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Supporting Information

Boosting the Oxygen Evolution Reaction Performance of CoS_2 Microspheres by Subtle Ionic Liquid Modification

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Experimental section

Materials

Cobalt sulfate heptahydrate ($CoSO_4·7H_2O$), sodium sulfite (Na_2SO_3), potassium hydroxide (KOH), isopropanol and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. Diethylenetriamine (DETA) was purchased from Alfa Aesar by Thermo Fisher Scientific. Pt/C (20 wt% Pt on carbon) was purchased from Shanghai Macklin Biochemical Co., Ltd. Ruthenium (IV) oxide (RuO_2, 99.9% metals basis) was purchased from Aladdin Co., Ltd. Nafion® perfluorinated resin solution (5.0 wt%) and 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene [MTBD] were purchased from Sigma-Aldrich. Lithium bis(trifluoromethylsulfonyl)imide [NTf_2] was purchased from IoLiTec Ionic Liquids Technologies GmbH. All chemicals were used as received without further purification. All aqueous solutions were prepared with deionized (DI) water.

Synthesis of 3D flower-like CoS_2 microspheres

In a typical procedure, 1 mmol cobalt sulfate heptahydrate ($CoSO_4·7H_2O$) and 2 mmol sodium sulfite (Na_2SO_3) were added into a mixed solution (40 mL) with a volume ratio of V_{DETA}/V_{DI} = 1:1 (DI = deionized water) under vigorous stirring. The obtained solution was sealed, transferred into a 50 mL Teflon-lined autoclave and maintained at 180 ^{o}C for 16 h and then naturally cooled to room temperature. The black precipitate was collected and washed with distilled water and ethanol, then vacuum dried at 60 ^{o}C for 6 h.

Synthesis of the [MTBD][NTf_2] IL.

The IL was synthesized following a protocol from the literature.[1] Briefly, the lithium salt of bis(trifluoromethylsulfonyl)imide [NTf_2] (33.9 mmol) was dissolved in water with HNO_3. Equimolar amounts of 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene [MTBD] was neutralized by adding HNO_3 dropwise to the [MTBD] solution. Then, the Li[NTf_2] solution was slowly added and the IL precipitated as a viscous fluid phase beneath the water phase. The IL was washed several times with DI water and then placed in a rotary evaporator at 60 ^{o}C for 24 h to remove the residual water. The IL was further dried under high vacuum.

Synthesis of the CoS_2-IL System.

The CoS2-IL systems were prepared by dispersing the CoS_2 microsphere in isopropyl alcohol solution containing [MTBD][NTf2], followed by multistep solvent evaporation. Specifically, 20.0 mg of CoS_2 catalyst was mixed with 4 mL of isopropyl alcohol solution containing a specific amount of IL under intense stirring. After 20 min ultrasonic treatment of this mixture, isopropyl alcohol was slowly removed from the slurry by rotary evaporation under low vacuum (60 ^oC). Then the sample was dried under high vacuum (room temperature) overnight in order to ensure the complete removal of the solvent. The IL amount in the isopropyl alcohol solution was varied to adjust the pore filling degree.

Calculation of pore filling degree α

The pore filling degree α was calculated based on the mass of the catalyst (20 mg in the experiment) and the measured density of the IL (ρ_{IL}, 1.5 g cm^{-3}) with α being defined as:

$$\alpha = \frac{m_{cat}}{m_{cat} + m_{IL}}, m_{IL} = \rho_{IL} * V_{IL}$$

where m_{IL} and V_{IL} are the mass (g) and volume (mL) of the IL used in the preparation of the CoS_2-IL systems, and m_{cat} is the mass (g) of the CoS_2 catalyst. In this work, α varied from 5 to 55% (corresponding to the samples named CoS_2-IL-α). According to the OER experiment the best α value results CoS_2-IL-45.

