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# Ti/Co-S Catalysts Covered Amorphous Silicon Based Photocathodes with High Photovoltage for Hydrogen Evolution Reaction in Non-Acid Environment

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## Experimental details

**Materials.** The ethyl alcohol and acetone were of analytical grade and used as received without further purification. The Potassium phosphate dibasic ($K_2HPO_4$, ≥ 99.0%), Potassium phosphate monobasic ($KH_2PO_4$, 99.5-100.5%), Thiourea ($CH_4N_2S$, ≥ 99.0%) and Cobalt(II) choride ($CoCl_2$, 97%) were purchased from Sigma-Aldrich.

### Fabrication Ti/Co-S catalyst

FTO is rinsed thoroughly with water and acetone, and dried in air. The metal Ti was deposited on FTO by DC sputtering with power 15 W, air pressure 2 mTorr, gas flow of argon 30 sccm, temperature 25℃. Cobalt sulfide catalyst was prepared via a room temperature electrochemical deposition synthesis with Cobalt chloride hexahydrate (0.018 M, Aladdin) and Thiourea (1 M, Aladdin) reagents, which is mixed with deionized water. The working and counter electrode was FTO/Ti, and a saturated Ag/AgCl reference electrode was used. Consecutive linear scans from −1.2 V vs Ag/AgCl to 0.2 V vs Ag/AgCl was conducted at a scan rate of 5 mV $s^{-1}$. After deposition, the FTO/Ti working electrode is removed from the deposition bath, washed with water, followed by drying at room temperature in air and annealing at 180 °C for 1 h under nitrogen.

### A-Si/a-Si tandem solar cell preparation

All the thin film silicon layers in the devices were deposited on the wet-etched AZO glass substrates at temperature of 175℃ by a plasma enhanced chemical vapor deposition technique (PECVD) in a multi-chamber system. A mixture of silane ($SiH_4$) and hydrogen ($H_2$) gases were used for the i-a-Si:H absorber layers, and the methane ($CH_4$), trimethylborane (TMB), phosphine ($PH_3$), carbon dioxide ($CO_2$) gases were added to the $SiH_4$-$H_2$ mixture for the i-a-SiC:H buffer layers, p-nc-SiC:H/p-a-SiC:H p-type layers and n-a-Si:H/n-nc-Si:H/n-nc-$SiO_x$:H n-type layers. The a-Si:H/a-Si:H tandem solar cell structure is AZO/p-nc-SiC:H/p-a-SiC:H/i-a-SiC:H/i-a-Si:H/n-a-Si:H/n-nc-Si:H/p-nc-Si:H/p-a-SiC:H/i-a-SiC:H/i-a-Si:H/n-a-Si:H/n-nc-Si:H/n-nc-$SiO_x$:H/BZO.

### A-Si/a-Si/Ti/Co-S photocathode preparation

Using DC sputtering deposit Ti metal on a-Si/a-Si tandem solar cell. And then the a-Si/a-Si/Ti as working electrode was immersed into electrodeposition solution to deposit Co-S material.

### Electrochemical and Potoelectrochemical characterization

In this study, electrochemical and photoelectrochemical (PEC) characterization of catalyst is performed in a three-electrode configuration immersed in 1.0 M potassium phosphate buffer of pH 7 water and 1.0 M potassium hydroxide of pH 13.6 solution under 1-sun conditions [air mass (AM) 1.5G, 25 ℃, 100 mW $cm^{-2}$] using a Wacom WXs-156s-l2 dual-beam solar simulator. The potential of the working electrode is controlled with a Princeton potentiostat (PARSTAT 4000). A Pt counter electrode, an Ag/AgCl reference electrode (saturated KCl and AgCl solution), and catalyst acting as the working electrode deployed the three-electrode configuration. Linear sweep voltammetry (LSV) measurements with a scan rate of 1 mV $s^{-1}$ for electrochemical and 50 mV $s^{-1}$ for photochemical were carried out to record the current density–potential (*J*–*E*) data of catalyst. To study the catalytic activity at the material/electrolyte interface of catalyst, potential EIS measurements were also performed from 10000 Hz to 0.1 Hz at

-0.3 V *vs*. RHE.

