Electronic Supplementary Material (ESI) for Nanoscale.

New enhancement mechanism of ether-based electrolyte in cobalt sulfide-containing potassium-ion batteries

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Experiment

Synthesis

Graphene oxide (GO) was obtained in our previous works. Typically, 1 mmol $CoCl_2 \cdot 6H_2O$, and 3 mmol thioureas were dissolved into a 60 mL aqueous solution with 100 mg GO under stirring and subsequently transferred into a 100 mL Teflon container for hydrothermal treatment under 180 °C for 16 hours. After the washing and drying, the precipitate was calcined at 800 °C for 2 h under the Ar atmosphere to obtain the CoS@RGO hybrid. The simplified synthetic schematic is shown in Figure S1a.

Characterization

The morphologies of the CoS@RGO hybrid were tested by field emission scanning electron microscope (SEM, Zeiss-U55) and high-resolution transmission electron microscope (TEM, JEOL-2100F). The structures were confirmed by X-ray diffraction (XRD, Rigaku) and Raman spectrometer (Horiba). The surface properties were measured by X-ray photoelectron spectroscopies (XPS, Thermo Fisher) and atomic force microscope (AFM, (Bruker dimension icon).

Electrochemical measurement

The electrochemical performance of our CoS@RGO hybrid was tested by the CR2032 coin-type half batteries. To obtain the electrode, 80wt% CoS@RGO hybrid, 10wt% Super P, and 10wt% sodium carboxymethyl cellulose were mixed into water under grinding to form a homogeneous slurry and then coated on the Cu foil. After thoroughly drying, the resulting electrode was cut into discs with a diameter of 14 mm. The half batteries were packaged in an argon-filled (O_2<0.1 ppm, H_2O<0.1 ppm) glove box (Etelux-Lab2000). Generally, Metallic K foil was used as a counter electrode and glass fiber membrane was adopted as the separator. For the ester-based electrolyte, 1, 3, and 5 M potassium bis(fluorosulfonyl) imide (KFSI) dissolved into ethylene carbonate/propylene carbonate (1:1/v:v) mixed solution, which was devoted as EP-KFSI, EP-KFSI-3M and EP-KFSI-5M, respectively. For ether-based electrolytes, 1, 3, and 5 M KFSI dissolved into glycol dimethyl ether, which is devoted as DME-KFSI-1M, DME-KFSI-3M, and DME-KFSI, respectively. About

0.2 mL electrolyte was added to each battery. The galvanostatic charge-discharge (GCD) curves and cycling performances were recorded by a battery test system (Neware, BTS-4000). Cyclic voltammetry (CV) was measured by an electrochemical workstation (ChenHua, CHI 1030C) at a scan rate of 0.2 mV s^{-1} unless otherwise noted. Electrochemical impedance spectroscopies (EIS) were evaluated by Princeton electrochemical workstation (Veras STAT 3400).

***In-situ* visualization observation**

For the in-situ visualization measurement, we used the same electrode with battery measurement. The glass fiber membrane was punched into a hole with a diameter of 2 mm as a separator and Metallic K foil was punched into a hole with a diameter of 2 mm as a counter electrode. After that, the corresponding electrolyte was injected from the hole, and then used quartz glass to encapsulate the battery. After the packaging of the electrochemical reaction cell, the electrode could be observed from the quartz glass by the metallographic microscope (Leica). During the measurement, the electrochemical reaction cell was scanned by the electrochemical workstation (ChenHua, CHI 660E) with a scan rate of 0.6 mV s^{-1}.

DFT computational methods

The charge density distribution, the binding energies, the highest occupied molecular orbital (HOMO), and lowest unoccupied molecular orbital (LUMO) energy levels of the solvents and solvated structures were calculated by density functional theory (DFT) in the Vienna ab initio simulation package (VASP). The binding energy (E_b) between solvents and FSI was defined as follows:

$$E_b = E_{total} - E_{FSI} - E_{solvent}$$

E_{total}, E_{FSI} , and $E_{solvent}$ are the total energies of the ion−solvent complex, FSI, and solvent molecules, respectively.