Electrocatalytic measurements

OER activity measurements were carried out on a three-electrode system using an electrochemical workstation (CHI660B) equipped with high-speed rotators from Pine Instruments. Pt wires and Ag/AgCl/KCl (saturated) were used as counter and reference electrodes, respectively. To prepare the working electrode, 5 mg catalysts powder were dispersed in 1 mL of 3:1 v/v water/isopropanol with 40 µL Nafion solution (Sigma-Aldrich, 5 wt%). Then, the mixtures were ultrasonicated for 30 min, and 8 µL catalyst ink were transferred onto the glassy carbon electrode (GCE) (geometric area: 0.196 cm^2) to obtain a loading amount of ~ 0.2 mg cm^{-2}. Finally, the as-prepared electrode was dried at room temperature. The same amount of commercial Pt/C or RuO_2 catalyst suspension was loaded on the GCE surface for comparison. The OER performance of the catalysts was evaluated from the current density which was normalized to the geometric surface. Before the electrochemical measurement, the electrolyte (0.1 M KOH, pH ~ 13) was degassed by bubbling O_2 for 30 min. Polarization curves were obtained by sweeping the potential from 0 to 0.8 V vs. Ag/AgCl, with a scan rate of 5 mV s^{-1} and speed of 1600 rpm. The data were recorded after applying a number of potential sweeps until a stable behavior was reached. All the polarization curves were corrected with iR-compensation. The resistance of 0.1M KOH, as determined by electrochemical impedance spectroscopy (EIS), is ~45 Ω. All potentials were referenced to the reversible hydrogen electrode (RHE) through RHE calibration described below. Tafel slopes were obtained by fitting the linear portion of the Tafel plots ($\eta = a + b\log|j|$, where η is the overpotential, b is the Tafel slope, and j is the current density) derived from the corresponding polarization curves.

Accelerated stability tests were performed in O_2-saturated 0.1 M KOH at room temperature by potential cycling between 0.3 and 0.8 V vs. Ag/AgCl at a sweep rate of 100 mV s^{-1} for 1000 cycles. At the end of the cycles, the resulting electrode was used for the OER polarization. For chronoamperometric tests, a static overpotential of 310 mV was applied for 10000 s during the continuous OER process to derive the time dependence of the current density.

RHE calibration:

In the all electrochemical tests, Ag/AgCl/KCl (saturated) was used as reference electrode. Potentials were referenced to the reversible hydrogen electrode (RHE) by adding a value of 0.965 V in 0.1 M KOH solution.

$$E\ (RHE) = E\ (Ag/AgCl) + E^{\theta}\ (Ag/AgCl\ vs\ NHE) + 0.059\ pH$$
$$E\ (RHE) = E\ (Ag/AgCl) + 0.198\ V + 0.059*13\ V$$
$$E\ (RHE) = E\ (Ag/AgCl) + 0.965\ V$$

Estimation of the turn over frequency (TOF):

The turnover frequency (s^{-1}) was calculated by following equation:

$$TOF = I/4nF$$

where I is the current density (mA) at a particular overpotential, F is the Faraday constant (96485.3 C mol^{-1}) and n is the number of active sites (mol) on the electrode. The factor 1/4 means that four electrons are required to give one O_2 molecule. Moreover, we assume that: (a) CoS_2 microspheres are totally composed of cobalt disulfide without DETA skeleton, (b) every cobalt atom present on the glassy carbon electrode is an active site involved in the OER and (c) the obtained value corresponds to the lower limit of the TOF. Considering that 16 μL (ρ_{IL}, 1.5 g cm^{-3}) of IL mixed with 20.0 mg of CoS_2 catalyst to form the CoS_2-IL-45. Considering these assumptions, the TOF value is given by the expression:

$$TOF_{CoS2} = \frac{10 \times 0.1963 \times 10^{-3}}{4 \times (0.2 \times 10^{-3}/123.06) \times 96485.3} = 0.0031\ s^{-1}\ (\eta = 370\ mV)$$

$$TOF_{CoS2\text{-}IL\text{-}45} = \frac{10 \times 0.1963 \times 10^{-3}}{4 \times (0.2 \times 10^{-3} \times 0.45/123.06) \times 96485.3} = 0.0070\ s^{-1}\ (\eta = 310\ mV)$$

$$TOF_{CoS2\text{-}IL\text{-}45} = \frac{26.6 \times 0.1963 \times 10^{-3}}{4 \times (0.2 \times 10^{-3} \times 0.45/123.06) \times 96485.3} = 0.0186\ s^{-1}\ (\eta = 370\ mV)$$

$$TOF_{RuO2} = \frac{4.66 \times 0.1963 \times 10^{-3}}{4 \times (0.2 \times 10^{-3}/133.07) \times 96485.3} = 0.0016\ s^{-1}\ (\eta = 310\ mV)$$

$$\mathrm{TOF}_{RuO2}=\frac{12.5\times 0.1963\times 10^{-3}}{4\times(0.2\times 10^{-3}/133.07)\times 96485.3}=0.0042\ \mathrm{s}^{-1}\ (\eta=370\ \mathrm{mV})$$

