

## Supporting Information

### Single-Atom-Catalyst with Abundant Co-S<sub>4</sub> Sites for Use as Counter Electrode in Photovoltaics

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## Chemicals

2,5-dihydroxyterephthalic acid (2.5-Dhba,  $\geq 99\%$ ) and hexadecyltrimethylammonium chloride (CTMAB,  $\geq 97\%$ ) were purchased from Alfa Aesar. Cobalt acetate tetrahydrate ( $\geq 98\%$ ) and Sodium thiosulfate pentahydrate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ,  $\geq 99.0\%$ ) were purchased from J&K Scientific Ltd. Potassium chloride (KCl,  $\geq 98.0\%$ ) and Sodium chloride (KCl,  $\geq 98.0\%$ ) as well as glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) were bought from Tianjin Kemiou. All reagents were used without further purification.

## Synthesis of Co-MOF-74 nanocrystals

Co-MOF-74 nanocrystals were synthesized in the light of the previous reported by Jide Wang and coworkers<sup>1</sup>. Specifically, 2,5-dihydroxyterephthalic acid (3 mmol) was well dissolved in 30 mL THF, the cobalt acetate (3 mmol) was dissolved in 30 mL water, followed with the addition of 2.00 g of CTMAB. Then, two aforementioned suspensions were mixed under vigorous stirring for 10 min. Next, the obtained solution was shifted to 100 mL sealed bottle and placed in an oil bath for 6 h with magnetic stirring. After that, Co-MOF-74 nanocrystals were washed and centrifugation with DI water and ethanol several times and dried in vacuum at  $60^\circ\text{C}$  overnight.

## Synthesis of Co@C

The Co@C was fabricated by the following steps: Co-MOF-74 nanocrystals were heated to  $800^\circ\text{C}$  with a heating rate of  $5^\circ\text{C min}^{-1}$  and kept at  $800^\circ\text{C}$  for 3h under flowing  $\text{N}_2$ , and then naturally cooled to room temperature. Finally, the obtained black powder named Co@C.

## Synthesis of Co-S/C-SAC

The Co-S/C-SAC were prepared by molten-salts-assisted pyrolysis. In detail, 40 mg Co-MOF-74, 0.3 g glucose and 0.8 g  $\text{Na}_2\text{S}_2\text{O}_3$  were poured into mill bottle. Next, 1.35 g NaCl and 1.65 g KCl were added into the bottle. Then, the mixture was milling several times using the ball mill to obtain homogeneous powder. Afterwards, the sample was transferred into a tube furnace at a heating rate of  $5^\circ\text{C min}^{-1}$  and heated at  $800^\circ\text{C}$  for 2 h under flowing  $\text{N}_2$ . After the furnace was cooled down to room temperature, the obtained sample was washed with DI water six times to remove the residual salt, and dried in vacuum at  $100^\circ\text{C}$  for 5 h.

## CE and DSSCs fabricaton

The Co-S/C-SAC based CE was obtained by the following steps: Firstly, the 10 mg Co-S/C-SAC sample was dispersing in 5.5 mL isopropanol. Secondly, the mixture was milled for 2 h and ultrasonic dispersed 2 h. Finally, the as-prepared CE slurry was sprayed onto FTO conductive glass at  $90^\circ\text{C}$  and heated continuously for 30min. The S/C CE was obtained by the same method. The  $\text{TiO}_2$  porous films are acquired by

commercial purchase (Yingkou Opvtech New Energy Co., Ltd, China). The TiO<sub>2</sub> films were sintered at 500°C for 30 min prior to the fabrication of the DSSCs. After cooling to 80°C, the TiO<sub>2</sub> films were immersed into a ethanol solution of N719 dye (5 x 10<sup>-4</sup> M, Solaronix SA, Switzerland) for 24 h to obtain the dye-sensitized TiO<sub>2</sub> photoanode. The DSSCs devices consisted of photoanode, a CE, a electrolyte incorporating 0.1 M LiI, 0.03 M I<sub>2</sub>, 0.1 M GuSCN, 0.5 M 4-tert-butylpyridine (TBP) and acetonitrile as solvent.

