

Supplementary Information

Cobalt oxysulphide/hydroxide nanosheets with a dual property based on electrochromism and charge storage mechanism

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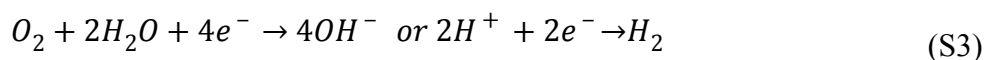
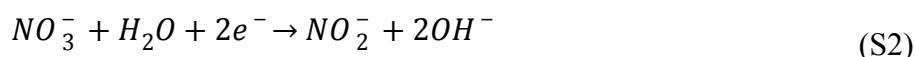
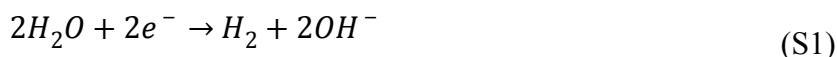
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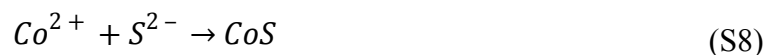
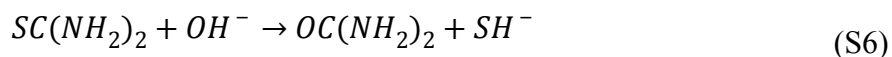
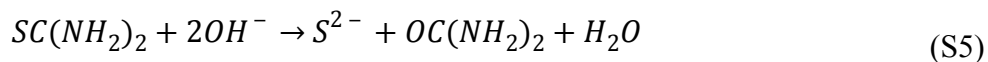
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1. Electrodeposition mechanisms

In this work, the electrodeposition method was used to produce Co(OH)₂ thin film on a conductive fluorine-doped tin oxide (FTO) glass substrate. FTO glass, Hg/HgO and Pt electrodes were used as working, reference and counter electrodes, respectively. Chronoamperometry method was used for the electrodeposition at an applied potential of -1.0 V vs. Hg/HgO. For the electrodeposition process, sodium nitrate (NaNO₃) was used as an auxiliary electrolyte and the reductions of water, oxygen, and nitrate can raise the local pH of electrolyte (see reactions S1-3). The precipitation of Co(OH)₂ can occur at the surface of FTO (see reaction S4).



For the electrodeposition of CoS, thiourea was used as a sulphur source for the electrodeposition process.^{1,2} The electrodeposition mechanisms of CoS follow reactions (S5-S8) below^{1,2};



2. Experimental details

2.1 Electrodeposition process

In this work, the FTO glass substrate was used as a conductive substrate for the electrodeposition process. A commercial FTO glass (TEC8, Dyesol Ltd., Australia) was cut to 1 cm × 2.5 cm. An FTO glass was cleaned with detergent, water and DI water (Milli-Q water), respectively. After that, it was rinsed with absolute ethanol and acetone before drying at room temperature. The cleaned FTO (1 cm × 1 cm) was used as a working electrode (WE) in the electrodeposition process. Platinum wire was used as a counter electrode (CE) and Ag/AgCl (3M KCl) was used as the reference electrode (RE). A solution of 0.1 M Co(NO₃)₂·6H₂O (analytical grad, UNIVOR) in 0.5 M Thiourea (analytical grad, HIMEDIA) was employed as an electrodeposition solution. Thiourea (CH₄N₂S) was served as sulphur source in the electrolyte. Three electrodes (WE, CE and RE) were immersed in the Co(NO₃)₂ in CH₄N₂S solution and then -1.0 V vs. Ag/AgCl was applied for 5 min via a chronoamperometry method using a Metrohm AUTOLAB potentiostat (PGSTAT 302N made in Netherlands running NOVA version 1.10.3 software). After the electrodeposition process, the yellowish-brown film of the cobalt oxysulfide/hydroxide film on the FTO glass substrate was obtained and then washed 3 times with DI water in Fig. S1b. Finally, the film was dried in a vacuum oven at 60 °C overnight.

