

Supporting information

Solution-based synthesis of pyrite film with enhanced photocurrent generation

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Experimental Details:

1. Preparation

All chemical include $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, S, KI and the commercial natural pyrite crystals were purchased from Aldrich and Wako and used as received. The flexible Fe foil (Wako, purity: > 99 %, thickness 0.01 mm) was cut into four identical pieces with the size of $\sim 2.2 \text{ cm} \times 2 \text{ cm}$. the Fe pieces were soaked in 100 mL distilled water with detergent. After being ultrasonically cleaned, the Fe pieces were taken out and rinsed gently with distilled sufficiently.

To prepare the FeS_2 thin film, 0.002 mol $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.004 mol S were dispersed in 30 mL distilled water. The as-obtained yellow dispersion was mixed with 10 mL Na_2S solution (0.008 mol) under magnetic stirring at 50 °C to give a black suspension. Ten mL of this suspension was added into a 20 mL Teflon-lined autoclave with a piece of clean iron foil, placed at the bottom. The autoclave was heated at 140-200 °C for 3-6 h, and cooled in air to room temperature. The iron foil was removed, washed with distilled water by ultrasonication for 30 min (US-4R, 620 W, 50/60 Hz), and finally dried for characterization. The experiment procedure of pyrite thin film synthesis is illustrated in **Fig. S1**.

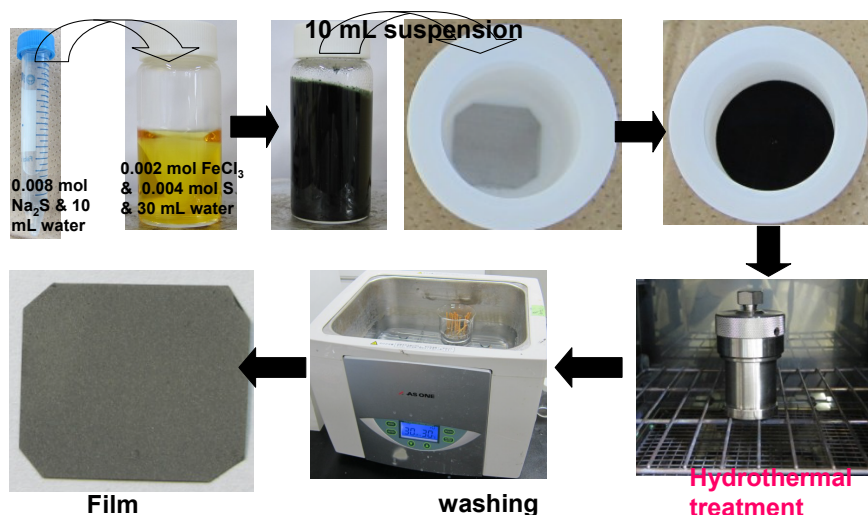


Fig. S1 The experiment procedure of pyrite thin film synthesis via hydrothermal route

In our synthesis approach, Fe³⁺ ions reacted with S²⁻ ions to produce FeS and elemental S via the equation¹ $2Fe^{3+} + 3S^{2-} \rightarrow 2FeS + S$ (1), when Na₂S solution was added into FeCl₃ solution. As Na₂S can also act as a strong base, the following reaction can also occur between Na₂S and FeCl₃: $2Fe^{3+} + 3S^{2-} + 3H_2O \rightarrow 2Fe(OH)_3 + 3H_2S$ (2). Hence, the black suspension obtained upon mixing the FeCl₃ and S dispersion with Na₂S solution is expected to contain Fe(OH)₃, FeS₂, FeS, and S. When the black suspension was transferred to the Teflon-lined autoclave containing Fe foil, Fe²⁺ clusters formed on the foil surface according to the reaction: $2Fe^{3+} + Fe \rightarrow 3Fe^{2+}$ (3). The Fe²⁺ clusters then likely acted as nuclei layers for FeS₂ growth in the presence of sufficient amounts of elemental S, FeS, and S²⁻ ions, a speculation that will be later confirmed by field-emission scanning (FESEM) and transmission electron microscopy (TEM) observations. It is worth noting that the pyrite film did not detach from the Fe foil, even after long periods of intense ultrasonication, suggesting that the film strongly adhered to the substrate. This strong adhesion was presumably due to the *in-situ* nucleation of Fe²⁺ clusters resulting from the redox reaction between Fe metal and ferric ions, and the structural resemblance between the pyrite film and Fe foil substrate, which together, are expected to have enhanced the photocurrent.

