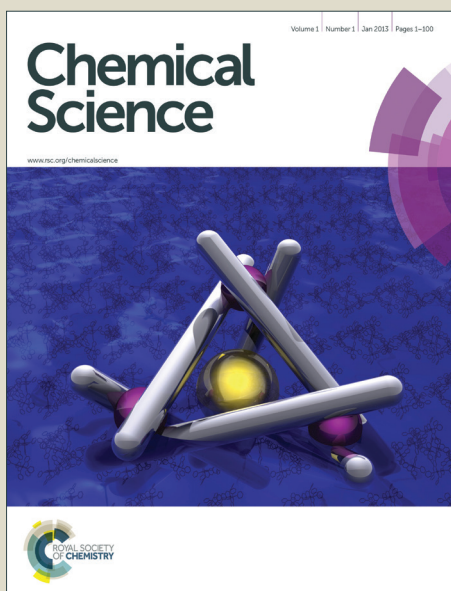


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EDGE ARTICLE

Cobalt Sulphide Microtube Array as Cathode in Photoelectrochemical Water Splitting with Photoanodes†

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We report on a cobalt sulphide (CoS) electrode prepared by simple and scalable chemical bath deposition (CBD), which performs as a highly efficient and robust electrocatalyst for the H₂ evolution reaction (HER) in both neutral and pH 13 electrolyte solution at a small overpotential ($\eta < 90$ mV). At $\eta = 390$ mV, turnover frequencies of 38.8 ± 1.9 and 52.1 ± 2.0 mol H₂ (mol Co)⁻¹ h⁻¹ were achieved with high stability (Faradaic efficiency > 95% for at least 72 h) and turnover numbers of approximately 2,600 and 3,400 in neutral and basic electrolyte solution, respectively. The rate of HER per geometric area is further enhanced by employing a CoS microtube array (*microCoS*), which is prepared by sulfuration of a cobalt hydroxide carbonate nanorod array template using CBD. *MicroCoS* shows excellent HER activity when it is coupled with a nanostructured hematite (α -Fe₂O₃) photoanode for H₂ generation from photoelectrochemical water splitting in basic electrolyte solution.

Introduction

Photoelectrochemical (PEC) water splitting is a promising approach to convert intermittent sunlight into a storable and renewable chemical fuel, H₂.¹ The success of clean water splitting systems will not only rely on the development of a device consisting of robust, efficient, inexpensive, and environmentally benign components, but also on the compatibility of the catalysts and light absorbers in an integrated system. The Earth-abundant light absorbers² and water oxidation electrocatalysts³ developed so far are mainly functional in neutral or basic conditions, whereas most non-noble metal-based H₂ evolution electrocatalysts (H₂-cats)⁴ require acidic conditions. Although some inexpensive electrocatalysts, such as molybdenum boride/carbide,⁵ metal nitrides,^{4f} have been reported as promising H₂-cats at room temperature in alkaline solution, their preparation often involves costly and energy-intensive processes,^{4f} which makes large-scale production and their integration into the photoelectrodes difficult. As a result, in the fuel generation step, the development of an inexpensive, robust, and highly efficient electrocatalyst pair, which operates under the same condition, is an essential challenge, and there is an urgent need for a scalable and inexpensive H₂-cat that operates at pH ≥ 7 .

Cobalt based H₂-cats, including metallic Co⁶ and molecular Co complexes,⁷ have been proposed as alternative electrocatalysts to noble metals for the hydrogen evolution reaction (HER). However, the requirement of a high overpotential to achieve a reasonable H₂ evolution rate in neutral aqueous electrolyte solution or poor stability is an unsolved problem. Recently, a HER catalyst (H₂-CoCat) composed of metallic cobalt nanoparticles with a cobalt-oxo/hydroxophosphate layer was prepared by prolonged electrodeposition of a cobalt salt in phosphate buffer.⁸ The H₂-CoCat shows considerably higher activity than metallic cobalt in a pH neutral electrolyte solution (TOF of H₂-CoCat ~ 80 h⁻¹ at η of 385 mV at

pH 7⁸), and to further explore H₂-cats with better HER activity, we therefore decided to explore the HER activity of different cobalt species. Recently, cobalt sulphide has been explored as an effective electrocatalyst for the reduction of tri-iodide,⁹ poly sulphide,¹⁰ and oxygen.¹¹ However, as compared with other metal sulphides,^{4a-e, 12} the application of cobalt sulphide to HER received little attention,^{4d, 13} which can be attributed to the facts that studies have often been carried out under strongly acidic conditions, where cobalt sulphide is prone to dissolution and generation of H₂S.

In this study, the HER activity of cobalt sulphide (CoS), prepared by a simple and scalable chemical bath deposition (CBD) method, was thoroughly investigated under neutral and basic conditions. Subsequently, a CoS microtube array was prepared using CBD to further increase the H₂ evolution rate per geometric surface area. Finally, we demonstrate that *microCoS* can be employed as a cathode in efficient PEC water splitting systems, where the use of alkaline electrolyte is often indispensable.

Experimental section

General considerations. Starting materials for the synthetic part of the work were purchased from commercial suppliers and of the highest available purity for the analytical work. Fluorine-doped tin oxide (FTO) coated glass (sheet resistance 7 ohm sq⁻¹, TEC GlassTM 7) substrates (1.0 \times 3.0 cm²) were cleaned with an ammonia-hydrogen peroxide-deionised water mixture (volume ratio: 1:1:5) at 70 °C for 20 min, followed by sonication in water for 15 min and drying at room temperature.