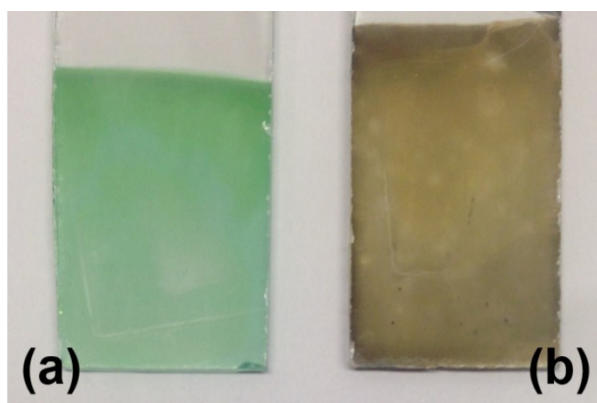


Fig. S1. The as-electrodeposited film; (a) cobalt hydroxide and (b) cobalt oxysulfide/hydroxide.

2.2 Physicochemical characterizations

Field-emission scanning electron microscopy (FE-SEM, JSM-7001F (JEOL Ltd., Japan)) and Transmission electron microscopy (TEM, JEM 1220 (JEOL Ltd., Japan)) were used to study the morphology of the as-prepared materials. For FESEM, the cobalt oxysulfide/hydroxide film on the FTO glass was cut and then attached on the sample holder and sputtered with Platinum at 10 mA for 90s to increase the surface conductivity before the measurement. SEM images were taken from both top-view and cross-section modes with a JEOL JSM-7610F at a low landing energy (0.8–2.0 keV) in a gentle beam (GB high) mode. The top-view image was taken with 100000x magnification at a working distance (WD) of 4.7. Note that, Energy-dispersive X-ray spectroscopy (EDS) technique was equipped with FESEM to investigate an element ratio. For TEM, 0.1 mg of cobalt oxysulfide/hydroxide powder obtained from the as-electrodeposited cobalt oxysulfide/hydroxide film was diluted in 5 ml of absolute ethanol and then ultra-sonicated for 15 min before dropped on Cu grid. The dried grid was inserted in TEM machine and bright field high-resolution TEM (HRTEM) image (e.g., the observation of lattice spacing) was performed with a JEOL JEM ARM200F transmission electron microscope operating at 200 kV and 500000x magnification. The film was also investigated by XRD and XPS. For XRD, the crystallographic structure was measured with XRD machine (Bruker D8 advance) with Cu X-ray tube source. The wavelength of Cu-K α is 1.54060 Å. For XPS, the cobalt oxysulfide/hydroxide film was cut and then attached on the sample holder. X-ray Photoelectron Spectroscopy (XPS) was used to analyse the surface with a diameter of 6 mm of the analysed area of each sample. XPS was recorded on JEOL JPS-9010MC with a Mg K α source (1253.6 eV) at 12 kV and 25 mA. The XPS spectrum was

measured under a high vacuum pressure of 10^{-8} Pa at a room temperature. Software for running experiment is SpecSurf ver.1.9.3. The survey scan spectra were measured with a pass energy of 50 eV, a binding energy range of 0-1000 eV and an electron-volt step of 1 eV. The binding energy value was referenced to the carbon peak C 1s at 284.70 eV.

2.3 *In situ* electrochemical UV-Visible measurements

For the measurement, the cobalt oxysulfide/hydroxide film was used as the working electrode, while the Hg/HgO and Pt wire were used as a reference electrode and a counter electrode, respectively. The films were investigated by cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) to study their electrochemical properties in 1 M KOH.

The specific capacity of cobalt oxysulphide/hydroxide nanosheets was calculated from the GCD using Equation (S9).

$$C = \frac{I \times \Delta t}{m} \quad (\text{S9})$$

where C is the specific capacity (mAh g⁻¹), I is the applied current (A), Δt is the discharge time from the GCD curve (h), and m is the mass of the active material (g).