Characterizations

The samples morphology was characterized by field-emission scanning electron microscopy (Hitachi FE-SEM S4800) and transmission electron microscopy (TEM, JEOL 2000). Raman spectra were acquired on the LabRAM XploRA (HORIBA JOBIN YVON S.A.S). Powder X-ray diffraction (XRD) patterns were collected using an X'Pert Pro MPD diffractometer (PANalytical, Holland) with Cu Kα radiation. X-ray photoelectron spectra (XPS) were acquired on a Perkin-Elmer Physical Electronics 5600 spectrometer. FT-IR spectra were recorded on a Nicolet-6700 spectrometer (Thermal, USA).

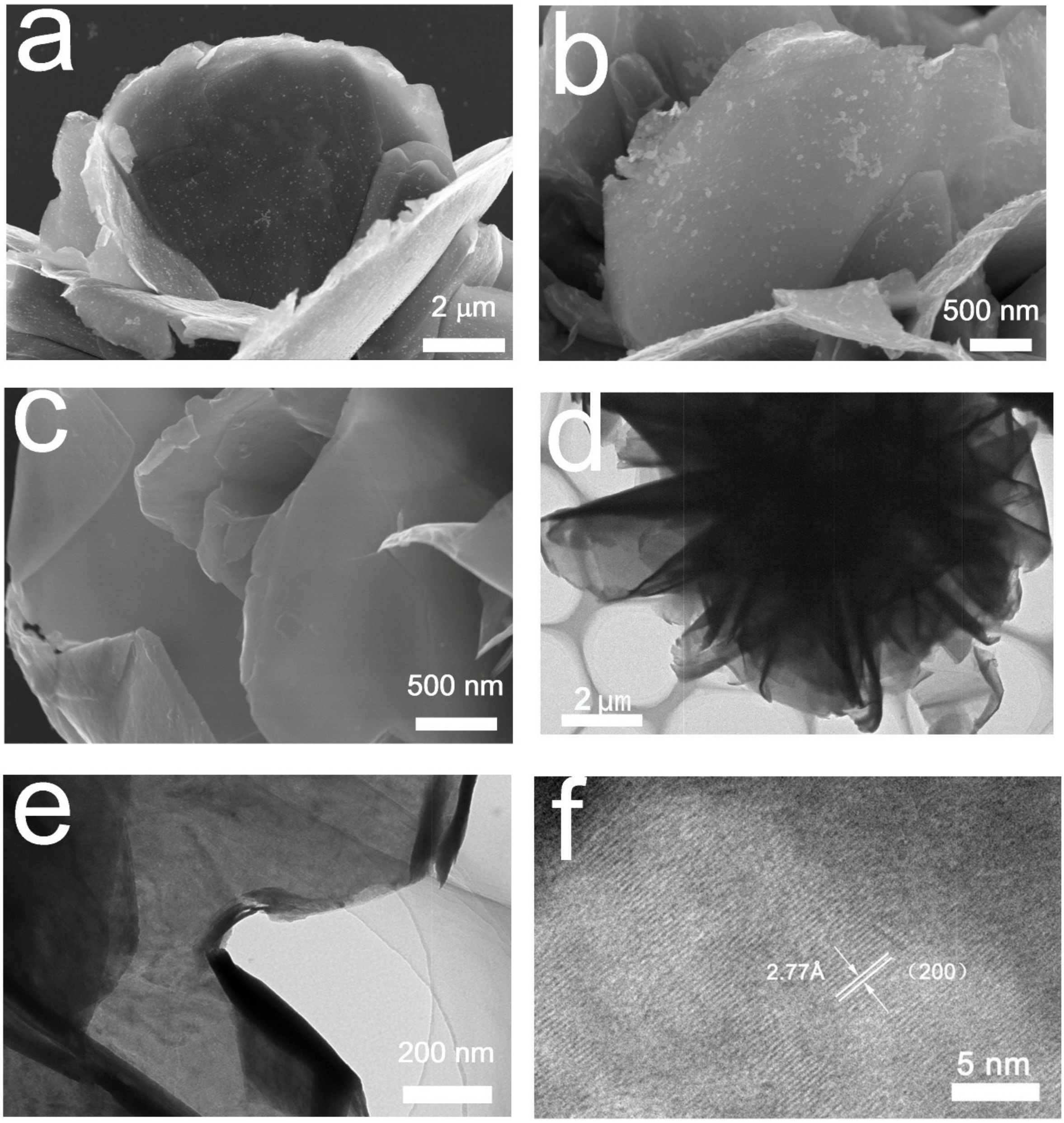

Figure S1. (a, b, c) SEM images, (d, e) TEM images and (f) HR-TEM image of the CoS_2 microsphere.

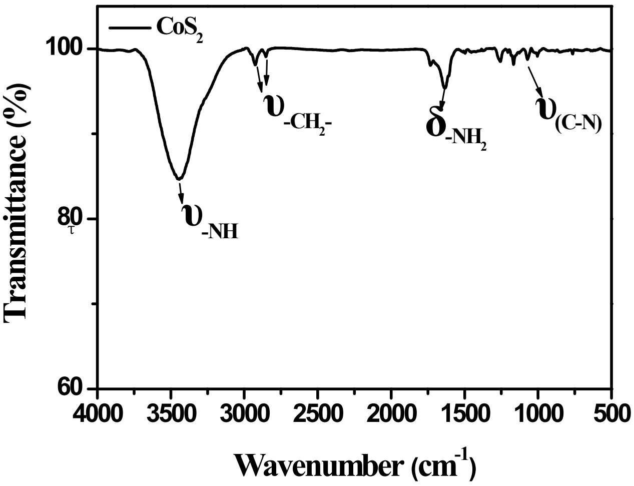

Figure S2. FT-IR spectrum of the CoS_2 microspheres.

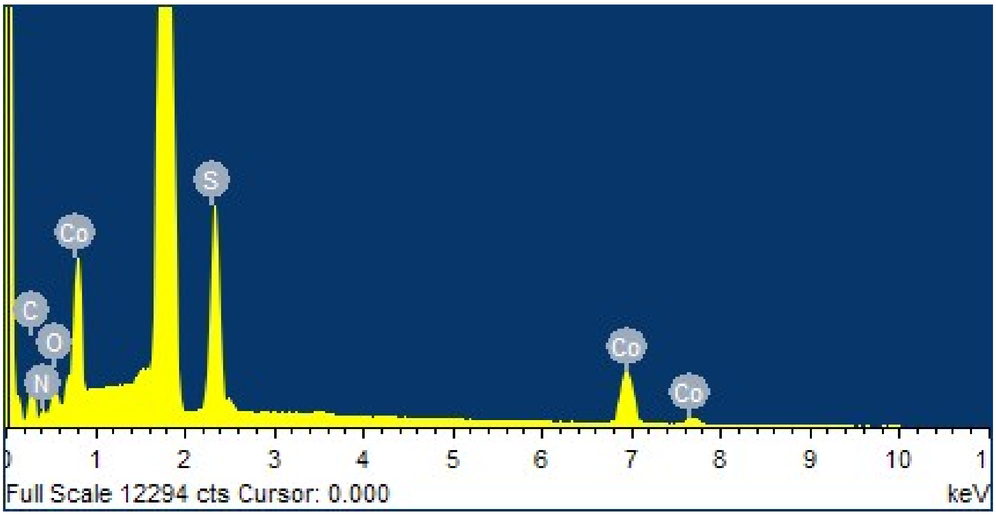

Figure S3. EDX pattern of the CoS_2 microspheres.