2. Sample Characterization

The structural characteristics of the samples were measured by X-ray diffraction (XRD) at room temperature on a Rigaku SmartLab 2080B202 diffractometer. The data were collected from $2\theta = 15-70^\circ$ in a step-scan mode. Raman spectra were recorded using a JY-HR800 spectrometer with a Confocal Raman microspectroscopy (Renishaw) with a 514-nm laser. The morphologies of the samples were investigated by a field-emission scanning electron microscopy (SEM) using a JEOL JSM-6700 apparatus and transition electron microscopy (TEM) on a Hitachi HF-2000 instrument under an acceleration voltage of 200 kV. The absorption spectra of the thin were recorded using a UV-2550 spectrophotometer (Shimadzu). The ionic characteristics and surface composition were studied by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer, 5600). The binding energy data are calibrated with the C 1s signal at 284.6 eV.

3. Electrode fabrication and evaluation of photoelectrochemical property

3.1 Electrode fabrication

Firstly, the as-obtained was cut into a desired size for the electrode. The back surface of the film was then polished with sandpaper. A copper wire with heat shrinkable tube was attached to the polished back surface with silver epoxy. After 30 min, the back surface and the four side faces of the electrode were protected with the epoxy glue. For the commercial natural pyrite crystal, the surface of the pyrite crystal was treated with Ga-In alloy. The following fabrication processes were the same as that of pyrite thin film electrode.

3.2 Valuation of photoelectrochemical properties

Photoelectrochemical performance of the as-obtained film electrodes was tested by using Hokuto Denko HSV-100 potentiostat. The light source was a Xenon arc lamp with a UV filter (Y-44) or an IR transmissive filter (R-70). The electrolyte was 4 M KI solution. Prior to measurements, the solution was bubbled with Ar gas to purge the dissolved oxygen for at least 30 min. A platinum electrode was used as the counter

electrode, and reference electrode was Ag/AgCl. For linear sweep voltammetry, potential was swept to the positive direction with a scan rate of 5 mV/S. Handed chopped light was used to record both the dark and photocurrent during a single scan. The time dependence of the photocurrent under constant electrode polarization was obtained with hand chopped light.

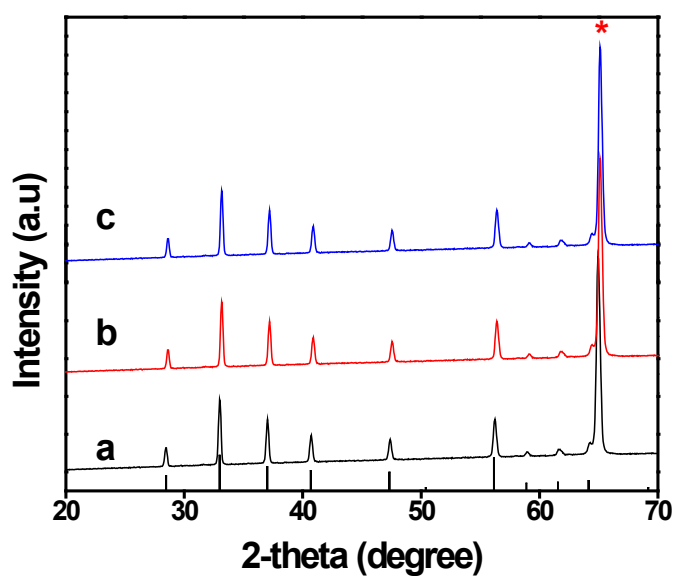


Fig. S2 XRD pattern of the as-obtained films obtained after hydrothermal treatment at (a) 160 °C, (b) 180 °C, and (c) 200 °C for 6 h