The intermediate state of the cobalt oxysulfide/hydroxide was studied by two *in situ* electrochemical UV-Visible techniques; *in situ* AvaSpec UV-Visible spectrometer with CV and *in situ* UV-Visible technique with chronoamperometry. For *in situ* AvaSpec UV-Visible spectrometer with CV, AvaSpec-UV/VIS spectrometer (2048L made in Netherlands) was used in the wavelength range of 200-1000 nm. The experiments were operated with NOVA version 1.10.3 software joined with AvaSoft version 8.0 software. For *in situ* UV-Visible technique with chronoamperometry, UV-Visible-Near IR spectrometer (UV/Vis/NIR Lambda 1050, PerkinElmer, USA) was substituted to AvaSpec-UV/VIS spectrometer to obtain better resolution UV-Visible spectra with chronoamperometry. The measurement was set up in a quartz cell. The oxidation states of cobalt oxysulfide/hydroxide electrodes were also studied by an *in situ* electrochemical X-ray absorption spectroscopy (XAS) technique with Co K-edge fluorescence mode. The Ge(220) double-crystal monochromator and 4-element silicon drift detector were applied for recording the spectroscopic data. The Co K-edge were calibrated using the Co foil before measurement. The mechanism of cobalt oxysulfide/hydroxide electrode was studied through the *in situ* XAS technique together with the chronoamperometry in 1 M KOH electrolyte by applying the potential stepped from -0.5, 0.0, 0.35, and 0.65 V vs.

Hg/HgO and the following backward process from 0.5, 0.2 and -0.5 V vs. Hg/HgO. The redox reaction of the cobalt oxysulfide/hydroxide in 1 M KOH electrolyte was setup in an acrylic electrochemical cell and the intermediate state can be observed as shown in **Figure S2**. This experiment was done at a beamline No. 5.2 at the Synchrotron Light Research Institute (Public Organization), Nakhon Ratchasima, Thailand.

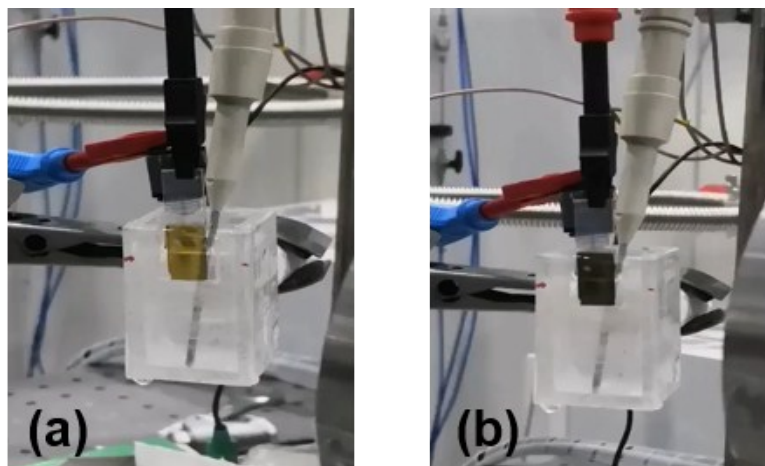


Fig. S2. *In situ* electrochemical XAS measurement setup. The colour change of the electrode can be clearly observed from the redox reactions in 1 M KOH.