MD Simulations

MD simulations were performed using the Large Scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) code and Optimized Potential for Liquid Simulations-all atom (OPLS-AA) force field. The initial atomic coordinates were

generated with Packing Optimization for Molecular Dynamics Simulations (Packmol) program.

FEA Simulations

Two physical models of Transport of Diluted Species and Electrostatic were coupled to conduct the simulation in the finite element analysis (FEA). Diffusion and electric field migration were used to calculate the movement of solvated structures and the diffusion and electromigration processes were based on Fick's law and the Nernst-Einstein relationship, respectively.

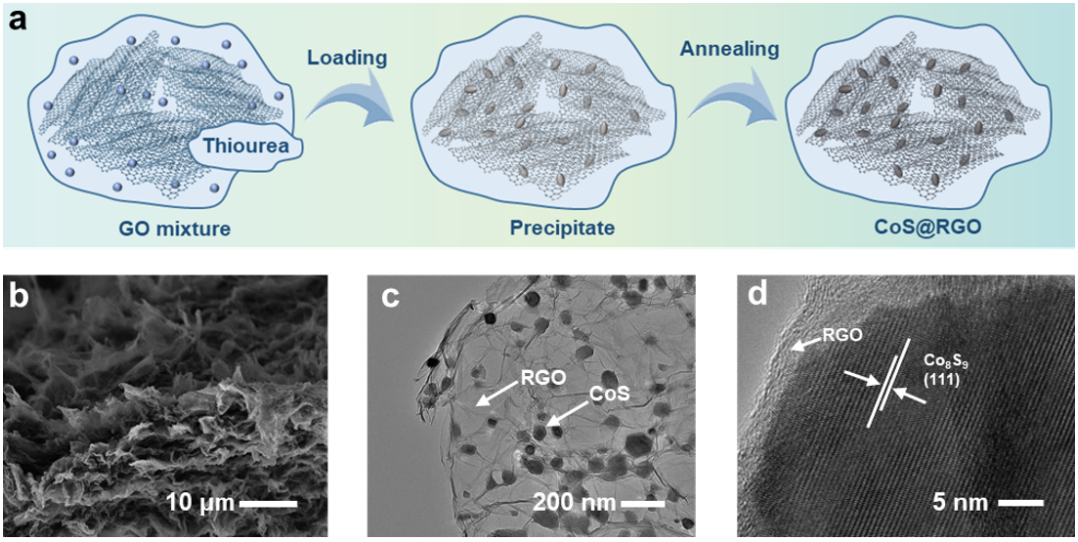

Figure S1 The synthetic schematic of CoS@RGO hybrid; (b) SEM, (c) TEM, and high-resolution TEM images of CoS@RGO hybrid.