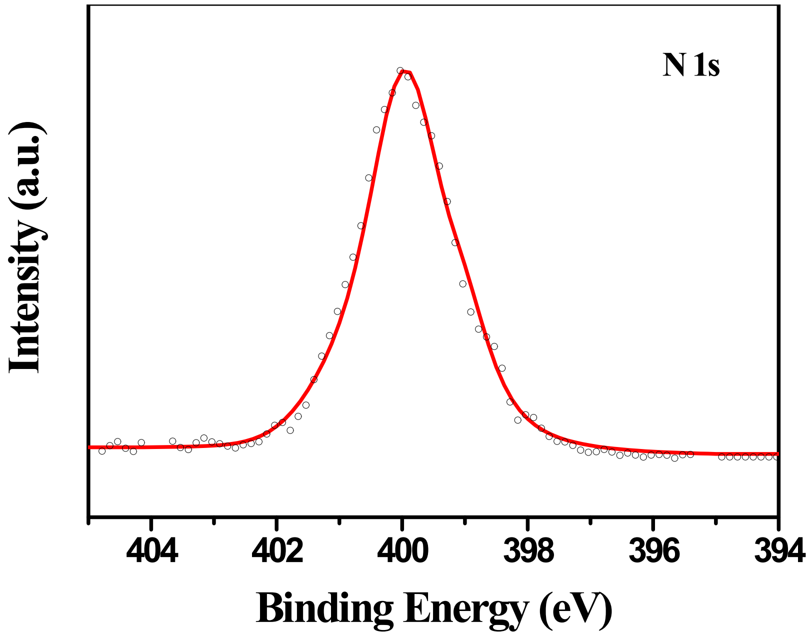

Figure S4. High-resolution N 1s XPS spectrum of the CoS_2 microspheres, which is derived from the protonated amine in DETA template.

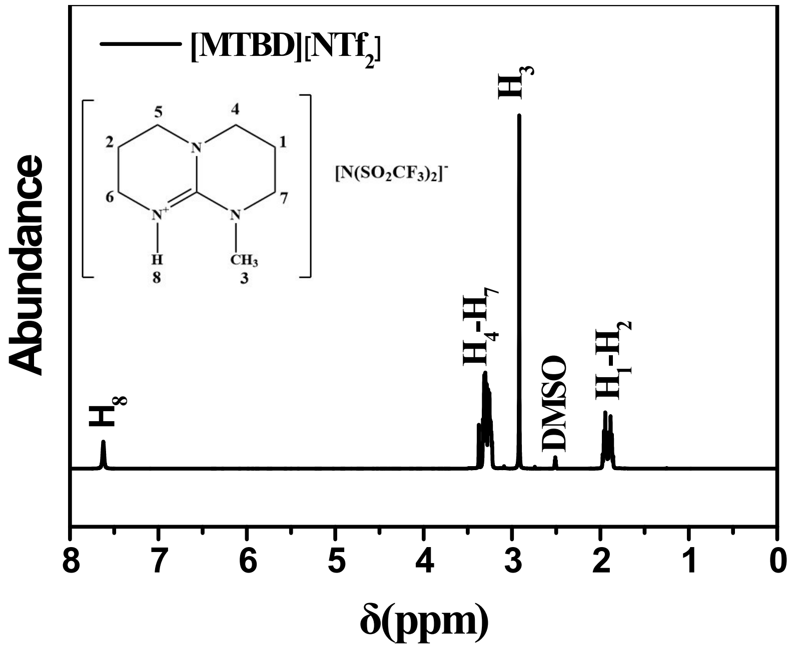

Figure S5. ^{1}H NMR spectrum of the [MTBD][NTf$_2$] IL.

