Supporting Information

Unraveling the Mechanism of Water-mediated Sulfur Tolerance via Operando Surface Enhanced Raman Spectroscopy

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Figure S1. (a) XRD data of BZCYYb powder. (b) Comparison of BZCYYb Raman intensity using SERS versus ordinary Raman spectroscopy. (c) *In situ* SERS measurement of Ni-BZCYYb model electrode at different temperatures.



Figure S2. (a) Top left : TEM image of Ag NPs, top right : TEM image of Ag@SiO₂ NPs, bottom left : SEM image of Ag NPs, bottom right : SEM image of Ag@SiO₂ NPs. (b) LSPR profile of Ag and Ag@SiO₂ NPs. (c) Raman Intensity comparison of diluted Rhodamine solution between ordinary Raman spectroscopy and SERS using Ag@SiO₂ NPs.



Figure S3. *In situ* SERS analysis of Ni-BZCYYb model electrode upon exposure to wet 100 ppm H₂S/H₂ at 500°C. Laser was focused on BZCYYb.



Figure S4. *In situ* Raman spectroscopic evolution of a BZCYYb model electrode acquired in 3 vol% H₂O introduction which was originally contaminated with dry 100 ppm H₂S/H₂ at 500°C. Intensity of v(-SO₄) fast decreasing upon water introduction and v(SO₂) develops at \sim 3,034 s as an indication of sulfate removal by water.



Figure S5. (a) *In situ* SERS analysis of Ni-BZCYYb model electrode upon exposure to wet 100 ppm H₂S/H₂ at 500°C. Laser was focused on Ni-BZCYYb interface. (b) Integrated peak intensities of key spectral features as function of time.

To gain information on the reaction on Ni-BZCYYb interface when wet atmosphere is introduced with sulfur, the Raman laser was focused on interface of model electrode. Figure S5 shows *in situ* Raman spectroscopic evolution of HSO₄⁻, –OH, and H₂O^{*}.



Figure S6. Comparison of v(-SO₄) intensity in pure BaSO₄, BZCYYb in Dry H₂S, BZCYYb in wet H₂S.



Figure S7. *In situ* SERS analysis of Ni-BZCYYb model electrode upon exposure to (a) dry and (b) wet 100 ppm H_2S/H_2 at 500 °C. Laser was focused on Ni surface. (c), (d) Integrated peak intensities of key spectral features as function of time for dry and wet respectively.

To investigate the reaction on the Ni surface, the Raman laser was focused on the Ni region of the model electrode. Figure S7a shows *in situ* Raman spectroscopic evolution when Dry 100ppm H_2S/H_2 was introduced at 500°C. A slight hump on ~460 cm⁻¹ may be attributed to v(S-S)

formation, which is sign of sulfur accumulation on Ni. In the higher vibrational region, v(-SH) was found at ~2,600 cm⁻¹.¹⁻³ It has been hypothesized by previous work⁴ that Ni can be an active metal to dissociate H_2S into S*. The elemental step of H_2S dissociation reaction on Ni was proposed as follows:

 $H_2S \to H_2S \ast$

 $H_2S^{\boldsymbol{*}} \rightarrow SH^{\boldsymbol{*}} + H^{\boldsymbol{*}}$

 $\mathrm{SH}^* \to \mathrm{S}^* + \mathrm{H}^*$

Therefore, Raman evolution of v(-SH) could be corresponds to H_2S^* or $-SH^*$ on Ni metal surface. Integrated Peak intensity shown in Figure S7c shows v(-SH) intensity increases over time, indicating –SH is aggregating on Ni surface.

The same experiment was repeated with 3 vol% water introduced. *In situ* Raman spectroscopic evolution of wet 100 ppm H₂S/H₂ at 500°C is shown in Figure S7b. There was no specific sign of v(S-S) formation. However, v(-SH) was also found ~2,600 cm⁻¹. It is very likely H₂S dissociation on Ni does not have great effect upon water presence in the system. Unlike dry atmosphere, v(-SH) does not increase over time. Rather, it decreases over time (Figure S7d). It seems water facilitates the sulfate dissociation reaction so that there are no accumulation of v(-SH) is found on Ni.



Figure S8. Molecular representation of (a) SO_4^{2-} and (b) BaZrO₃ used in computational modeling.