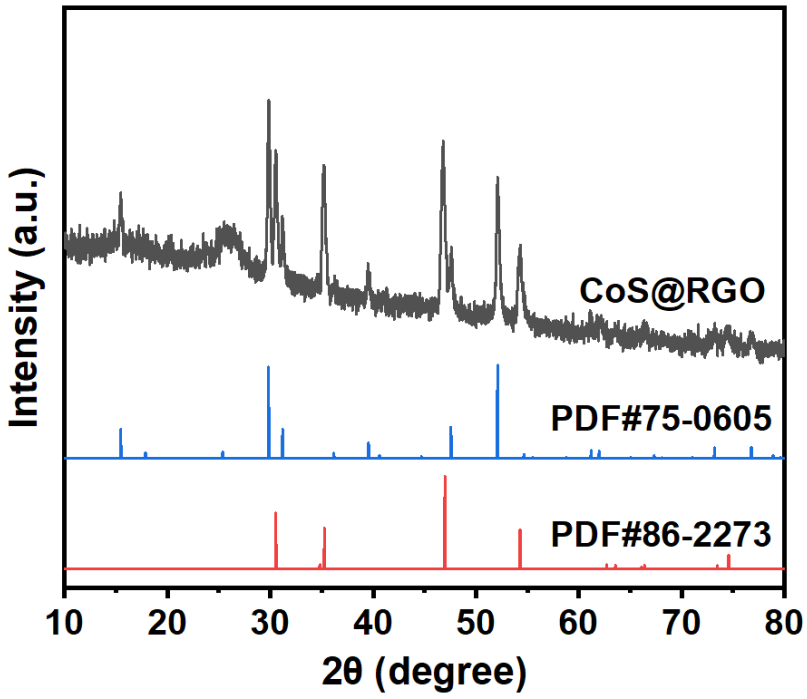

Figure S2 XRD pattern of CoS@RGO hybrid.

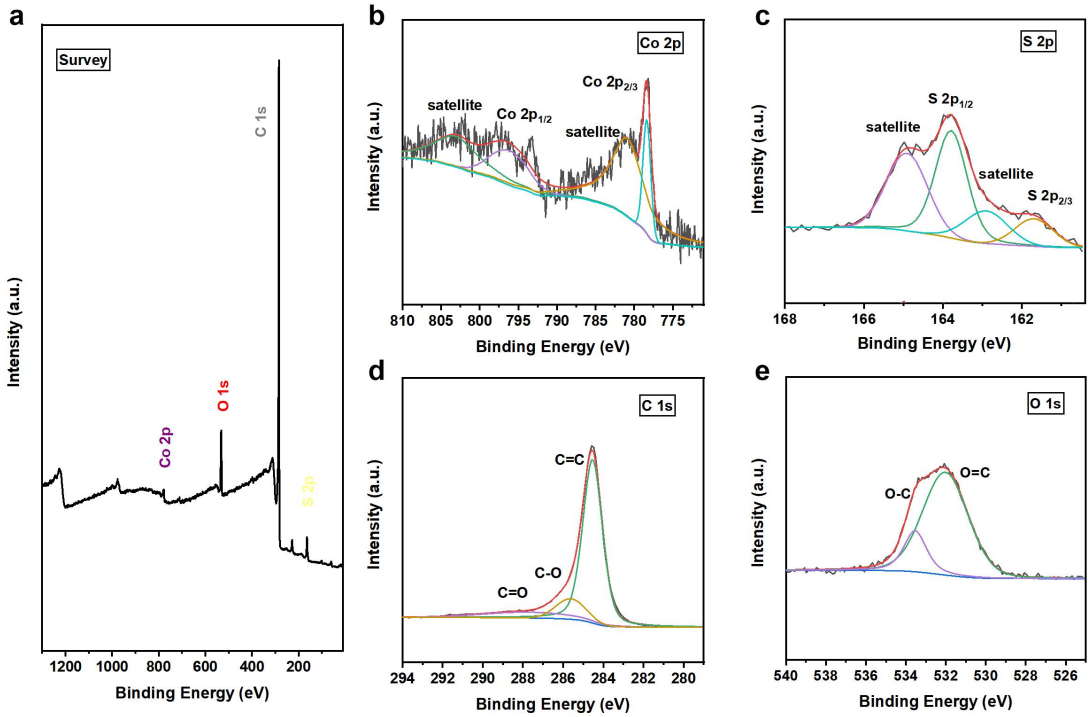

Figure S3 (a) Survey XPS, (b) Co 2p, (c) S 2p, (d) C 1s and (e) O 1s High resolution XPS of CoS@RGO hybrid.