## Characterizations

The Brunauer–Emmett–Teller (BET) specific surface area was measured at 77 K with a ASAP 2020-Physisorption Analyzer. X-ray diffraction (XRD) of samples were recorded by the Bruker-D8 diffractometer with Cu radiation. Scanning electron microscopy (SEM) were performed with a NOVA Nano Scanning electron microscope 450 Schottky field emission scanning electron microscope. X-ray photoelectron spectroscopy (XPS) measurements were performed with a Thermo Escalab 250Xi unit. The AC-HAADF-STEM images were recorded on a JEOL ARM-200F (S)TEM equipped with CEOS CESCOR aberration corrector at 80 kV. The XAFS spectra at the Co-edge were carried out at the 1W1B beamline of Beijing Synchrotron Radiation Facility (BSRF), China. The X-ray absorption fine structure spectra (Co K-edge) were collected at 1W1B beamline of Beijing Synchrotron Radiation Facility (BSRF). The data were collected in transmission mode using a Lytle detector. The sample were grinded and uniformly daubed on the special adhesive tape.

## XAFS Analysis and Results

The acquired EXAFS data were processed according to the standard procedures using the ATHENA module of Demeter software packages. The EXAFS spectra were obtained by subtracting the post-edge background from the overall absorption and then normalizing with respect to the edge-jump step. Subsequently, the  $\chi(k)$  data of were Fourier transformed to real (R) space using a hanning windows ( $dk=1.0 \text{ \AA}^{-1}$ ) to separate the EXAFS contributions from different coordination shells. To obtain the quantitative structural parameters around central atoms, least-squares curve parameter fitting was performed using the ARTEMIS module of Demeter software packages. The following EXAFS equation was used:

$$\chi(k) = \sum_j \frac{N_j S_0^2 F_j(k)}{k R_j^2} \cdot \exp[-2k^2 \sigma_j^2] \cdot \exp\left[\frac{-2R_j}{\lambda(k)}\right] \cdot \sin[2kR_j + \phi_j(k)]$$

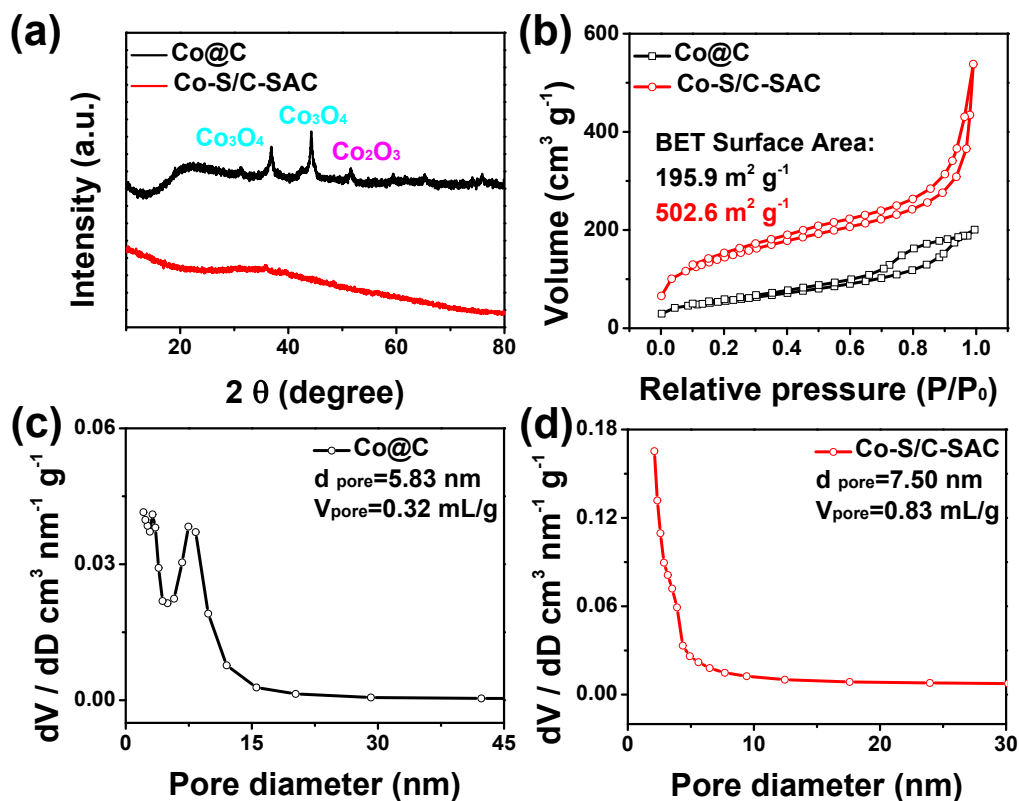
The theoretical scattering amplitudes, phase shifts and the photoelectron mean free path for all paths calculated.  $S_0^2$  is the amplitude reduction factor,  $F_j(k)$  is the effective curved-wave backscattering amplitude,  $N_j$  is the number of neighbors in the  $j^{\text{th}}$  atomic shell,  $R_j$  is the distance between the Xray absorbing central atom and the atoms in the

$j^{\text{th}}$  atomic shell (backscatterer),  $\lambda$  is the mean free path in Å,  $\phi_j(k)$  is the phase shift (including the phase shift for each shell and the total central atom phase shift),  $\sigma_j$  is the Debye-Waller parameter of the  $j^{\text{th}}$  atomic shell (variation of distances around the average  $R_j$ ). The functions  $F_j(k)$ ,  $\lambda$  and  $\phi_j(k)$  were calculated with the ab initio code FEFF9. The additional details for EXAFS simulations are given below.