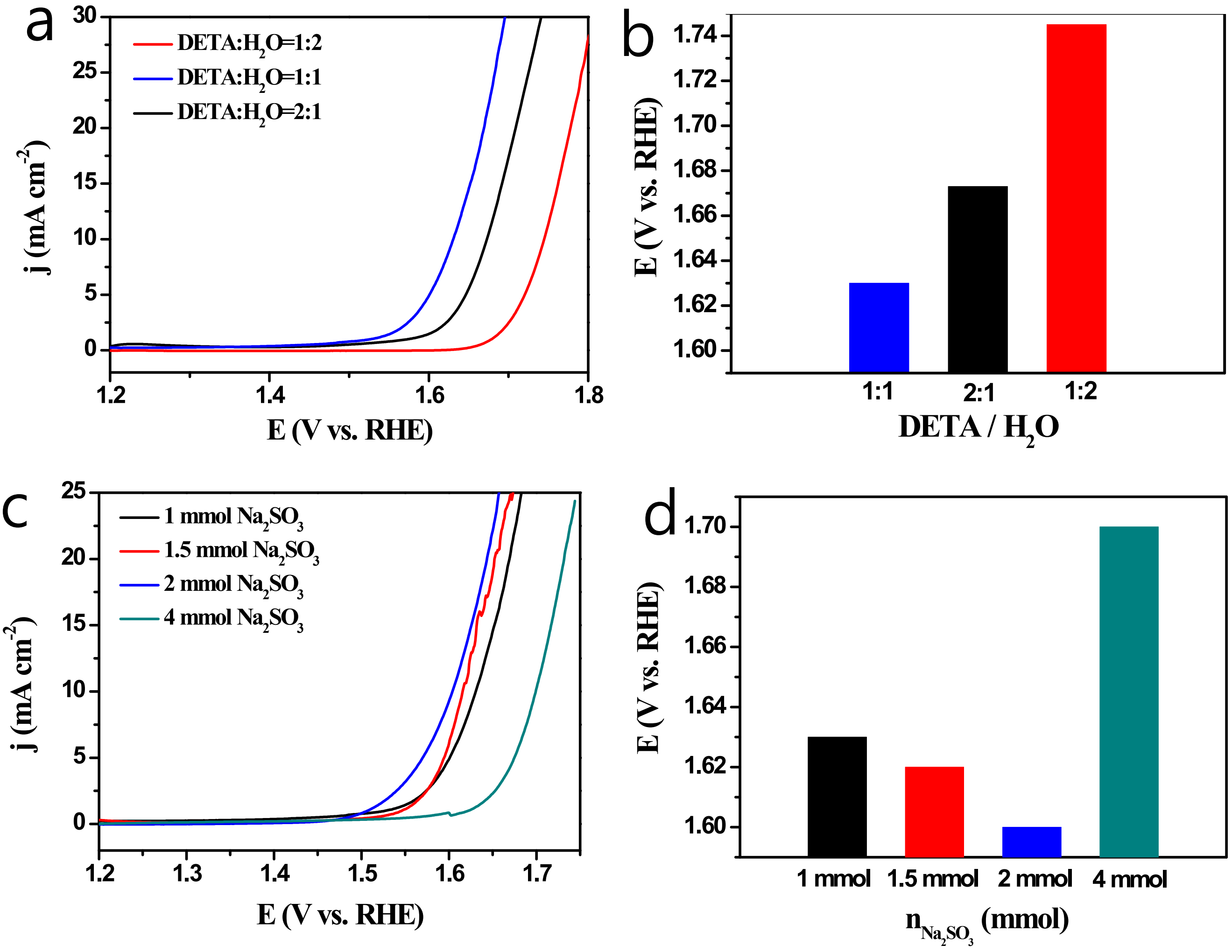

Figure S6. (a) OER polarization curves of the CoS_2 microspheres with different ratios of DETA and H_2O. (b) Corresponding potentials to achieve the current density of 10 mA cm^{-2}. (c) OER polarization curves of the CoS_2 microspheres with different initial Na_2SO_3 concentration. (d) Corresponding potentials to achieve the current density of 10 mA cm^{-2}.