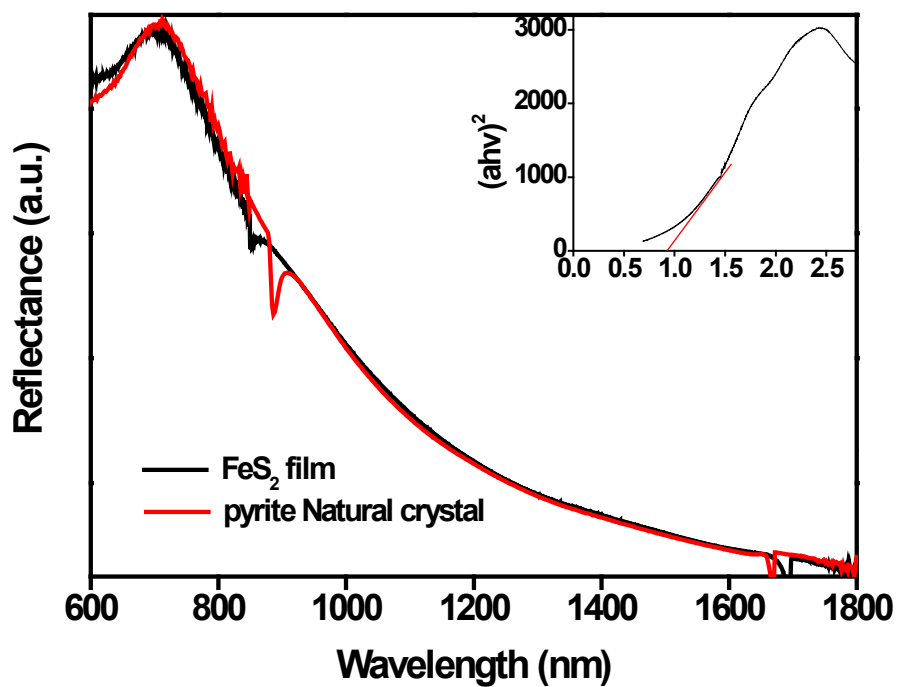


Fig. S3 Comparative studies of the UV-vis reflectance spectra of the as-obtained film and the commercial natural crystals. inset: relationship between $(ahv)^2$ and photo energy.