Preparation of CoS, Co₃O₄, and Co₉S₈ electrodes. CoS was deposited onto the FTO substrate (exposed area of 2.0 cm²) with epoxy tape (0.14 mm thickness) as spacer by using chemical bath deposition (CBD) in an aqueous solution (10 mL) containing urea (50 mM), CoCl₂·6H₂O (50 mM), and thioacetamide (0.1 M) at 90

°C for 4 h. The obtained electrode, designated as FTO/CoS, was rinsed with water and dried at room temperature. To prepare FTO/Co₃O₄ and FTO/Co₉S₈, FTO/CoS was annealed in air and nitrogen at 500 °C for 2 h, respectively. The film thickness of Co₃O₄, Co₉S₈, and CoS are approximately 150 nm. The amount of cobalt species on these electrodes was determined by UV-vis spectrophotometry (0.59 μmol cm⁻², *vide infra*).

Preparation of Co(OH)₂ electrode. α-Co(OH)₂ plates, with average film thickness of ~5 μm, was deposited onto the FTO substrate (exposed area of 2.0 cm²) using CBD in an aqueous solution (10 mL) containing CoCl₂·6H₂O (50 mM) and hexamethylenetetramine (0.1 M) at 90 °C for 4 h. The amount of cobalt species was determined by UV-vis spectrophotometry (2.25 μmol cm⁻², *vide infra*). The obtained electrode, designated as FTO/Co(OH)₂ electrode, was rinsed with water and dried at room temperature.

Preparation of metallic Co electrode. Electro-deposition of metallic cobalt was carried out following a published procedure.¹⁴ Briefly, metallic cobalt (~0.5 μm) was electrodeposited onto the FTO substrate (exposed area of 1.0 cm²) from an aqueous solution (20 mL, pH 4.6) containing ammonium chloride (1 M) and CoCl₂·6H₂O (0.01 M) at -1.0 V vs. Ag/AgCl for 5 min. The averaged charge passed is 0.68 C cm⁻². The amount of metallic cobalt was determined, by UV-vis spectrophotometry (1.59 μmol cm⁻², *vide infra*), corresponding to a Faradaic efficiency of 45%. The obtained electrode, designated as FTO/Co electrode, was rinsed with water and dried at room temperature.

Preparation of FTO/microCoS. CoS microtubes (with closed end) were grown on an FTO substrate by first growing layered hydroxide cobalt carbonate acicular nanorods (FTO/nanoLHCC), followed by the conversion of FTO/nanoLHCC into FTO/microCoS under CBD conditions. The FTO/nanoLHCC electrode was prepared following a previously reported procedure.¹⁵ The conversion of FTO/nanoLHCC into FTO/microCoS was achieved by immersing FTO/nanoLHCC into a bath solution containing urea (50 mM), CoCl₂·6H₂O (50 mM), and thioacetamide (0.1 M) at 90 °C for 6 h.

Preparation of FTO/nanoZnO/CdS_{NP}. This electrode consists of cadmium sulphide nanoparticles (CdS_{NP})-sensitised ZnO nanosheets (nanoZnO) on a FTO substrate. Firstly, layered hydroxide zinc carbonate nanosheets (nanoLHCC), ~15 μm in thickness, were grown on the FTO substrate (2.0 cm²) with epoxy tape as spacer by using CBD in a solution containing urea (16.7wt%) and zinc nitrate hexahydrate (0.15 M) at 90 °C for 4 h, followed by thermal conversion of nanoLHCC into nanoZnO at 300 °C in air for 30 min.¹⁶ The sensitisation of nanoZnO with CdS_{NP} was achieved by using a procedure reported elsewhere.¹⁷ Briefly, the FTO/nanoZnO electrode (exposed area of 2.0 cm²) was immersed into a solution (10 mL) containing cadmium chloride (10 mM) and thioacetamide (10 mM) at room temperature for 90 min. Finally, the obtained electrode was rinsed with water and dried at room temperature.

Preparation of FTO/nanoFe₂O₃. To prepare a tin doped α-Fe₂O₃ nanorod electrode (FTO/nanoFe₂O₃), β-FeOOH nanorods, with ~600 nm in length and ~50 nm in diameter, were firstly grown onto the FTO substrate (2.0 cm²) with epoxy tape as spacer by using CBD in a bath solution containing iron chloride

hexahydrate (0.15 M) and urea (6.25wt%) at 90 °C for 4 h. Thereafter, 20 μL of 20 mM SnCl₄ ethanolic solution was drop-coated onto the β-FeOOH nanorods three times, followed by annealing at 750 °C for 30 min. Note that, to remove the excess SnO₂, the annealed electrodes are treated in 1 M NaOH at room temperature for 12 h.¹⁸