## Material characterization

The crystal structures of the Co-S film were characterized by X-ray diffraction (XRD, Philips PANalytical X'Pert Pro) with a copper x-ray source. Scanning electron microscopy (SEM) analysis is carried out on a Hitachi SU8010 machine in a high vacuum mode. A PHI5000VersaProbe X-ray photoelectron spectroscopy (XPS) spectrometer is used to characterize Co-S sample surfaces. The open voltage of a-Si/a-Si cell is measured under 1-sun conditions [air mass (AM) 1.5G, 25 ℃, 100 mW cm$^{-2}$] using a Wacom WXs-156s-l2 dual-beam solar simulator.

## Supporting Figures

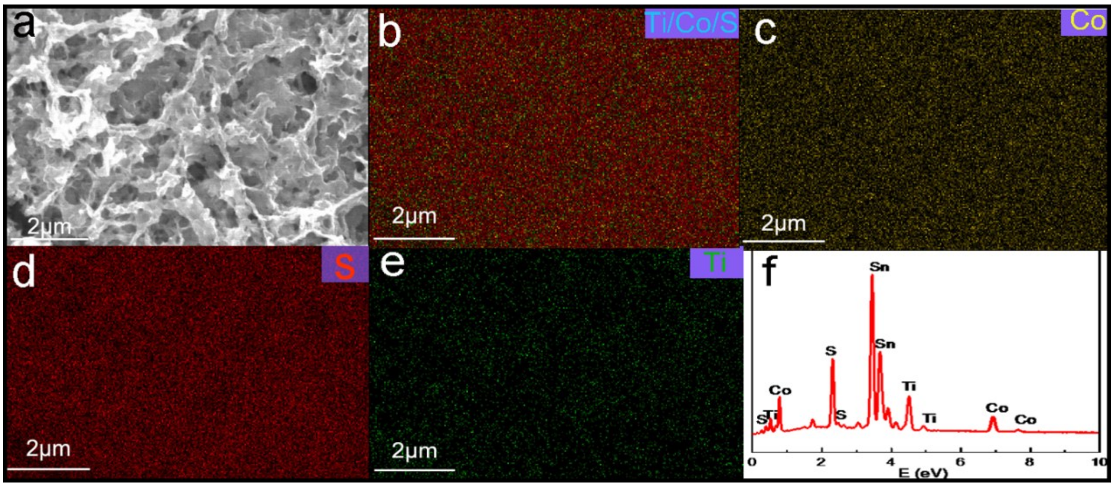

Fig. S1 The SEM image (a) and elemental mapping images of (b) overlap of Ti/Co/S, (c) Co, (d) S, and (e) Ti. (f) EDS spectra of the Ti/Co-S catalyst.

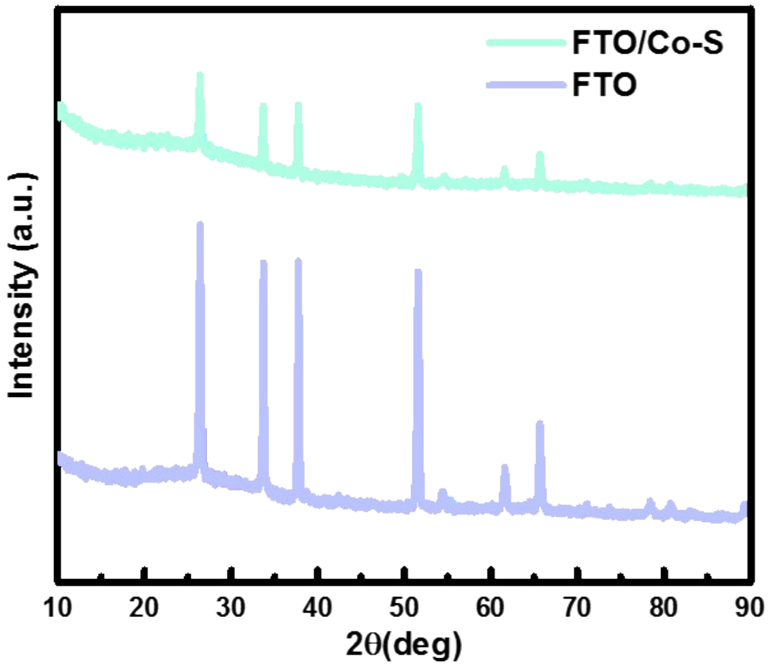

Fig. S2 The XRD patterns of Co-S deposited on FTO.