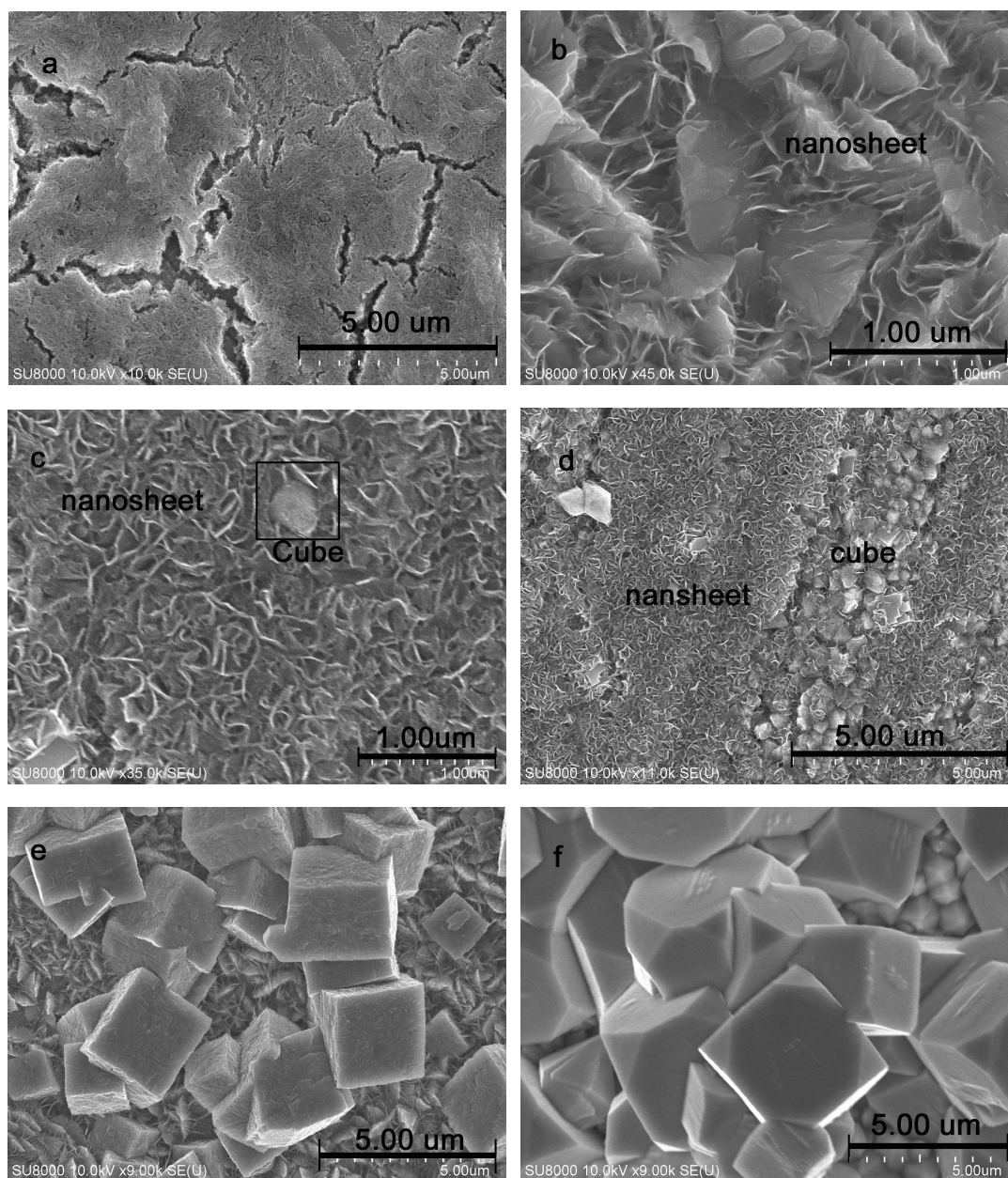


Fig. S4 FESEM images of the pyrite film obtained at 160 °C after various treatment times. (a) 3 h without ultrasonic rinsing. (b) and (c) 3 h after ultrasonic rinsing. (d) 3.5 h after ultrasonic rinsing. (e) 4 h after ultrasonic rinsing. (f) 5 h after ultrasonic rinsing.