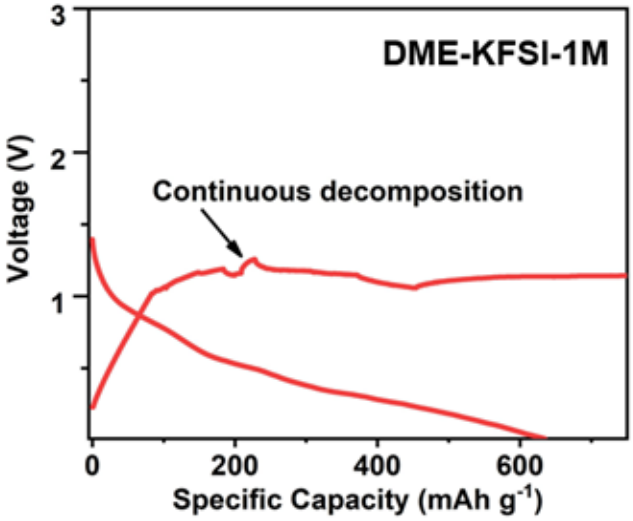

Figure S4 GDC curves of CoS@RGO electrode in DME-KFSI-1M.

Figure S5 Photograph of EP- KFSI-5M.

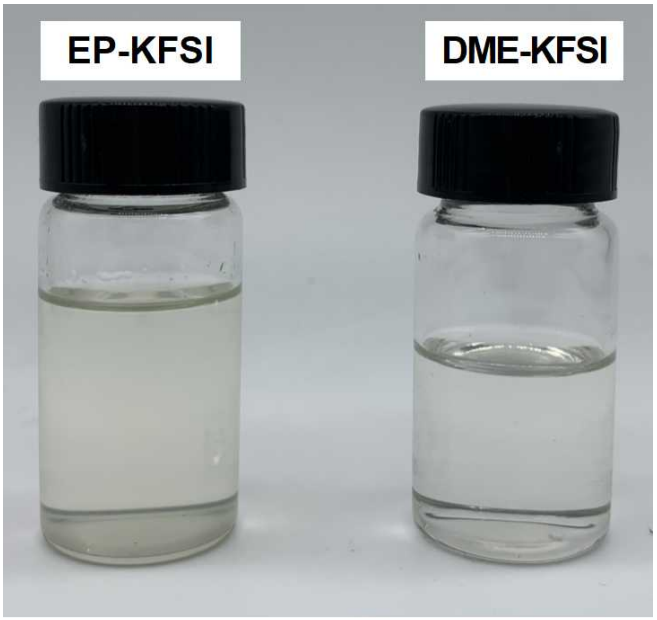

Figure S6 Photograph of EP-KFSI and DME-KFSI electrolyte.

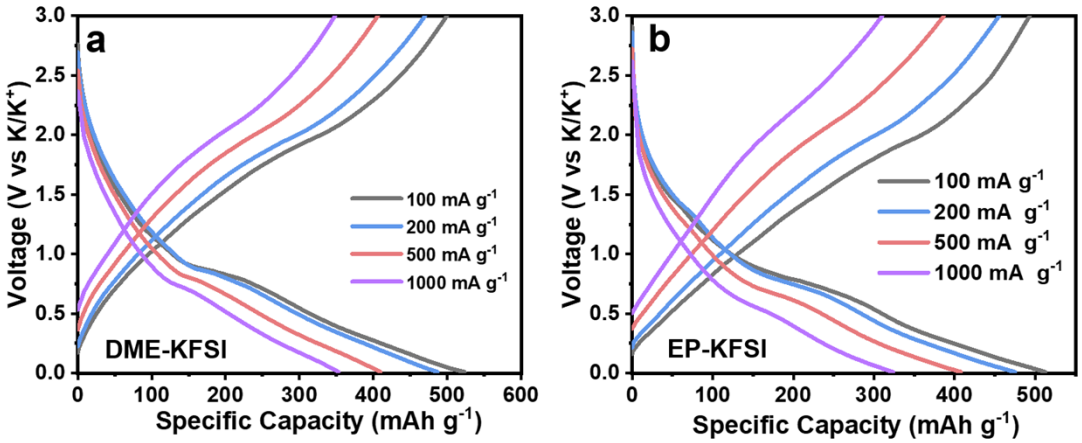

Figure S7 GCD curves of CoS@RGO hybrid at different current densities in (a) DME-KFSI and (b) EP-KFSI electrolytes

