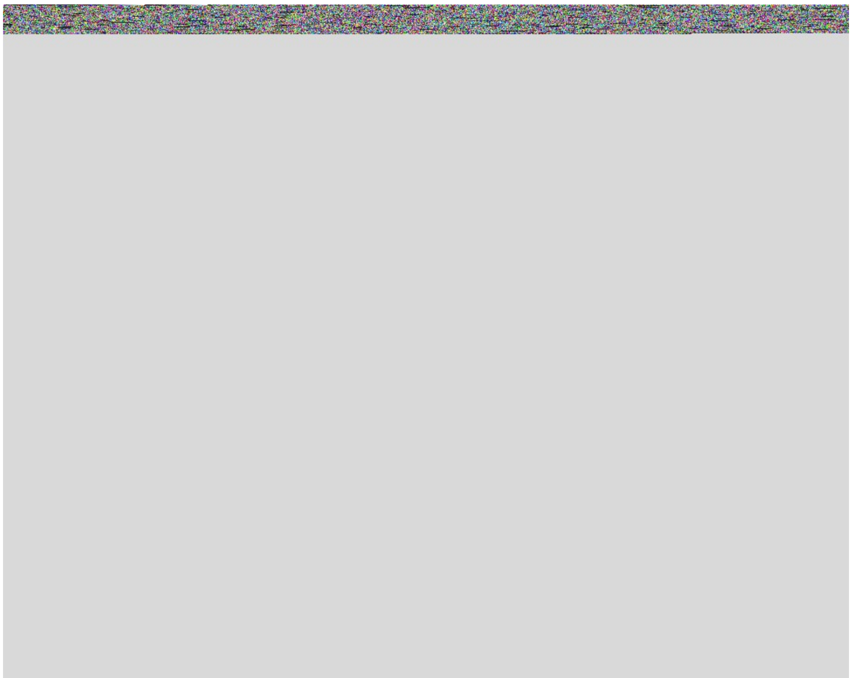

Fig. S8 Amplitude butterfly loop (a, c) and phase lag loop (b, d) of CdS/In_2S_3-T and CdS/In_2S_3-TC films

Fig. S9 SEM patterns of CdS/In_2S_3-T(a) and CdS/In_2S_3-TC(b) after the stability test

Fig. S10 The oxygen measurement data and Faraday efficiency of CdS/In_2S_3-T and CdS/In_2S_3-TC films