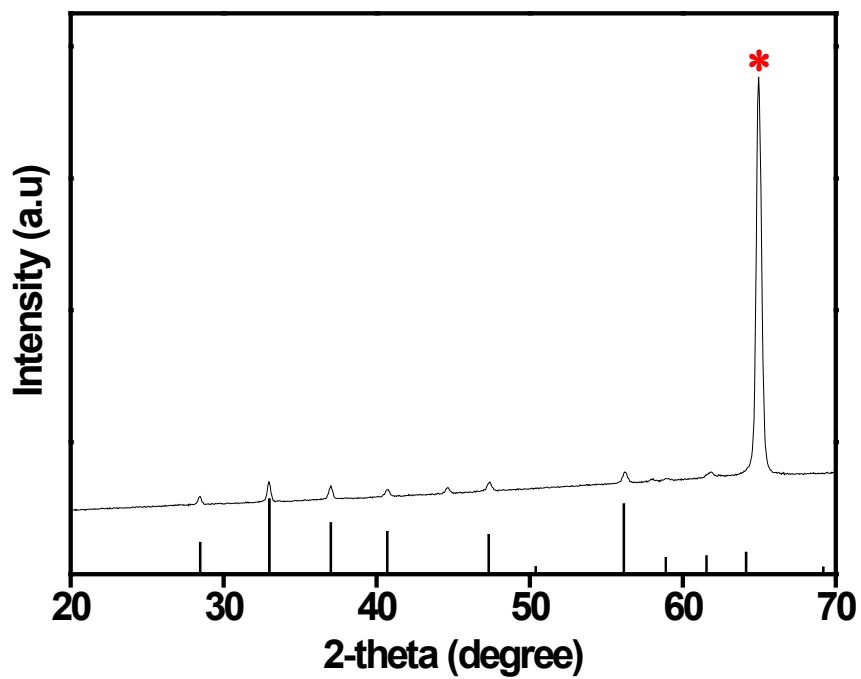


Fig. S5 XRD pattern of the as-obtained films obtained after hydrothermal treatment at 160 °C for 3.5 h.

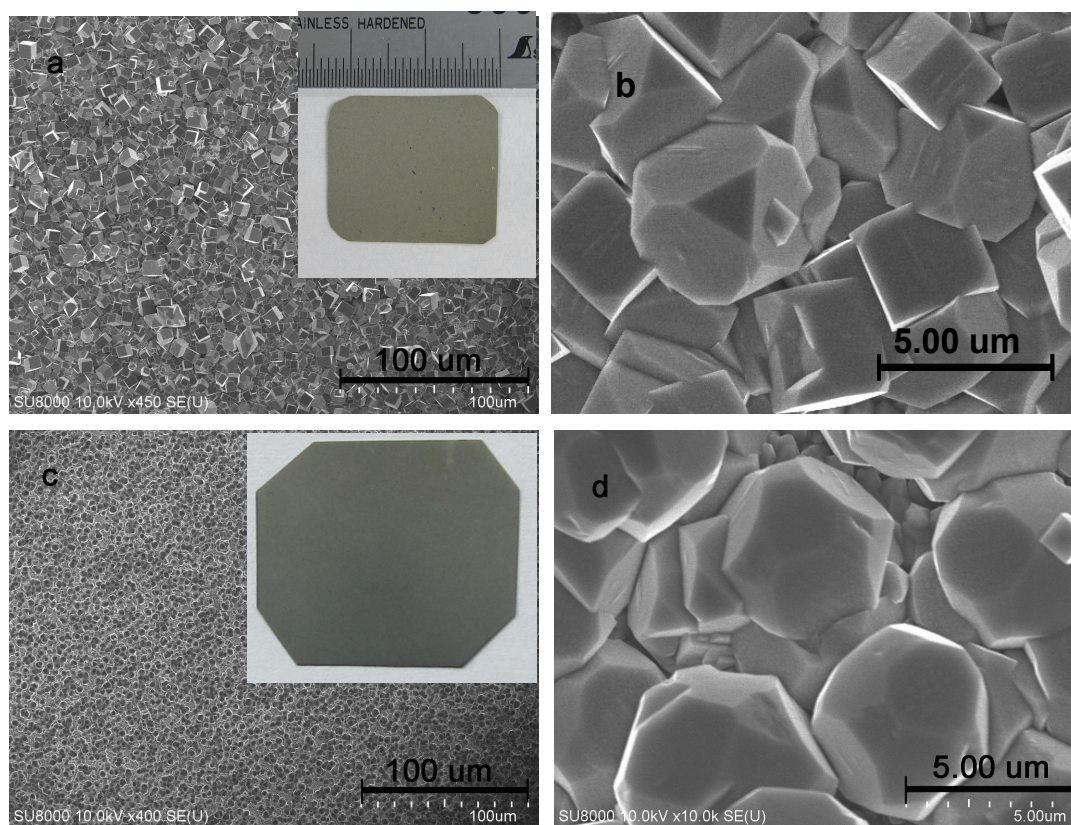


Fig. S6 SEM images of the thin films obtained after 6 h hydrothermal treatment at different temperature. (a) and (b) 180 °C, (c) and (d) 200 °C, Inset: the corresponding photographs.