Physical characterisation. The surface morphology of the electrodes was characterised using a Phillips XL30-SFGE scanning electron microscope (SEM). The nanoscale images of the microCoS tubes were obtained using a JEOL 3011 high resolution transmission electron microscope (HR-TEM) with samples made by scratching the film off the FTO substrate and dispersing the powder in acetone under ultrasonication for 5 min. X-ray diffraction (XRD) analyses were carried out using an X'Pert PRO X-ray diffractometer (PANalytical B.V., The Netherlands). To determine the amount of cobalt on the electrode, these cobalt species were dissolved to form [CoCl₄]²⁻ complex ions by ultrasonication of the electrodes (exposed area of 2 cm²) in a concentrated HCl solution (12 N, 10 mL) for 20 min. [CoCl₄]²⁻ ions were quantified by measuring the absorbance at 624 nm using a calibration curve of absorbance at 624 nm vs. concentration of [CoCl₄]²⁻. The surface composition of the films was verified by X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe system, ULVAC-PHI, Chigasaki, Japan), using a microfocused (100 μm, 25 W) Al X-ray beam, with a photoelectron take off angle of 45°. The Ar ion source for XPS (FIG-5CE) was controlled by using a floating voltage of 0.2 kV. The binding energies obtained in the XPS analyses were corrected for specimen charging, by referencing the C 1s peak to 285.0 eV.

Electrochemical and PEC measurements. Electrochemical experiments were performed with an Ivium CompactStat (Ivium Technologies BV) at 25 °C and all potentials are reported against the reversible hydrogen electrode (RHE) by using the equation $E(\text{V vs. RHE}) = E(\text{V vs. Ag/AgCl}) + 0.197 + 0.059 \times \text{pH}$.^{2e} A conventional one-compartment three-electrode electrochemical cell was employed for linear sweep voltammetry (LSV) unless otherwise noted; FTO/CoS, FTO/CoS, FTO/Co(OH)₂, FTO/Co₃O₄, or FTO/Co was used as the working electrode connected to a Pt foil counter electrode and a Ag/AgCl_{sat} reference electrode. The electrocatalytic activity of the electrodes (all with exposed area of 1.0 cm²) was evaluated using LSV at a scan rate of 0.05 mV s⁻¹ either in an aqueous pH 7 solution containing triethanolamine (TEOA, 0.05 M) and sodium sulphate (0.1 M), in an aqueous pH 13 solution containing KOH (0.1 M) and sodium sulphate (0.1 M), or in an another basic solution at pH 12.5 with Na₂S (0.1 M) and TEOA (0.05 M). Note that a TEOA buffer was used due to the irreversible oxidation of TEOA at the Pt counter electrode (preventing oxidation products to interfere with the reduction at the working electrode) and CoS is also stable in TEOA (in contrast to phosphate buffer; *vide infra*). When an aqueous basic electrolyte solution was used, the LSVs were carried out with three-electrodes in two-compartments separated by a Nafion[®] 117 film. It is noted that the electrolyte solution was prepared under N₂ when Na₂S is used to avoid the possible formation of polysulphides.

Controlled potential electrolysis with a FTO/CoS, FTO/Co, FTO/Co(OH)₂, FTO/Co₃O₄, and FTO/Co₉S₈ working electrode

was performed at $\eta = 390$ mV to allow for quantitative H_2 detection (vide infra). Measurements at low η resulted in correspondingly lower amounts of H_2 produced and difficulty to determine the FE accurately.

PEC properties of FTO/*nano*Fe₂O₃ and FTO/*nano*ZnO/CdS_{NP} (exposed area of 1.0 cm²) were examined in a two-compartment electrochemical cell with an aqueous basic electrolyte using LSV at a scan rate of 10 mV s⁻¹ under illumination provided by a solar light simulator (Newport Oriel, 100 mW cm⁻²; calibrated with Newport High Power Detector equipped with a Newport 1916-R Handheld Optical Power Meter) equipped with an air mass 1.5 global filter and an IR water filter. FTO/*nano*Fe₂O₃ or FTO/*nano*ZnO/CdS_{NP} was used as working electrode, whereas Pt foil or FTO/*micro*CoS was used as counter electrode, and Ag/AgCl_{sat} was used as the reference electrode (a reference electrode was only employed during LSV). The *i*-*t* transients and product measurements were carried out in a two-electrode configuration (electrode separation: ~10 cm). A bias of 1.23 V was applied with the FTO/*nano*Fe₂O₃ based PEC water splitting system, whereas zero bias was applied with the FTO/*nano*ZnO/CdS_{NP} PEC H_2 generation system.

Hydrogen and oxygen measurements. The amount of O₂ and H₂ generated from the two-compartment two-electrode PEC systems was detected and quantified by headspace gas analysis with an Ocean Optics fluorescence O₂ probe (FOSPOR-R) and an Agilent 7890A Series gas chromatography (GC) equipped with a 5 Å molecular sieve column (N₂ carrier gas at a flow rate of approximately 3 mL min⁻¹), respectively. The O₂ probe was inserted in an anodic compartment through a tightly sealed septum and continuous O₂ readings (O₂ partial pressure) at 1 s intervals throughout the experiment. For H₂ quantification, 20 μ L aliquots of the headspace gas were removed from the cathodic compartment of the PEC cell for GC analysis at the end of the experiment. The GC oven holding the columns was kept at 40 °C, and a thermal conductivity detector was used. The two-compartment electrochemical cell was purged with 2% CH₄ in N₂ (methane acts as internal standard for H₂ quantification by GC). The two-electrode PEC cell was operated at an applied bias of 1.23 V: a dark period of 30 min (control experiment) was followed by 2 h water splitting under standardised light illumination (100 mW cm⁻²) and another 30 min in the dark.