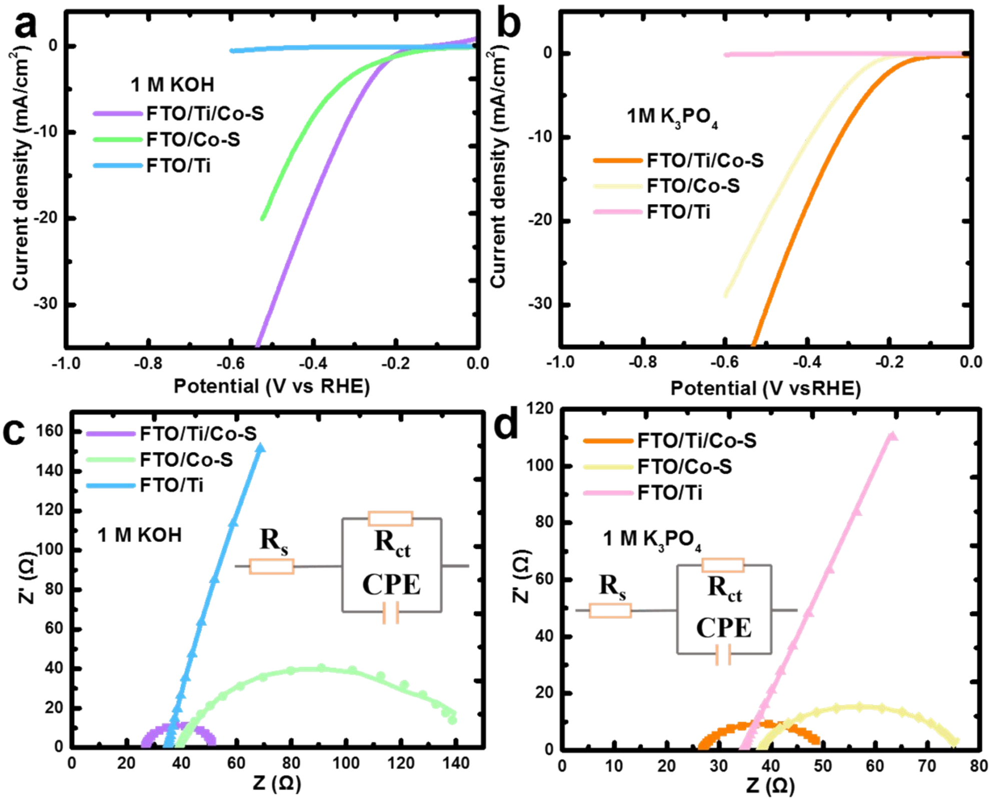

Fig. S3 The LSV curves before IR-correction (a) and (b), and the EIS curves (c) and (b) of FTO/Ti/Co-S, FTO/Co-S, FTO/Ti in alkaline and neutral solution respectively. Equivalent electrical circuit inset of (b) and (c).