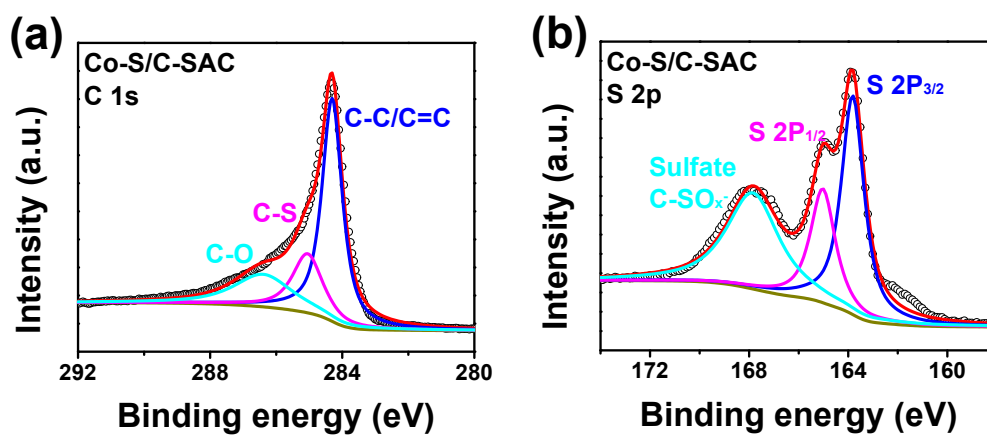
All fits were performed in the  $R$  space with  $k$ -weight of 2. The coordination numbers of model samples were fixed as the nominal values. The obtained  $S_0^2$  was fixed in the subsequent fitting. While the internal atomic distances  $R$ , Debye-Waller factor  $\sigma^2$ , and the edge-energy shift  $\Delta$  were allowed to run freely.

## Electrochemical Measurements

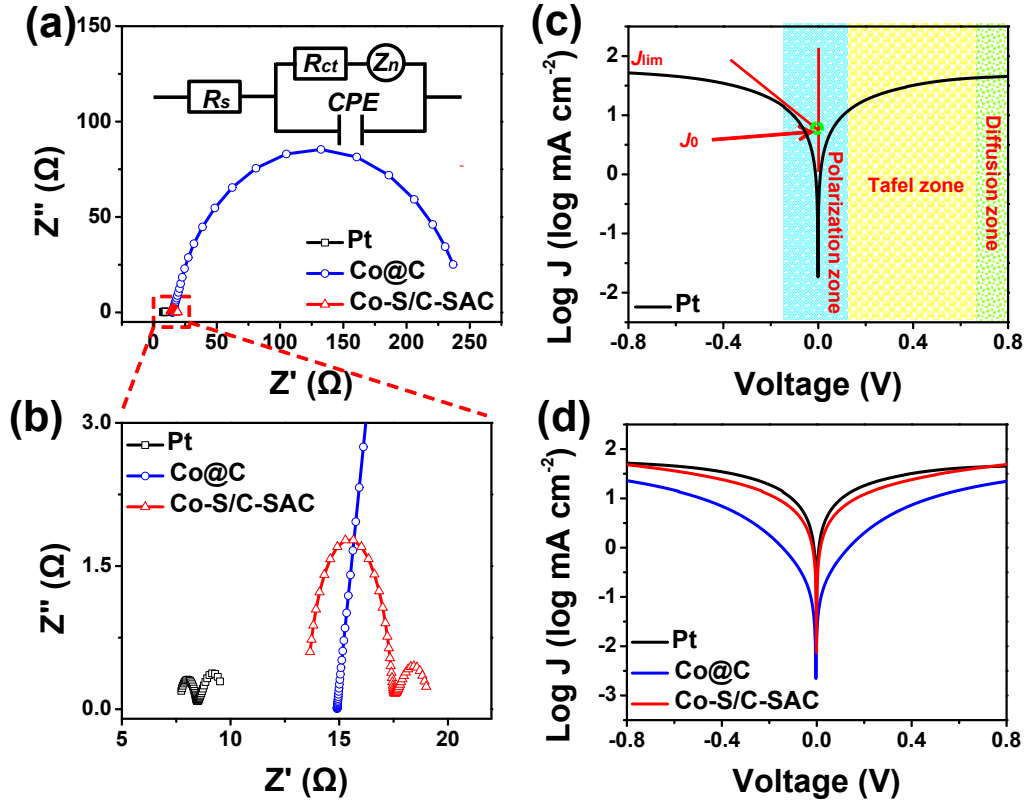
The cyclic voltammetry (CV) was executed using a CHI660E electrochemical workstation (SHANGHAI CHEN HUA) in a three-electrode system in an Ar-purged acetonitrile solution of 0.1 M LiClO<sub>4</sub>, 10 mM LiI and 1 mM I<sub>2</sub> at a scan rate of 10 mV s<sup>-1</sup>. The as-prepared Co-S/C-SAC (S/C) CE served as the working electrode, a Pt electrode acted as counter electrode, and a Ag/AgCl electrode was used as reference electrode. Tafel polarization measurements was employed with CHI660E in a symmetric dummy cell with a scan rate of 50 mVs<sup>-1</sup>. The electrochemical impedance spectroscopy (EIS) was acquired with electrochemical workstation (ZeniumZahner, Germany) in the dark. The measured frequency ranged from 100 mHZ to 1 MHz, and the AC amplitude was set at 10 mV. The photovoltaic performance of the DSSCs was acquired by using a Keithley digital source meter (Keithley 2601, USA) under simulated sunlight illumination conditions (Xe arc lamp, 1.5 AM, 100 mW cm<sup>-2</sup>, PEC-L15, Peccell, Japan).