3. Additional Results

3.1 Energy-dispersive X-ray spectroscopy (EDX)

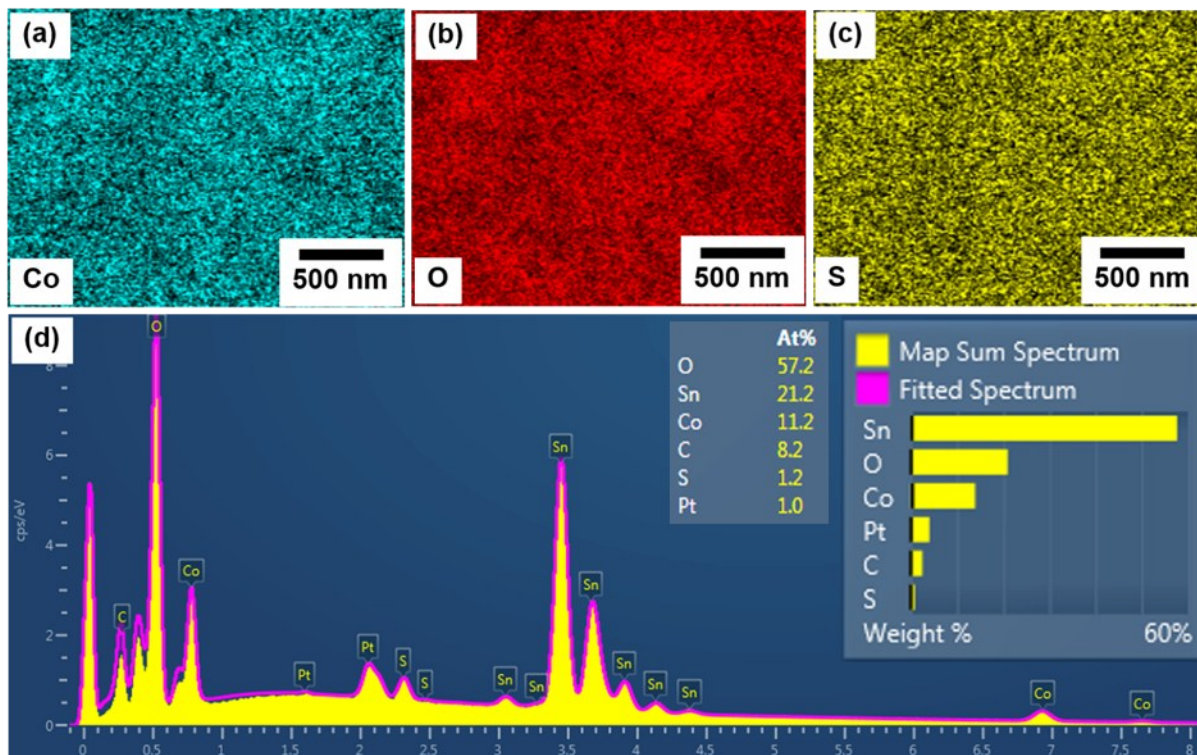


Fig. S3. EDX patterns and the elemental mapping analysis (Co, O, and S) of the as-electrodeposited cobalt oxysulfide/hydroxide.

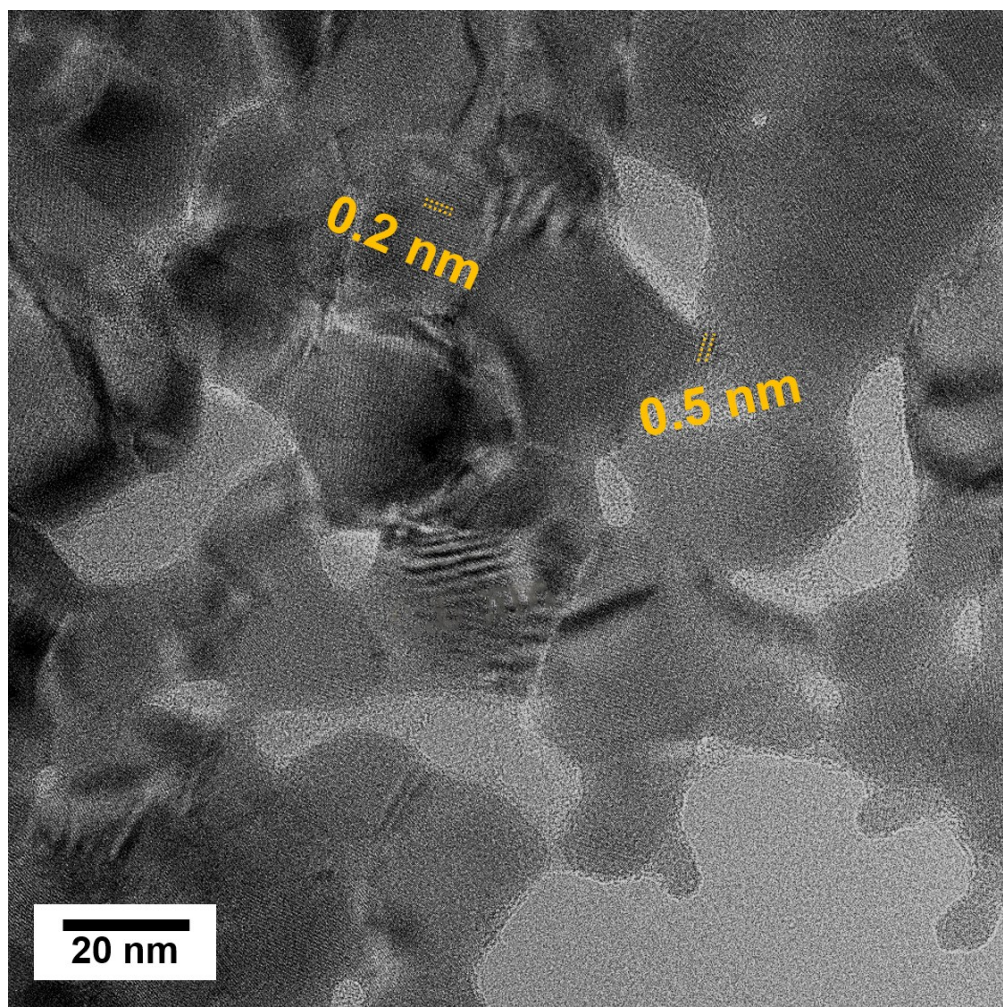


Fig. S4. FESEM image of the cobalt oxysulfide/hydroxide nanosheets.