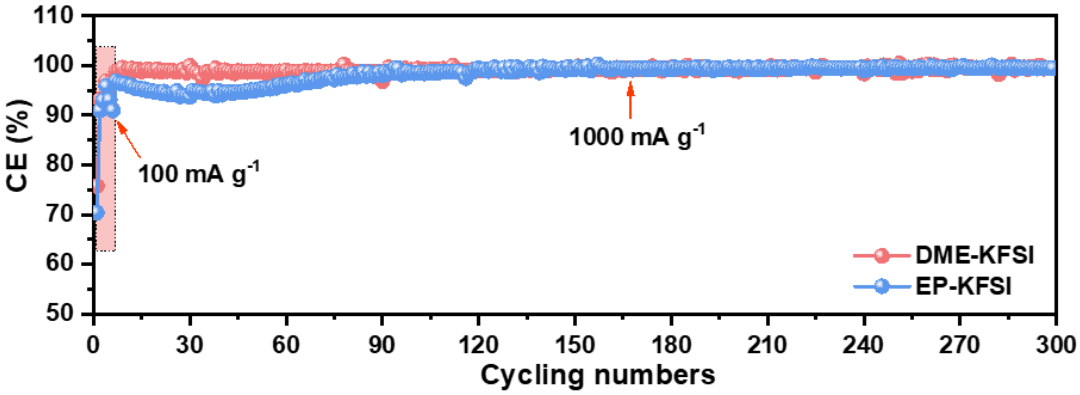

Figure S8CEs of the electrode in DME-KFSI and EP-KFSI electrolyte

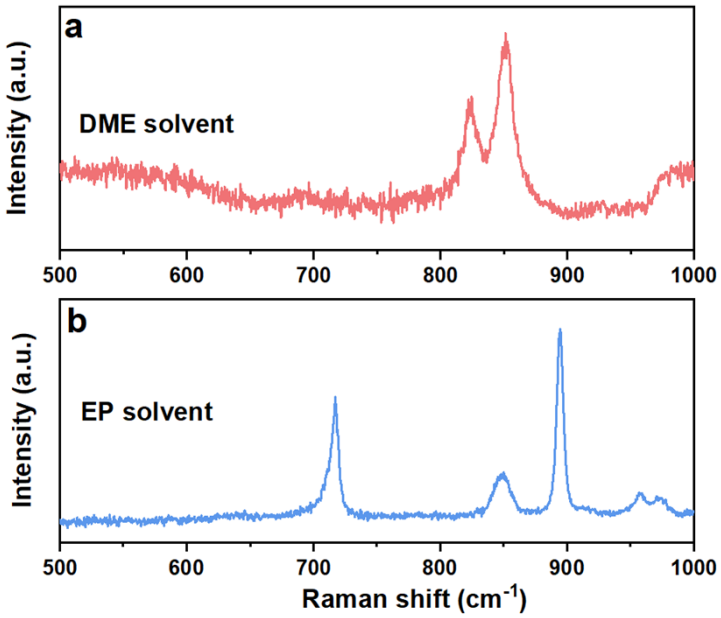

Figure S9 Raman spectra of (a) DME and (b) EP solvent.