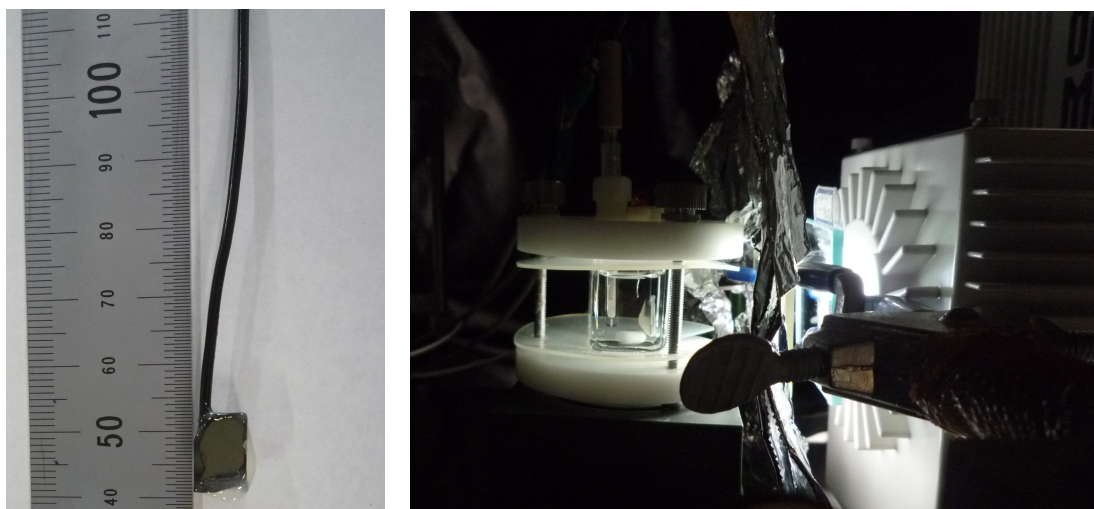


Fig. S7 The photographs of the thin film electrode (a) and the cells for the photoelectrochemical studies (b).

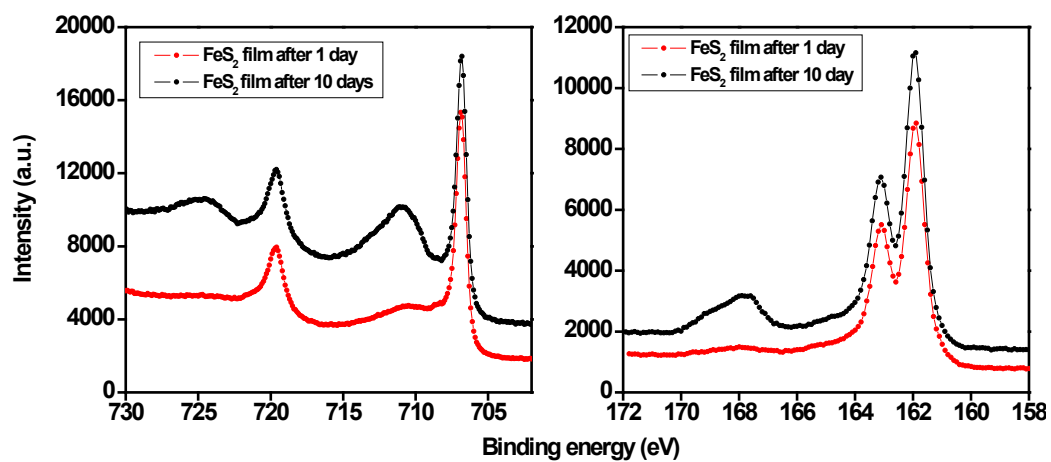


Fig. S8 Comparative studies of the XPS of the films after kept in air for different days, (a) Fe 2p core-level spectra, (b) S 2p core-level spectra.