**Fig. S1** (a) XRD pattern for Co-S/C-SAC and Co@C. (b) Nitrogen adsorption/desorption isotherm of Co-S/C-SAC and Co@C. (c) and (d) Corresponding pore size distributions of Co-S/C-SAC and Co@C.



**Fig. S2** The high-resolution XPS spectra for Co-S/C-SAC (a) C 1s and (b) S 2p.



**Fig. S3** (a) Nyquist plots for Pt and Co@C as well as Co-S/C-SAC symmetric cell with corresponding equivalent circuit. (b) Corresponding Nernst diagram of high frequency region. (c) The annotation of Tafel curve. (d) Tafel polarization curves of three samples symmetrical cells used in the EIS measurement.

**Table S1.** Structural parameters extracted from the K-edge Co  $\chi(R)$  space spectra fitting of Co-S/C-SAC ( $S_0^2=0.94$ ).

	Reduced Chi-square ( $\chi_v^2$ )	R-factor (%)	amp/ $S_0^2$	$N_{(\text{Co-S path})}$	$R_{(\text{Co-S path})}$ (Å)	$\sigma^2_{(\text{Co-S path})}$ ( $10^{-3}\text{Å}^2$ )	$\Delta E_0$ (eV)
Co-S-C	1468.90	0.0161	0.96	4+/-0.56	$2.097 \pm 0.068$	7.7+/-1.7	2.73 +/- 0.96
			amp/ $S_0^2$	$N_{(\text{Co-S-C path})}$	$R_{(\text{Co-S-C path})}$ (Å)	$\sigma^2_{(\text{Co-S-C path})}$ ( $10^{-3}\text{Å}^2$ )	$\Delta E_0$ (eV)
			0.80	2+/-0.24	$3.192 \pm 0.094$	8.7+/-2.0	6.74 +/- 0.78

**Table S2.** CV and EIS parameters of DSSCs based on Pt, Co@C and Co-S/C-SAC CE.

Sample	$E_{pp}$ (V)	$J_{cp}$ (mA cm <sup>-2</sup> )	$R_s$ ( $\Omega$ )	$R_{ct}$ ( $\Omega$ )	$Z_n$ ( $\Omega$ )
Pt	0.28	0.16	7.62	0.78	1.38
Co@C	0.43	0.04	14.90	4.79	229.30
Co-S/C-SAC	0.19	0.36	13.51	3.86	1.82

**Table S3.** Photovoltaic performance parameters of the DSSCs based on Pt, Co@C and Co-S/C-SAC CE.

Sample	$V_{oc}$ (V)	$J_{sc}$ (mA cm <sup>-2</sup> )	FF	$\eta$ (%)
Pt	0.80	12.71	0.77	7.80
Co@C	0.78	12.61	0.51	5.01
Co-S/C-SAC	0.80	13.24	0.78	8.18