Results and discussion

Electrocatalytic HER activity of FTO/CoS thin film. Coating of FTO with a thin film of CoS (FTO/CoS) was accomplished by CBD with CoCl₂, urea and thioacetamide on FTO-coated glass in water at 90 °C for 4 h. For comparison, other cobalt species, including Co(OH)₂, Co₃O₄, metallic Co, and Co₉S₈ were also prepared (see Experimental Section). Physical characterisations, including XRD and SEM, of these five cobalt species confirm the identity of the different Co species (Figs. S1 and S2). Fig. 1 shows the linear sweep voltammetry (LSV) of the five cobalt species modified electrodes in a pH neutral electrolyte solution (50 mM TEOA and 0.1 M Na₂SO₄) at a scan rate of 0.05 mV s⁻¹. The reduction of aqueous protons on FTO/CoS onsets at a relatively low overpotential (η) of approximately 20 mV, which is comparable to FTO/Co. FTO/CoS shows a catalytic current density of -1.0 mA cm⁻² at an overpotential of 330 mV, which is

only 120 mV more cathodic than that of a Pt electrode (Fig. 1a). The overpotential requirement for FTO/CoS to obtain -1.0 mA cm⁻² is lower than that for FTO/Co ($\eta \sim 380$ mV), FTO/Co(OH)₂ ($\eta \sim 400$ mV), FTO/Co₃O₄ ($\eta \sim 450$ mV; all data uncorrected for *i*-R drop). FTO/Co₉S₈ exhibits the lowest electrocatalytic activity and -0.45 mA cm⁻² were observed at $\eta = 450$ mV. The difference in the HER activity of these cobalt species could be attributed to the difference in chemical composition, amount of Co loaded on the electrode, and surface morphology (see Fig. S2). At this electrochemical screening stage, however, we only investigated the effects of chemical composition in more detail.

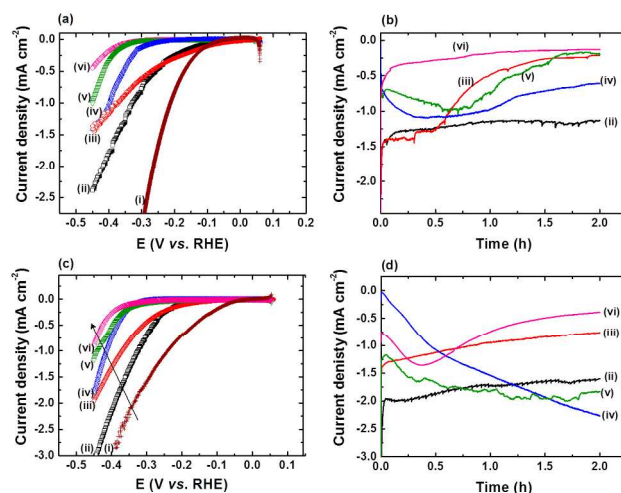


Figure 1. Linear sweep voltammetry (LSV), recorded at 0.05 mV s⁻¹, of cobalt species in (a) pH 7 and (c) pH 13 electrolyte solution (data not corrected for any uncompensated resistance losses). Chronoamperometric curves of the cobalt species at $\eta = 390$ mV in (b) pH 7 and (d) pH 13 solution. The neutral pH contains TEOA (50 mM) and Na₂SO₄ (0.1 M), whereas the pH 13 solution contains KOH (0.1 M) and Na₂SO₄ (0.1 M) in water. Samples (i) to (vi) are Pt foil (brown), FTO/CoS (black), FTO/Co (red), FTO/Co(OH)₂ (blue), FTO/Co₃O₄ (green), and FTO/Co₉S₈ (pink trace), respectively.

All cobalt species were subjected to 2-h electrolysis in pH neutral electrolyte solution. The chronoamperometric (*I*-*t*) traces at various η are shown in Figs. 1b and S3 the corresponding turnover frequency (TOF) and Faradaic efficiency (FE) at $\eta = 390$ mV in Table 1. FTO/CoS showed the highest stability and activity: A TOF of 38.8 ± 1.9 h⁻¹ was reached after 2-h electrolysis and a turnover number (TON) of approximately 2,600 with a FE of $96.2 \pm 2.8\%$ was observed after 72-h electrolysis at $\eta = 390$ mV (see Fig. S4). FTO/Co showed a slightly lower catalytic onset potential than FTO/CoS, FTO/Co, but it was unstable at $\eta > 90$ mV with a lower TOF and FE after 2-h electrolysis at $\eta = 390$ mV (see Table 1 and Fig. 1). The initial *i*-*t* transients of both FTO/Co(OH)₂ and FTO/Co₃O₄ at $\eta > 90$ mV indicate low activity and accompanying electrochemical reaction processes (Figs. 1 and S3). Reduction of Co(OH)₂ to metallic Co was reported to occur prior to HER,¹⁹ and we therefore suggest that the initial increase in cathodic current results from the reduction of Co(OH)₂ to metallic Co, which accompanies HER. FTO/Co₃O₄ shows two regions with an increasing cathodic current, which might be assigned to the

regions where the reductions of Co^{3+} to Co^{2+} (Eq. 1) and Co^{2+} to Co^0 (Eq. 2) occur.²⁰ These side reactions would further reduce the FE of Co_3O_4 and $\text{Co}(\text{OH})_2$ towards HER. In addition, we observed that the Co_3O_4 and $\text{Co}(\text{OH})_2$ films de-attached from the electrode during electrolysis, which can be attributed to the surface stress from structural changes induced by the electrochemical reduction processes during the electrolysis, and therefore, Co_3O_4 and $\text{Co}(\text{OH})_2$ are unstable and their corresponding HER activity is lower than FTO|CoS (Table 1).