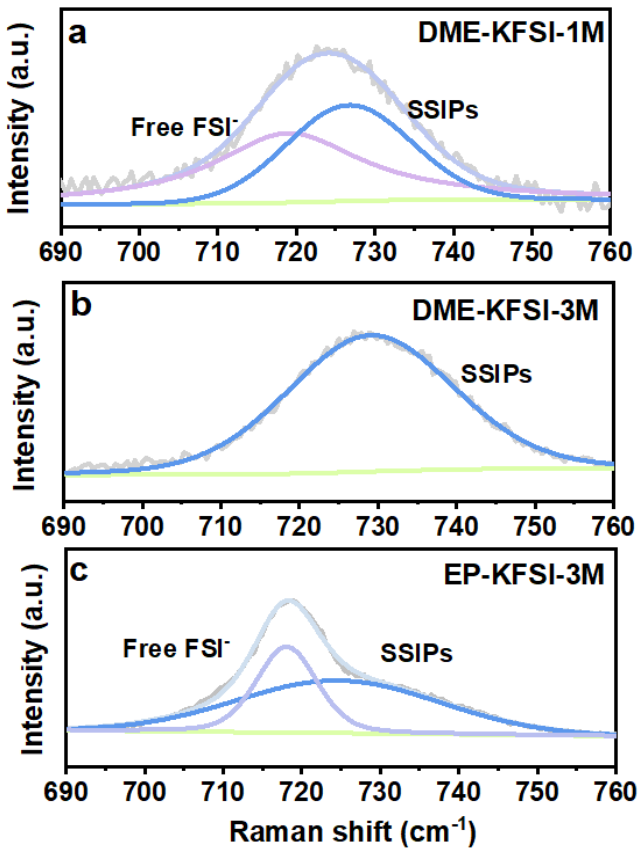

Figure S10 Raman spectra of (a) DME-KFSI-1M, (b) DME-KFSI-3M and (c) EP-KFSI-3M electrolytes.

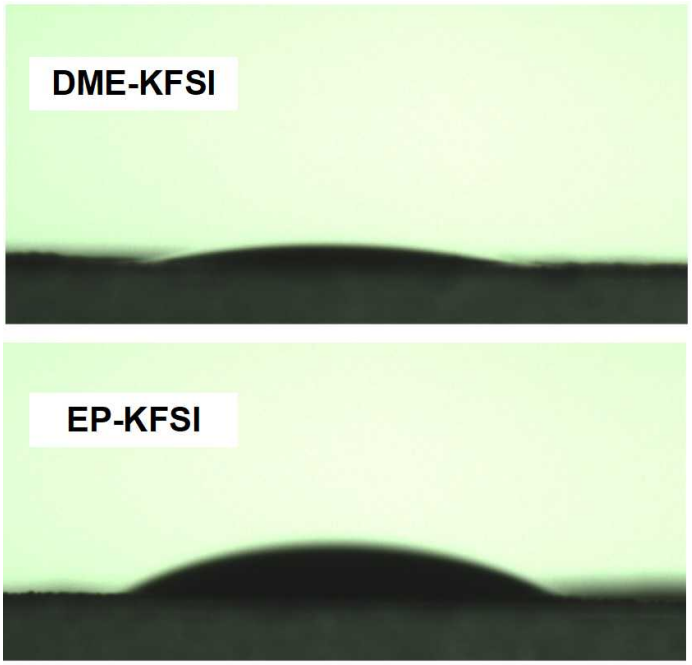

Figure S11 Contact angles of DME-KFSI and EP-KFSI electrolytes on our CoS@RGO electrode.