3.2 FTIR

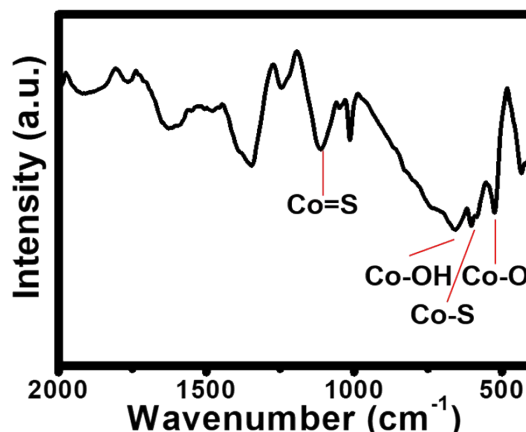


Fig. S5. FTIR spectrum of cobalt oxysulfide/hydroxide.

The peaks at 700 and 1095 cm⁻¹ can be assigned to Co-S and Co=S stretching, respectively.^{3, 4} The stretching vibrations of Co-OH and Co-O are at 730 and 510 cm⁻¹, respectively.⁵

3.4 Optical properties

The optical properties of cobalt oxysulfide/hydroxide were investigated by several techniques under ambient condition. UV-Visible-Near IR spectrometer (UV/Vis/NIR Lambda 1050, PerkinElmer, USA), Ultraviolet photoelectron spectrometer (UPS, RIKEN KEIKI, AC-2, USA) and Raman spectroscopy (Senterra Dispersive Raman Microscope, Bruker, with an excitation wavelength of 785 nm) were employed.