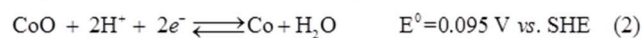
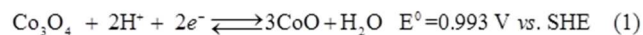


Table 1 Summary of the TOF and FE obtained from H_2 measurements after 2 h controlled-potential electrolysis at $\eta = 390$ mV.

Sample	TOF ^c (h^{-1})	FE (%)
pH 7^a		
CoS ^d	38.8 ± 1.9	99.1 ± 2.0
Co	8.2 ± 1.7	91.8 ± 2.5
$\text{Co}(\text{OH})_2$	6.8 ± 0.9	83.4 ± 10.0
Co_3O_4	15.1 ± 1.1	82.1 ± 1.0
Co_9S_8	5.9 ± 0.8	72.6 ± 2.3
pH 13^b		
CoS ^d	52.1 ± 2.0	96.3 ± 3.7
Co	8.3 ± 1.5	92.0 ± 8.4
$\text{Co}(\text{OH})_2$	8.4 ± 1.2	75.5 ± 1.2
Co_3O_4	38.6 ± 3.7	74.6 ± 3.8
Co_9S_8	28.4 ± 7.7	74.4 ± 4.2

^a: TEOA (0.05 M) and Na_2SO_4 (0.1 M); ^b: KOH (0.1 M) and Na_2SO_4 (0.1 M); ^c: Amount of Co on electrodes quantified by dissolving the film in concentrated HCl (~12 M) and measuring the absorbance of $[\text{CoCl}_4]^{2-}$ by UV-vis spectrophotometry. The TOF values were calculated taking all Co ions, including bulk Co, into account and are therefore an underestimated activity of these cobalt species; ^d: A TON of approximately 2,600 with a FE of $96.2 \pm 2.8\%$ was obtained at pH 7 and a TON of $> 3,400$ with a FE of $94.1 \pm 4.8\%$ after 72-h electrolysis at $\eta = 390$ mV at pH 13.

Fig. 2 shows the XPS spectra of Co 2p and S 2p for the FTO|CoS electrodes before and after 2-h controlled-potential electrolysis at various η . The Co 2p and S 2p spectra display similar features for all measured samples. All Co $2\text{p}_{3/2}$ peaks appear at a binding energy of approximately 778.0 eV with Co $2\text{p}_{3/2}$ - $2\text{p}_{1/2}$ peak separation of ca. 15.0 eV (Fig. 2a), which is typical for metallic Co or cobalt sulphide.²¹ The S $2\text{p}_{3/2}$ peaks at binding energy of approximately 161.8 eV, and S $2\text{p}_{3/2}$ and $2\text{p}_{1/2}$ doublet separation of 1.18 eV (Fig. 2b), which corresponds to S^{2-} of CoS.^{21b} The integration of the S 2p and Co $2\text{p}_{3/2}$ peaks for samples (i) to (v) show that the loss of sulfur in CoS is minimal ($< 20\%$) after 2-h controlled potential electrolysis. In addition, in prolonged electrolysis (24-h electrolysis at $\eta = 390$ mV), FTO|CoS kept its crystalline structure (Fig. S5). The results are in agreement with the previous report, in which CoS decomposed only when the applied potential was more negative than -1.0 V (vs. NHE, pH 6.1).²²

Figs. 1c-d show the HER activity of all the cobalt species in

basic electrolyte solution (0.1 M KOH and 0.1 M Na_2SO_4 at pH 13). The general trends are similar to pH 7, and FTO|CoS shows the highest HER activity and stability under basic conditions. The TOF and FE values after 2-h electrolysis at $\eta = 390$ mV for FTO|CoS, FTO|Co, FTO| $\text{Co}(\text{OH})_2$, FTO| Co_3O_4 , and FTO| Co_9S_8 are given in Table 1. In addition, when the electrolysis at $\eta = 390$ mV was extended to 72 h (Fig. S4), a TON of more than 3,400 with an FE of $94.1 \pm 4.8\%$ demonstrates that CoS is an efficient and robust catalyst for HER not only in pH neutral, but also in strongly alkaline conditions, where many other state-of-the-art catalysts such as MoS_x are not stable.⁵

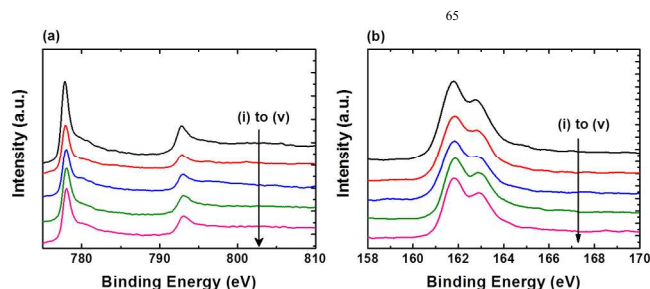


Figure 2. XPS spectra of FTO|CoS before electrolysis (i), and after 2-h electrolysis at (ii) $\eta = 90$ mV, (iii) $\eta = 190$ mV, (iv) $\eta = 290$ mV, (v) $\eta = 390$ mV in pH neutral solution (pH 7) containing TEOA (50 mM) and Na_2SO_4 (0.1 M). (a) Co 2p region. (b) S 2p region.