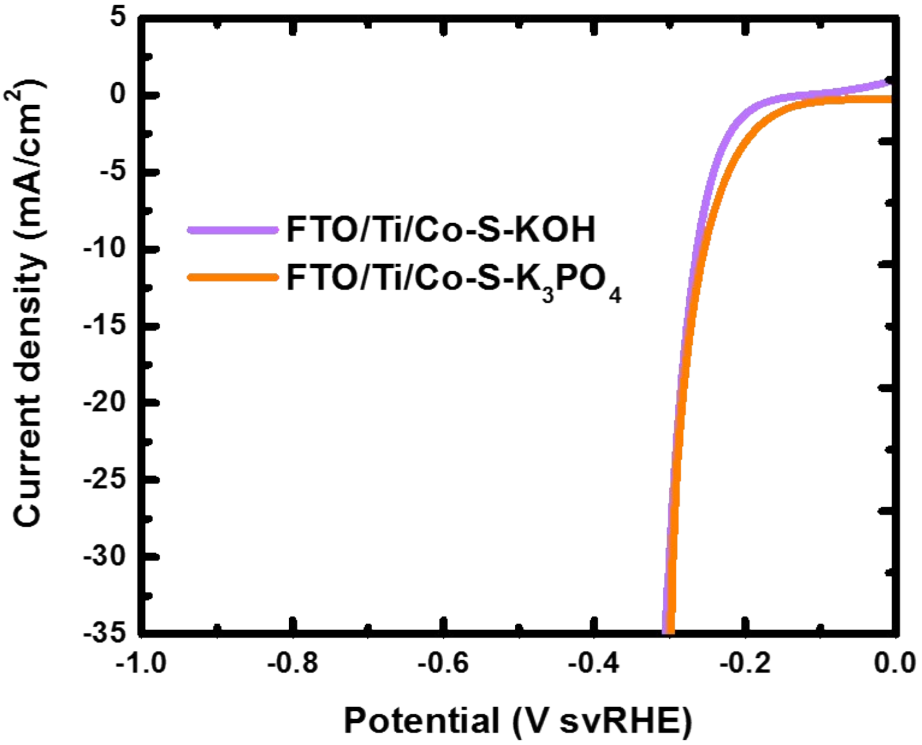

Fig. S4 Comparison of electrochemical activity of Ti/Co-S catalyst on FTO in 1 M KOH and 1M $K_3PO_4$ at 1 mV/s.

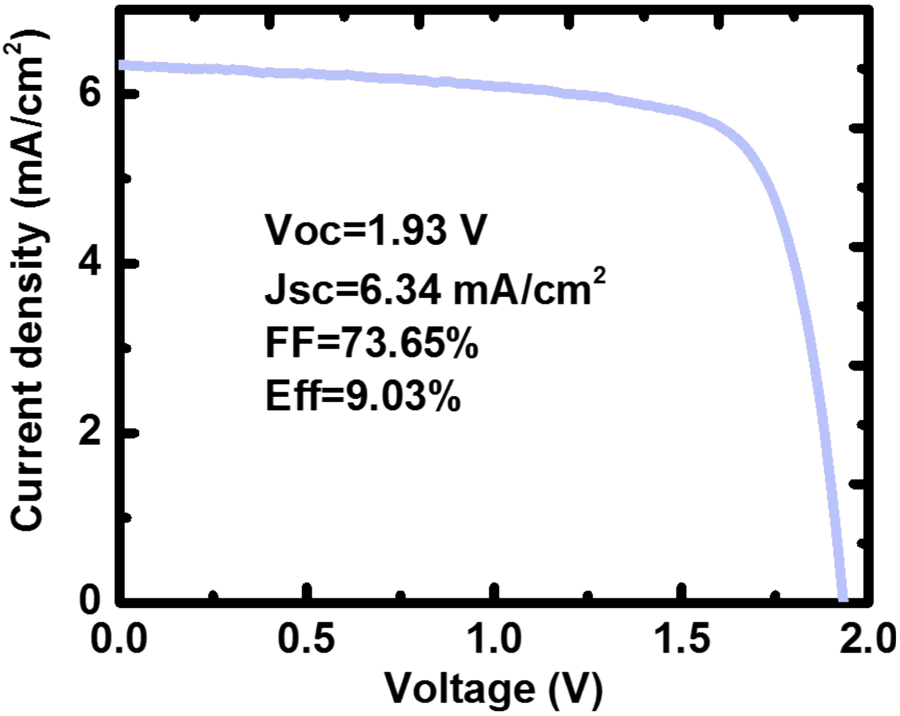

Fig. S5 Photocurrent–voltage measurement of the investigated a-Si/a-Si tandem junction solar cell with a ZnO:B back reflector.