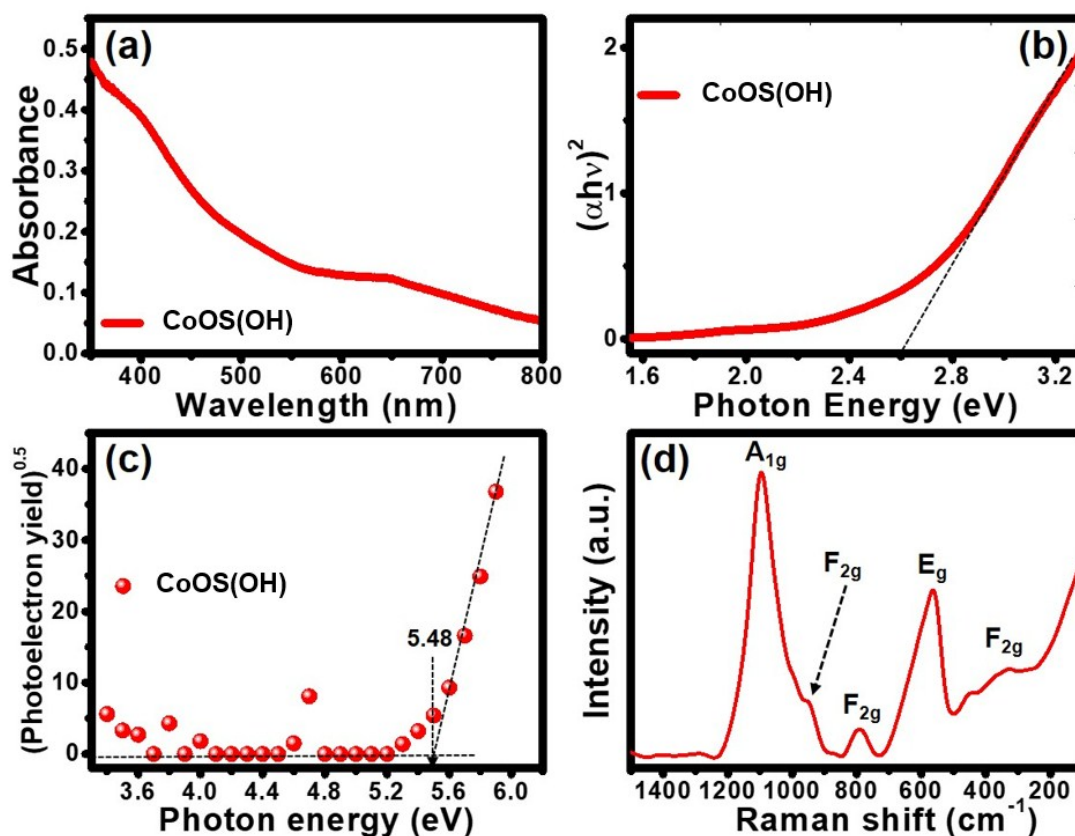


Figure S6. (a) UV-Visible diffuse reflectance spectrum of cobalt oxysulfide/hydroxide film, (b) Tauc plots or $(\alpha h\nu)^n$ as a function of Photon energy, (c) $(\text{photoelectron yield})^{0.5}$ as a function of Photon energy, and (d) Raman spectrum with an excitation wavelength of 785 nm.

3.5 *In situ* EXAFS measurement

Table S1 EXAFS curve fitting parameters of cobalt oxysulfide/hydroxide (CoOS(OH))

Name path	N	S 0^2	S 2 (\AA^2)	E $_0$	R (\AA)
[CoO $_2$] Co-O $_{1,1}$	6.000	0.596	0.00604	3.551	2.00752
[CoO $_2$] Co-Co $_{0,1}$	6.000	0.596	0.00925	3.551	3.10761
[CoS $_2$] Co-S $_{1,1}$	6.000	0.404	0.03058	7.468	2.28509
[CoS $_2$] Co-S $_{1,2}$	6.000	0.404	0.00739	7.468	3.56010
[CoS $_2$] Co-Co $_{0,1}$	12.000	0.404	0.02744	7.468	3.69724

3.6 Cycling stability

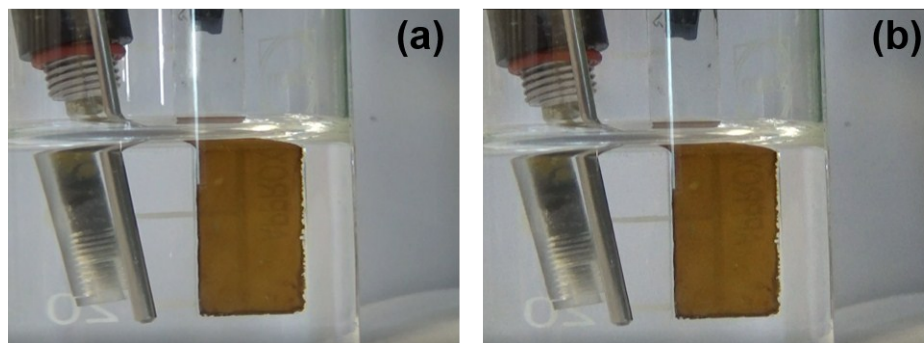


Figure S7. Electrode (a) before and (b) after cycling stability test from GCD over 10000 cycles at 5 A/g.

3.7 Electrochemical properties

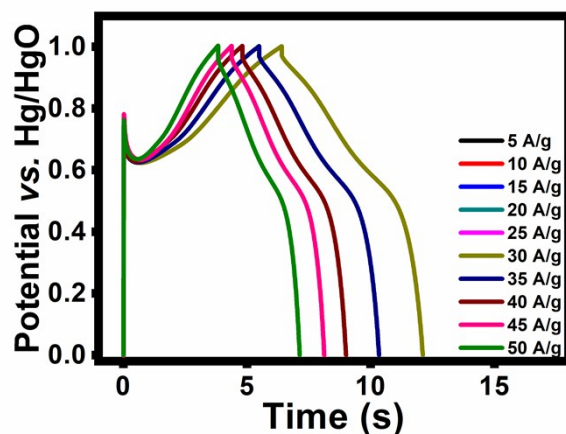


Figure S8. The GCDs at 30-50 A/g of half-cell electrode of cobalt oxysulphide/hydroxide nanosheets in 1 M KOH electrolyte.

References

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