CoS shows enhanced HER activity in phosphate buffer (Fig. S6),²³ but we note that employing CoS in phosphate buffer (0.5 M, pH 7) results in the conversion of CoS into a cobalt hydroxide phosphate species with P/Co/O ratio of 1:0.99:9.79 (Figs. S6). A high HER activity was also reported for CoS_2 ($\sim 4 \text{ mA cm}^{-2}$ at $\eta = 225$ mV) prepared from expensive and energy-intensive e-beam evaporation and high temperature annealing process.^{13b} However, HER activity of CoS_2 was only examined under strongly acidic conditions (0.5 M H_2SO_4). In this study, we prepared CoS by a simple and scalable CBD method, whereas the synthesis of other metal sulphides, such as MoS_x and WS_x typically requires an inert atmosphere, tedious, costly and/or energy intensive procedures.^{4a, 4c-e, 4i, 12b, 13} In addition, our studies show that CoS is highly active over a wide pH range (pH 7 and pH 13) with the cobalt sulphide structure remaining intact during the electrochemical experiments.

Electroactivity of CoS microtube array. We increased the surface roughness of CoS by micro-structuring to enhance the rate of HER per geometric area. An array of layered hydroxide cobalt carbonate acicular nanorods (FTO|*nano*LHCC) was first grown onto an FTO substrate in water containing CoCl_2 and urea at 90°C for 4 h, followed by its conversion into a CoS microtube array (FTO|*micro*CoS) via CBD at 90°C for 6 h (see Experimental Section). The conversion of FTO|*nano*LHCC into FTO|*micro*CoS was confirmed by XRD and XPS (Fig. S7). As compared with the CoS thin film (Fig. S2a), *nano*LHCC has a tubular structure and its diameter increases with prolonged reaction time (Figs. 3a-b and S8), indicating the growth of a CoS layer on *nano*LHCC. TEM images (Fig. S9a) confirm that *nano*LHCC has a solid interior, but polycrystalline shells (Figs. S9b-d) and voids form when the sulfurisation process started. A tubular structure is formed after 6 h, which indicates the

conversion process involves not only the deposition of CoS onto *nano*LHCC from the reaction of Co^{2+} and S^{2-} ions in the bulk solution, but also the reaction of Co^{2+} ions inside *nano*LHCC with S^{2-} ions close to the *nano*LHCC|bath solution interface via the nanoscale Kirkendall effect.²⁴

A possible mechanism for the formation of CoS microtubes is proposed as follows (Fig. 3c): first, S^{2-} ions are released into the bath solution upon decomposition of thioacetamide at 90 °C and react with Co^{2+} ions and *nano*LHCC, resulting in the formation of a CoS shell. The higher diffusivity of cobalt ions than that of sulphide ions results in voids close to the interface, and the thickness of the CoS shell along with the number of voids in the core of the tube increases with reaction time. Finally, the voids connect to each other and form the tubular CoS structure as shown in the TEM images in Figs. 3c and S9.

The relative effective surface area between FTO/*micro*CoS and FTO/CoS is determined by measuring double-layer capacitance using cyclic voltammetry.²⁵ The results (Fig. S10) reveal that the effective surface area, *i.e.*, surface roughness, of FTO/*micro*CoS is about 17 times higher than that of FTO/CoS. Fig. S11 shows the LSVs of FTO/*micro*CoS in a basic electrolyte solution (pH 13) containing KOH (0.1 M) and Na_2SO_4 (0.1 M). It is found that the increased surface roughness indeed remarkably enhances the catalytic current per geometric area; FTO/*micro*CoS shows a current density of -0.44 mA cm^{-2} at $\eta = 190 \text{ mV}$, which is about 6 times higher than FTO/CoS (-0.08 mA cm^{-2} , Fig. S11a). However, the catalytic current of CoS does not scale proportionally with its surface area, *i.e.*, the catalytic current density of FTO/*micro*CoS is lower than that of FTO/CoS after normalisation with respect to the roughness factor (Fig. S11b), which can be attributed to the loss by (i) increasing *i*-R drop with increasing current, and (ii) the semiconducting properties of CoS and the short charge carrier diffusion length in CoS.⁴¹ The same behaviour has also been observed in neutral electrolyte (50 mM TEOA and 0.1 M Na_2SO_4), where the average current density of FTO/*micro*CoS during 24-h electrolysis at $\eta = 390 \text{ mV}$ is about -2.7 mA cm^{-2} , which is only about 2.25 times higher than that of FTO/CoS (see Fig S5a and Fig. S12a). We note that FTO/*nano*LHCC is inactive towards HER (see Fig. S13), and the maximal HER activity of FTO/*micro*CoS can therefore only be expected when *nano*LHCC is completely converted into *micro*CoS (6 h). FTO/*micro*CoS also kept its crystalline structure after 24-h electrolysis as confirmed by XRD (Fig. 12b). Nevertheless, the excellent geometric catalytic current of *micro*CoS motivated us to employ FTO/*micro*CoS as a cathode in PEC water splitting, where the use of alkaline electrolyte is often indispensable.