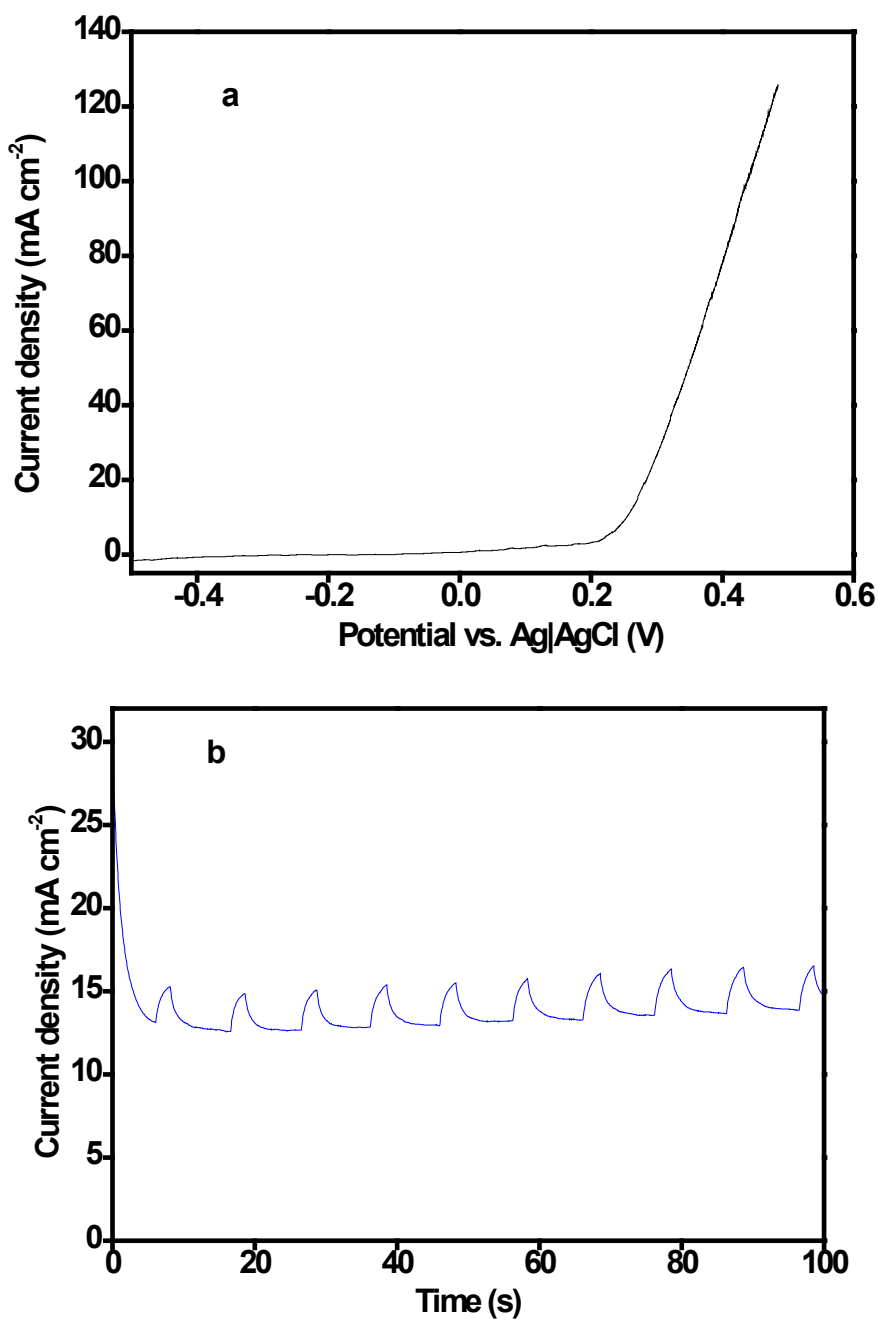


Fig. S9 (a) Current potential curves under chopped light irradiation with a UV filter for natural pyrite crystal electrode. (b) Current-time profiles for pyrite film electrode at an applied potential bias of 0.25 V vs Ag/AgCl under chopped light irradiation with an IR transmissive filter

References

- 1 D. W. Wei and K. Osseo-Asare, *Colloid Surf. A-Physicochem. Eng. Asp.*, 1997, **121**, 27-36.