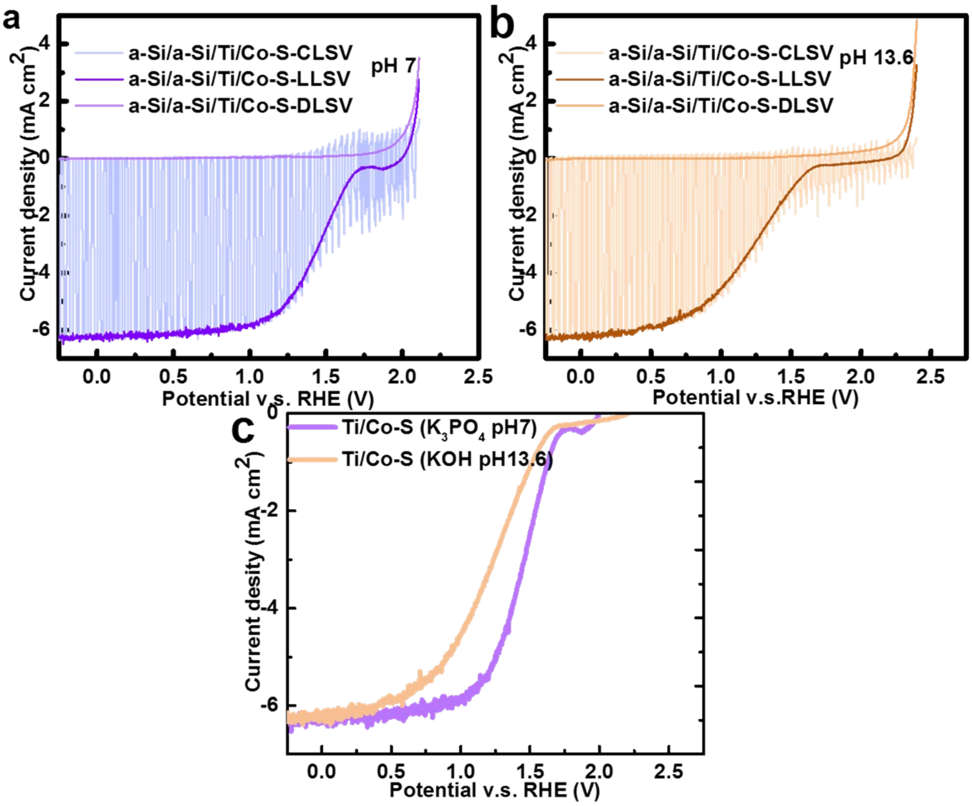

Fig. S6 The Linear sweep voltammetry curves of (a) a-Si/a-Si/Ti/Co-S photocathode in basic electrolyte and (b) a-Si/a-Si/Ti/Co-S in alkaline electrolyte under light, in the dark and during light chopping.