MicroCoS as cathode in PEC water splitting. Hematite ($\alpha\text{-Fe}_2\text{O}_3$), an Earth-abundant and chemically stable semiconductor, has a bandgap of 2.2 eV and favorable valence band potential for water oxidation, which makes itself a promising photoanode material for PEC water oxidation.^{2e-f,26} The conduction band level of hematite is more positive than the potential of proton reduction, and an external bias is therefore required when it is combined with a H_2 evolving cathode in a two-electrode PEC water splitting device.²⁶ In addition, the use of a hematite photoanode requires an alkaline electrolyte solution, which in the past has

limited the selection of cathode materials to noble metals such as Pt.^[2e-f] Here, we demonstrate that FTO/*micro*CoS can be used as an inexpensive alternative to Pt in this hematite based PEC water splitting system. A tin doped hematite nanorod (FTO/*nano* Fe_2O_3) photoanode is prepared by using a similar procedure reported previously (see Experimental Section).²⁷ Physical characterisations of FTO/*nano* Fe_2O_3 are shown in Figs. 4a and S14. FTO/*nano* Fe_2O_3 (2 cm^2) shows a photocurrent of approximately 0.6 mA at 1.23 V vs. RHE in a three-electrode, two compartment cell under standardised solar light irradiation (100 mW cm^{-2} , AM 1.5G, Fig. 4b).

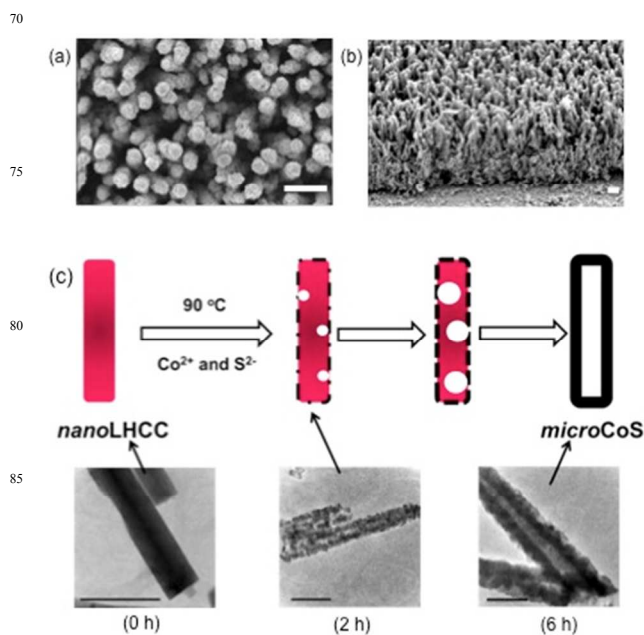


Figure 3. (a) Top-view and (b) tilted (45°) SEM images of FTO/*micro*CoS after 6-h CBD sulphurisation of FTO/*nano*LHCC. (c) Schematic illustration of the mechanism of *micro*CoS formation with TEM images at different CBD sulphurisation stages (*i.e.*, 0 h, 2 h, and 6 h, respectively). Scale bars in (a-b) and (c) are 1 and 0.5 μm , respectively.

FTO/*nano* Fe_2O_3 was subsequently combined with a Pt or FTO/*micro*CoS cathode (2.5 cm^2) in a two-electrode two-compartment PEC cell. A photocurrent of 0.15 to 0.20 mA was obtained at an external bias of 1.23 V (Fig. 4c). Note that the separation between photoanode and cathode is approximately 10 cm, and therefore, the loss in photocurrent by *i*-R drop would be significant.²⁸ The amount of H_2 and O_2 detected from PEC water splitting after 2-h irradiation (100 mW cm^{-2} , AM 1.5G) was (i) $4.3 \pm 0.4 \mu\text{mol H}_2$ and $2.3 \pm 0.4 \mu\text{mol O}_2$ with a Pt foil and $2.7 \pm 0.2 \mu\text{mol H}_2$ and $1.9 \pm 0.2 \mu\text{mol O}_2$ with FTO/*micro*CoS as cathode (Fig. S15). FTO/*micro*CoS therefore produces approximately 37% less H_2 than Pt. The lower H_2 production yield can be attributed to the additional 50 mV overpotential requirement for FTO/*micro*CoS to show comparable catalytic current with Pt (Fig. 4b). We note that there was no obvious change in surface morphology (SEM) and surface composition (XPS) of FTO/*nano* Fe_2O_3 after 2-h PEC experiment, indicating FTO/*nano* Fe_2O_3 is stable during PEC conditions (Figs. S14e-i).