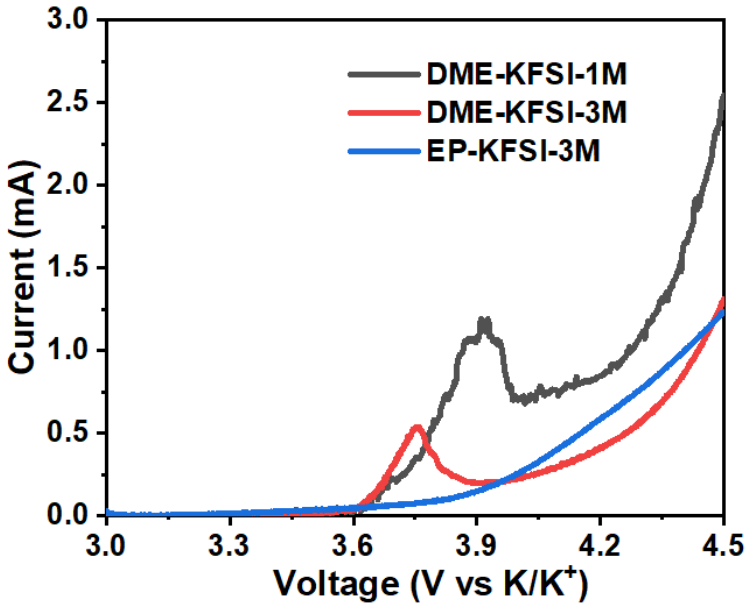

Figure S12. LSV curves of CoS@RGO hybrid in DME-KFSI-1M, DME-KFSI-3M, and EP-KFSI-3M electrolytes.

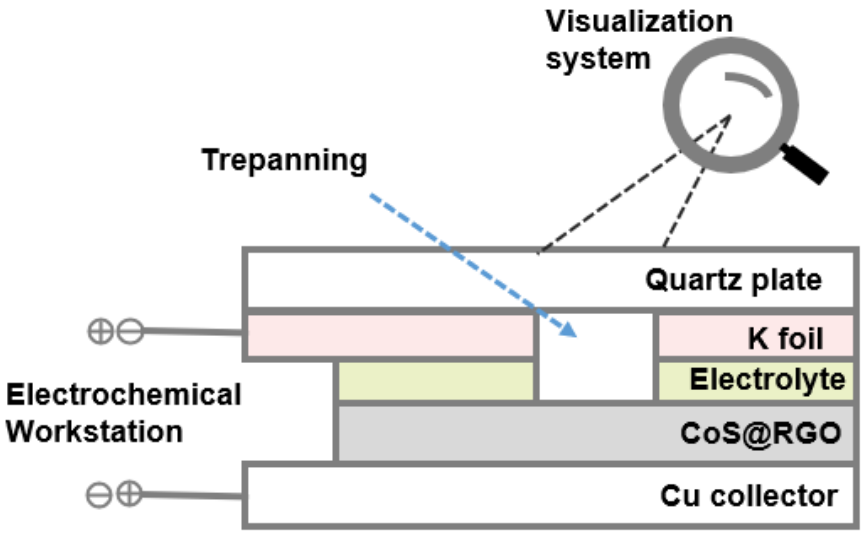

Figure S13. Testing schematic of *in-situ* visualization.

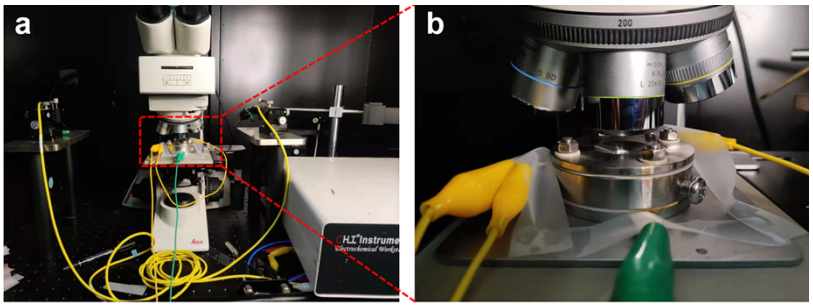

Figure S14. (a) Photograph and (b) enlarged photograph of the in-situ visualization testing system.

Table S1 The obtained parameters of adsorption models based on DFT calculation.

	Energy (eV)		Energy (eV)
DME-FSI	-135.74	FSI-EC-PC	-190.85
FSI	-48.92	FSI	-49.02
DME	-86.17	EC	-62.68
		PC	-79.44
E_b	-0.65	E_b	0.28