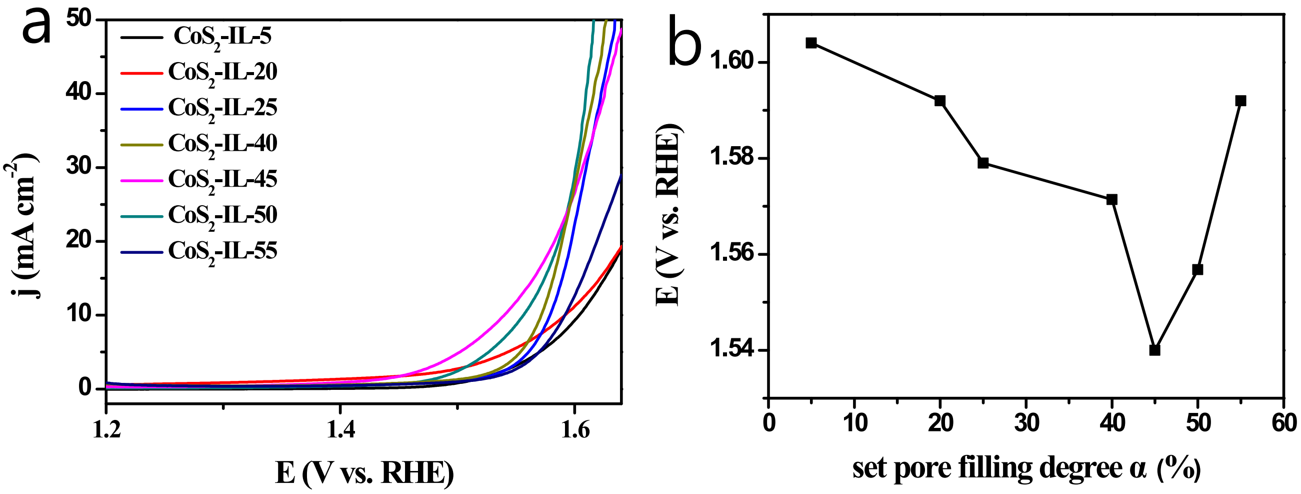

Figure S7. (a) Polarization curves of the different CoS_2-IL systems. (b) Broken line graph of the potential obtained with the catalysts at the current density of 10 mA cm^{-2}.

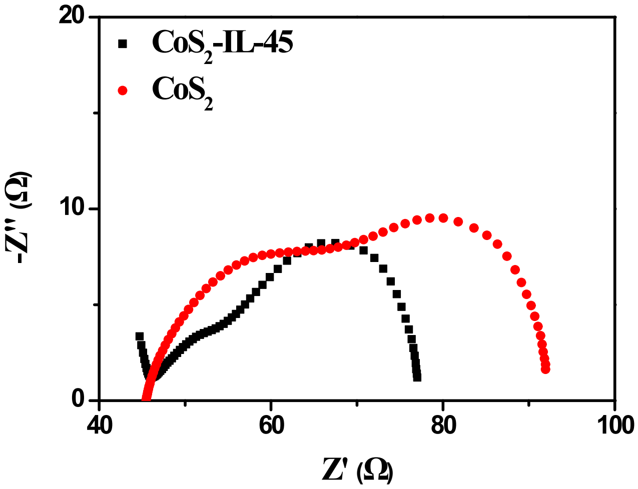

Figure S8. (a) EIS spectra of CoS_2 microspheres and CoS_2-IL-45 microspheres in 0.1 M KOH solution.

Table S1. Summary of the contents of the Co, S, C, N and O elements in the CoS_2 microspheres.

Surface Atomic Concentration (at. %)				
C1s	**N1s**	**O1s**	**S2p**	**Co2p**
55.69	**7.25**	**23.43**	**8.01**	**5.62**

Table S2. Comparison between the OER catalytic performance of CoS_2-IL systems with recently reported Co-based OER catalysts.

Catalysts	loading (mg cm^{-2})	Electrolyte	Tafel plots (mV/decade)	TOF (s^{-1})	E_{j10} (V *vs*. RHE)	η_{j10} (mV)	Ref.
CoS_2	0.2	0.1 M KOH	81.7	0.0031 (η = 370 mV)	1.60	370	This work
CoS_2-IL-45	0.2	0.1 M KOH	115.1	0.0070, 0.0186 (η = 310, 370 mV)	1.54	310	This work
RuO_2	0.2	0.1 M KOH	63.4	0.0016, 0.0042 (η = 310, 370 mV)	1.583	353	This work
CoS_2(400)/N,S-GO	0.25	0.1 M KOH	75	\	1.61	380	2
Co/N-C-800	0.25	0.1 M KOH	61.4	\	1.60	370	3
NG-$CoSe_2$	0.2	0.1 M KOH	40	0.03565 (η = 366 mV)	1.596	366	4
$CoTe_2$@NCNTFs	0.285	1 M KOH	82.8	\	1.56	330	5
CoO_x	9.5×10^{-3}	1 M KOH + 0.3 mM Fe^{3+}	27.6	0.08, 1.6, and 16.9 (η= 300, 350, and 400 mV)	1.539	309	6
CoO_x-4h	0.5	1 M KOH	67	0.0030, 0.0056 and 0.012(η=300, 320 and 350 mV)	1.536	306	7
a-$CoVO_x$	0.14	1 M KOH	51	\	1.577	347	8
CNT-CoS_2	\	0.1 M KOH	255	\	1.52	290	9
Co_xS_y@C-1000	0.1415	0.1 M KOH	\	\	1.7	470	10
Co_3O_4/CoS_2	0.34	1 M KOH	63	\	1.51	280	11
CoSSPIL/CNT	0.05	0.1 M KOH	42.1	0.29 (η= 400 mV)	1.64	410	12

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