SO ₄			
	1o-binding on b-site	1o-binding on active-o-	1o-binding on crystal-o-
		site	site
		(most stable adsorption)	
side-			
view			
top- view			
E _{total} (eV)	-1012.12	-1012.60	-1012.58

	2o-binding in Td form	3o-binding	4o-binding(so3-like)
side- view			
top- view			
Etotal	-1006.88	-1005.40	-1007.55
(eV)			

Figure S9. Geometrical illustration of -SO₄ on BaZrO₃ to find most stable adsorption site. The cyan, green, red, yellow and white spheres are represented as Zr, Ba, O, S and H atoms, respectively.

H ₂ S			
	on b-site	on active-o-site	on crystal-o-site
		(most stable adsorption)	
side- view			

top- view				
Etotal (eV)	-1009.05	-1011.43	-1009.29	
	· · ·			
	on active-o-site in			
	dissociative form			
side-				
view				
top- view				
Etotal	-1009.71			
(eV)				
Figure S10. Geometrical illustration of H ₂ S on BaZrO ₃ to find most stable adsorption site. The				

Figure S10. Geometrical illustration of H_2S on $BaZrO_3$ to find most stable adsorption site. In
cyan, green, red, yellow and white spheres are represented as Zr, Ba, O, S and H atoms,
respectively.

Steps	BZO	doping Y	doping Yb
R1 : $H_2S_{(g)} + O^{2-} \rightarrow H_2SO^{2-}_{(b)}$	-3.57	-3.94	-3.83
R2 : $H_2SO^{2-}(b) + O^{2-}(b) \rightarrow HSO^{2-}(b) + HO^{-}(b) + e^{-}$	-2.31	-2.23	-1.87
R3 : $\text{HSO}^{2-}(b) + \text{O}^{2-}(b) \rightarrow \text{SO}^{2-}(b) + \text{HO}^{-}(b) + \text{e}^{-}$	-2.42	-2.78	-2.98
R4: $SO^{2-}(b) + O^{2-}(b) \rightarrow SO_{2}^{2-}(b) + 2e^{-}$	-4.64	-4.26	-3.59
R5 : $SO_2^{2-}(b) + O^{2-}(b) \rightarrow SO_3^{2-}(b) + 2e^{-}$	-2.23	-2.13	-2.68
R6: $SO_3^{2-}(b) + O^{2-}(b) \rightarrow SO_4^{2-}(b) + 2e^{-}$	-2.04	-2.09	-1.90
ΔE for total oxidation reaction	-17.20	-17.46	-16.85

Table S1. ΔE for Oxidation reaction forming SO₄



Reaction Coodinate

Figure S11. PES and the related structures of intermediate states in each step for the oxidation process of $H_2S_{(g)} + 6O^{2-}_{(b)} \rightarrow SO_4^{2-}_{(b)} + 2OH^{-}_{(b)} + 8e^{-}$ on Y or Yb doped BaZrO_{3.}

Steps	BZO	doping Y	doping Yb
R7 : $SO_4^{2-}(b) + H_2O_{(g)} \rightarrow SO_4^{2-}(b) + H_2O_{(b)}$	-1.02	-0.94	-0.99
R8 : $SO_4^{2-}(b) + H_2O_{(b)} \rightarrow HSO_4^{-}(b) + OH^{-}(b)$	-0.09	-0.07	-0.13
R9 : $HSO_4^{-}(b) + 2e^{-} \rightarrow SO_3^{2-}(b) + OH^{-}(b)$	1.32	1.30	1.16
R10: $SO_3^{2-}(b) + H_2O_{(g)} \rightarrow SO_3^{2-}(b) + H_2O_{(b)}$	-0.79	-0.74	-0.71
R11 : $SO_3^{2-}(b) + H_2O_{(b)} \rightarrow HSO_3^{-}(b) + OH^{-}(b)$	0.72	0.81	0.88
R12: HSO ₃ ⁻ (b) \rightarrow SO _{2(b)} + OH ⁻ (b)	0.20	0.19	0.11
R13 : SO _{2(b)} \rightarrow SO _{2(g)}	0.44	0.40	0.32
ΔE for total reduction reaction	0.79	0.95	0.64

Table S2. ΔE for Reduction reaction for SO₄ removal



Reduction

Reaction Coordinate

Figure S12. PES and the related structures of intermediate states in each step for the reduction $(SO_4^{2-}_{(b)} removal)$ process of $SO_4^{2-}_{(b)} + 2H_2O_{(g)} + 2e^- \rightarrow SO_{2(g)} + 4OH^-_{(b)}$ on Y or Yb doped BaZrO₃.



