Supporting Information

Co$_9$S$_8$ Core-Shell Hollow Spheres for Enhanced Oxygen Evolution Reaction and Methanol Oxidation Reaction by Sulfur Vacancies Engineering

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1 Materials characterizations

The phase formation was identified using powder X-ray diffraction (XRD) (Bruker D8, Cu-Kα). The morphologies of the catalysts were observed by field emission scanning electron microscopy (FE-SEM, HITACHI S-4800) and transmission electron microscopy (TEM, JEOL JEM-2010). The linear scanning energy-dispersive X-ray spectrometry (EDX) and EDX elemental mappings were taken on TEM. The X-ray photoelectron spectroscopy (XPS) spectra were measured on ESCALAB 250 spectrometer (Perkin-Elmer). Raman spectra were analyzed using in-Via Raman spectrometer. The photoluminescence (PL) spectra were obtained by using a Cary Eclipse fluorescence spectrometer (Varian, USA) with Xe lamp as the excitation source. The electron paramagnetic resonance (EPR) spectra were collected at room temperature using a Bruker RPE Elexsys E500 spectrometer equipped with a SHQ with X band frequency in a continuous wave (around 9.8 GHz) cavity. The ICP-OES (PerkinElmer) was used to determine the element contents of the samples.

2 Electrochemical measurements

The electrochemical tests were conducted on CHI 760E electrochemical workstation. The Ag/AgCl (saturated KCl solution) as used as the reference electrode, a graphite rod was served as the counter electrode, and all catalysts were utilized as working electrode.

2.1 Electrochemical OER measurements

All electrochemical tests were performed in 1 M KOH aqueous electrolyte and the catalysts were dissolved in ethanol solution and then uniformly cast onto glassy carbon working electrode with a total loading of 0.4 mg cm⁻². All the linear sweep voltammetry (LSV) measurements were taken at a scan rate of 2 mV s⁻¹ to obtain the polarization curves. Chronoamperometric measurements were performed at corresponding potential to deliver a current density of 10 mA cm⁻². The Tafel slope was calculated according to the Tafel equation \( \eta = b \log (j/j_0) \) (\( \eta \) is the overpotential,
b is the Tafel slope, j is the current density, and \( j_0 \) is the exchange current density. Potentials were referenced to a reversible hydrogen electrode (RHE) using the following equation: 

\[
E_{\text{RHE}} = E_{\text{Ag/AgCl}} + (0.205 + 0.059pH) \ V.
\]

The double layer capacitance (\( C_{dl} \)) was obtained using cyclic voltammetry (CV) scanning from 1.18 to 1.24 V vs. RHE with different scan rates from 20 to 60 mV s\(^{-1}\) for OER. The electrochemical impedance spectroscopy (EIS) measurements were carried out by ranging the frequency from 100 k Hz to 0.1 Hz.

2.1 Electrochemical MOR measurements

MOR activities were characterized via cyclic voltammetry (CV) within the potential ranging from 1.0 – 1.8 V vs. RHE at a scan rate of 50 mV s\(^{-1}\). The solution was purged with \( N_2 \) for 30 min in prior to each measurement in 1.0 M KOH containing 1 M CH\(_3\)OH. The EIS measurements were carried out by ranging the frequency from 100 k Hz to 0.1 Hz in 1 M KOH containing 1 M CH\(_3\)OH. Chronoamperometric measurements were performed at corresponding potential to deliver a current density of 40 mA cm\(^{-2}\) in 1 M KOH containing 1 M CH\(_3\)OH.

2. Supplementary figures

![SEM image of the Co-precursor after sulfdation.](image)
Fig. S2 CVs tested at the potential range of 1.18 – 1.24 V vs. RHE with the scan rates increasing from 20 to 60 mV s⁻¹ for (a) Co₉S₈, (b) Co₉S₈₋ₓ-L, (c) Co₉S₈₋ₓ-M and (d) Co₉S₈₋ₓ-H spheres.
Fig. S3 SEM images of the Co$_9$S$_{8-x}$-M spheres after 10 h chronoamperometric test.

Fig. S4 TEM images of the Co$_9$S$_{8-x}$-M spheres after 10 h chronoamperometric test.
As shown in the XRD of the Co$_9$S$_{8-x}$-M spheres after 10 h chronoamperometric test, a new strong peak at 24° appears, which is correspond to the standard diffraction pattern of CoOOH. The existence of CoOOH in the Co$_9$S$_{8-x}$-M spheres after 10 h chronoamperometric test signifies that a part of Co$_9$S$_8$ transform into CoOOH during OER process, which is consistent with the transformation reported in the literature.$^{1-3}$

<table>
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<th>Table S1 The amount of Co and S, and the ratio of Co-to-S ratio of Co$<em>9$S$</em>{8-x}$-M spheres.</th>
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<tr>
<td>Sample</td>
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<tr>
<td>Co$<em>9$S$</em>{8-x}$-M spheres</td>
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The Co-to-S ratio of Co$_9$S$_{8-x}$-M spheres is 9:7.7 through ICP-AES, so the cobalt sulfide in this work is Co$_9$S$_8$ considering that their XRD characterization is correspond to the standard diffraction pattern of Co$_9$S$_8$ (JCPDS 75-2023).