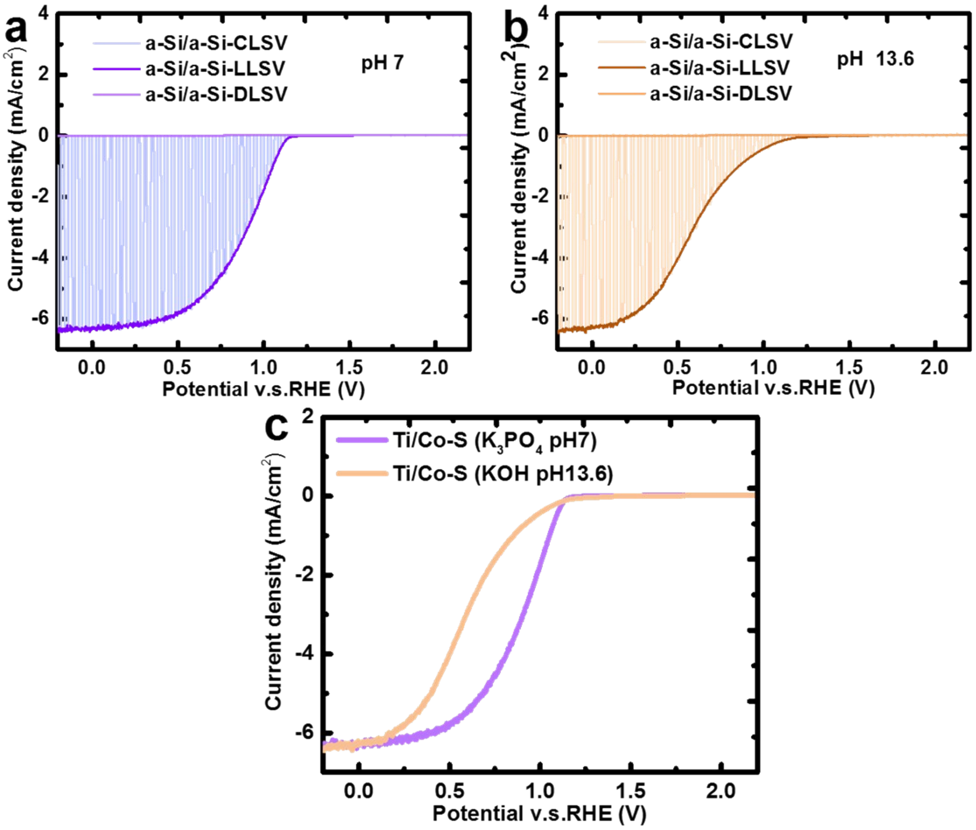

Fig. S7 The Linear sweep voltammetry curves of (a) a-Si/a-Si photocathode in basic electrolyte and (b) a-Si/a-Si in alkaline electrolyte under light and in the dark and during light chopping.

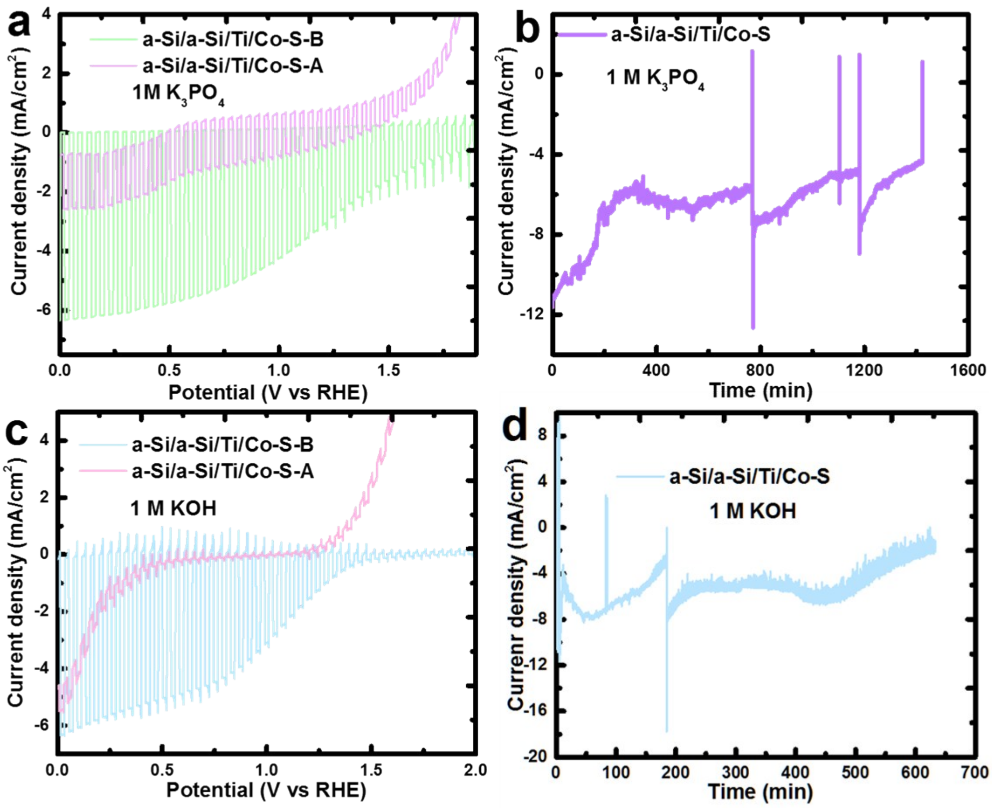

Fig. S8 The chop curves of J-V characteristics of before (a-Si/a-Si/Ti/Co-S-B) and after (a-Si/a-Si/Ti/Co-S-A) stability test in (a) neutral and (c) alkaline solution. The stability of a-Si/a-Si/Ti/Co-S photocathode in three-electrode system in (b) neutral and (d) alkaline solution.

## Supporting Tables

Table S1 The series resistence ($R_s$) values of different samples at -0.3 V vs RHE in both alkaline and neutral electrolyte.

| Electrolyte | $R_{FTO/Ti/Co\text{-}S}$ ( Ω ) | $R_{FTO/Co\text{-}S}$ ( Ω ) | $R_{FTO/Ti}$ ( Ω ) |
|---|---|---|---|
| KOH (pH 13.6) | 26.65 | 39.11 | 34.79 |
| $K_3PO_4$ (pH 7) | 26.78 | 38.17 | 34.45 |