Figure S13. (a) EIS of a Ni-BZCYYb model electrode measured in Dry H_2 with different anodic bias at 500 °C. Counter electrode of Ag is used. (b) Comparison of EIS when both electrodes are Ag.

EIS profile from 0 to 1.0 V was measured in dry H_2 at 500°C. While Ni-BZCYYb side was connected as working electrode (WE), the other side was brush-painted with Ag paste to perform as counter electrode (CE). For reference, a Ag-Ag symmetric cell with BZCYYb electrolyte of the same thickness was tested under the same conditions. Since Ag electrode resistance is relatively smaller than Ni-BZCYYb side, it can safely be assumed that major resistance change should come from Ni-BZCYYb (WE) side. Despite of applying anodic bias, R_p in H₂ does not change much.



Figure S14. (a) EIS of a Ni-BZCYYb model electrode measured in Dry 0.5ppm H_2S/H_2 with different anodic bias at 500°C. Counter electrode of Ag is used. (b) Comparison of EIS when both electrodes are Ag.

Then gas is switched with Dry 0.5 ppm H_2S/H_2 to track the R_p change of model electrode. Similarly, EIS profile from 0 V to 1.0 V is measured at 500°C. Unlike in pure H_2 , Ni-BZCYYb model electrode R_p increases as anodic bias is applied in dry H₂S condition. When DC bias is applied, R_p increases. On the other hand, Ag reference cell R_p does not change significantly, suggesting that the –SO₄ developed Ni-BZCYYb WE is responsible for the resistance increase. By EIS testing, it can be concluded that sulfur poisoning is deeply related with the bias applied to the cell.



Video S1. Animation for oxidation (SO₄²⁻(b) formation) process of $H_2S_{(g)} + 6O^{2-}(b) \rightarrow SO_4^{2-}(b) + O^{2-}(b) \rightarrow SO_4^{2-}(b) \rightarrow$

 $2OH^{\text{-}}{}_{(b)}+8e^{\text{-}}$



Video S2. Animation for reduction (water-mediated $SO_4^{2-}_{(b)}$ removal) process of $SO_4^{2-}_{(b)} + 2H_2O_{(g)} + 2e^- \rightarrow SO_{2(g)} + 4OH^-_{(b)}$

Table S3. Summary of experimentally found and DFT calculated vibrational frequency of sulfur ions (S=O stretching mode)

Species	Experimental (cm ⁻¹)	DFT (cm ⁻¹)
-SO4	980	987
-HSO4	1050	1050
SO ₂	1150, 1350	1038, 1229

The calculated frequencies of these vibration modes generally agree well with the experimental results, as summarized in the Table S3.

For -SO₄, the calculated frequency is 987 cm⁻¹ whereas the measured value is 980 cm⁻¹, corresponding to an S=O stretching mode.

For -HSO₄, the calculated frequency is 1050 whereas the experimental value is 1050 cm⁻¹, corresponding to an S=O stretching mode. Additionally, DFT calculations also suggest that O-H stretching at 3769 cm⁻¹ and the other S=O stretching at 1248 and 1110 cm⁻¹.

For SO₂, the calculated frequencies are 1229 and 1038 cm^{-1} whereas the measured values are1350 and 1150 cm^{-1} , corresponding to an asymmetrical and a symmetrical S=O stretching mode, respectively.





-HSO₄: 1248 cm⁻¹







SO₂: 1229 cm⁻¹

-SO₂: 1038 cm⁻¹







Figure S15. Calculated vibrational frequencies of the sulfur ions on the surface of BaZrO₃



Video S3. Animation for -HSO₄ vibration of -OH stretching at 3769 cm⁻¹



Video S4. Animation for -HSO₄ vibration of S=O stretching at 1248 cm⁻¹



Video S5. Animation for -HSO₄ vibration of S=O stretching at 1110 cm⁻¹



Video S6. Animation for -HSO₄ vibration of S=O stretching at 1050 cm⁻¹



Video S7. Animation for -SO₄ vibration of S=O stretching at 987 cm⁻¹



Video S8. Animation for SO₂ vibration of asymmetric S=O stretching at 1229 cm⁻¹



Video S9. Animation for SO₂ vibration of symmetric S=O stretching at 1038 cm⁻¹

References

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