Another demonstration (Figs. 4d and S16) of FTO/*micro*CoS in PEC H₂ generation is its coupling with a cadmium sulphide (CdS) nanoparticle sensitised ZnO nanosheet photoanode (FTO/*nano*ZnO/CdS_{NP}) in basic electrolyte (pH 12.5) containing TEOA (50 mM) and Na₂S (0.1 M). CdS has received much attention due to its suitable bandgap (~2.4 eV) and favourable conduction band position (-1.1 V vs. NHE, pH 7)²⁹ for H₂ generation. However, the use of hole scavenger, such as Na₂S, is necessary to prevent CdS from photocorrosion by the photo-generated holes in CdS, which is the reason that there is no O₂ evolution in this system. The physical characterisation of FTO/*nano*ZnO/CdS_{NP} is shown in Figs. S16a-d. The highly porous ZnO nanosheet architecture, which is prepared by growing layered zinc hydroxide carbonate using CBD, followed by thermal annealing, not only provides high surface area for CdS_{NP} loading, but also facilitates the diffusion of the sacrificial hole scavenger, resulting in a high photocurrent response with good stability. Fig. 4d shows that the photocurrent response of the PEC cell with FTO/*micro*CoS, operated at short-circuit condition, as cathode is higher than that with Pt foil as cathode, which can be attributed in part to poisoning of Pt by sulfur species.³⁰ After 2-h irradiation, the PEC cell with Pt as cathode generated 3.1 ± 0.4 μmol H₂, whereas FTO/*micro*CoS produced 4.0 ± 0.9 μmol H₂. As with FTO/*nano*Fe₂O₃, SEM and XPS analysis of FTO/*nano*ZnO/CdS_{NP} showed no signs of changes in surface morphology and surface composition after 2-h PEC experiment (Figs. S16d-h).

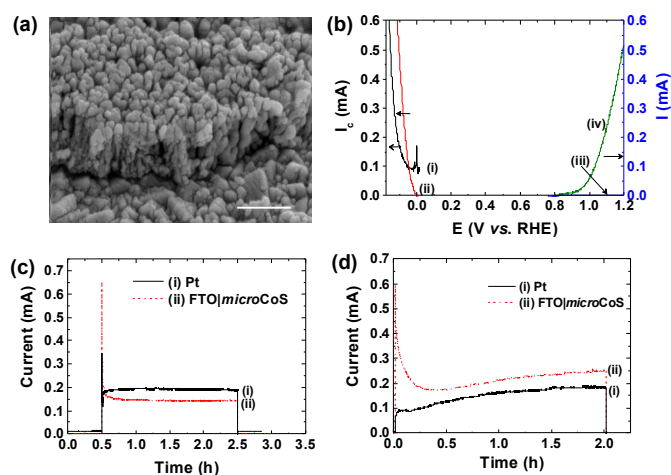


Figure 4. (a) SEM image of FTO/*nano*Fe₂O₃. Scale bar is 0.5 μm. (b) LSVs of FTO/*micro*CoS (i, 2.5 cm²), Pt (ii, 2.5 cm²), and FTO/*nano*Fe₂O₃ (2.0 cm²) in the dark (iii) and during irradiation (iv). LSVs for FTO/*micro*CoS and Pt were recorded at 0.05 mV s⁻¹, whereas LSVs for FTO/*nano*Fe₂O₃ was recorded at 5 mV s⁻¹. (c) Photocurrent transients of a two-electrode PEC cell with Pt or FTO/*micro*CoS combined with FTO/*nano*Fe₂O₃ at 1.23 V bias under irradiation. The electrolyte used for b-c contains KOH (0.1 M) and Na₂SO₄ (0.1 M) at pH 13. (d) Photocurrent transients of a two-electrode PEC cell with Pt or FTO/*micro*CoS combined with FTO/*nano*ZnO/CdS_{NP} at short-circuit condition under irradiation at pH 12.5. Light intensity: 100 mW cm⁻² (AM 1.5G). *Micro*CoS in (b) shows a 80 μA capacitive (non-Faradaic) current at 0 V vs. RHE in (curve i). The dark current shown in curve (ii) in (c) and (d) is negligible.

Conclusions

In this study, CoS has been selected from a series of different Co species as the most active and as a robust material in catalysing HER under both neutral (pH 7) and basic (pH 13) aqueous conditions. The three-dimensional morphology of microtubular CoS can easily be prepared by CBD and *micro*CoS displays a substantially enhanced catalytic current per geometric area for H₂ generation compared to flat CoS films. The *micro*CoS array was employed as efficient cathode in combination with a nanostructured α-Fe₂O₃ (hematite) photoanode, thereby allowing for water splitting in a PEC cell fully made of Earth abundant elements.

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Notes and references

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[†] Electronic Supplementary Information (ESI) available: experimental details, crystallographic data and spectral data. See DOI: 10.1039/b000000x/

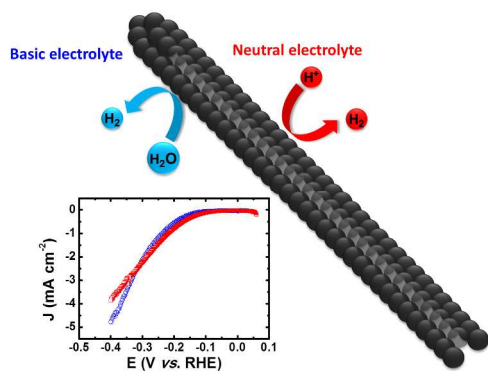
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Table of Content



A CoS microtube electrode catalyses hydrogen evolution efficiently in both neutral and basic aqueous electrolyte solution. The microtubular CoS electrode was also combined with a hematite photoanode to give a photoelectrochemical water splitting cell.