

## Supporting Information

### **Investigating the oxidation mechanism of facet-dependent pyrite: implications for the environment and sulfur evolution**

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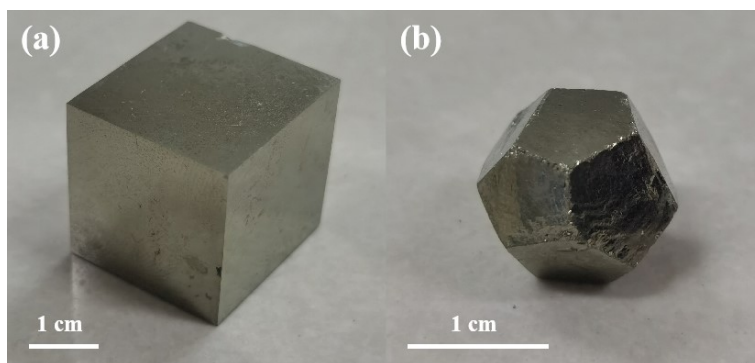
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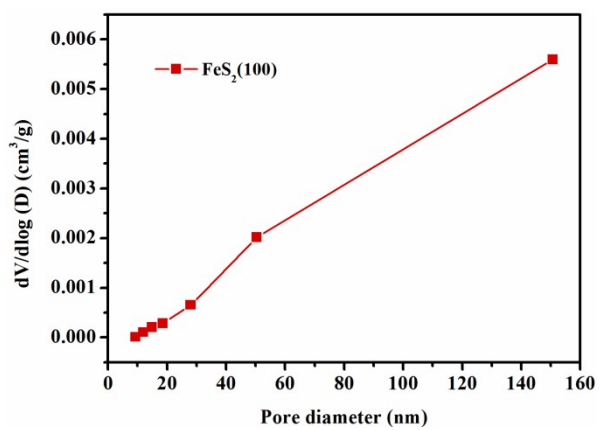
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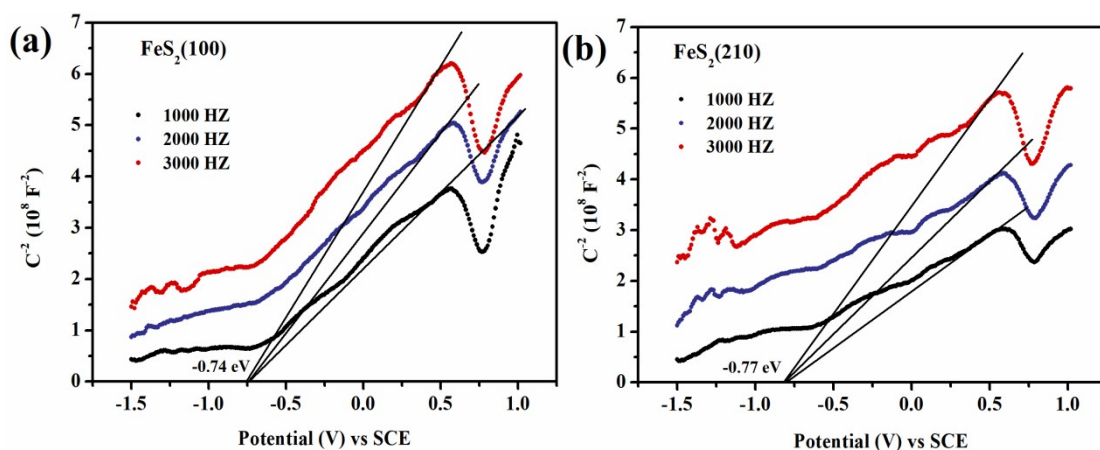
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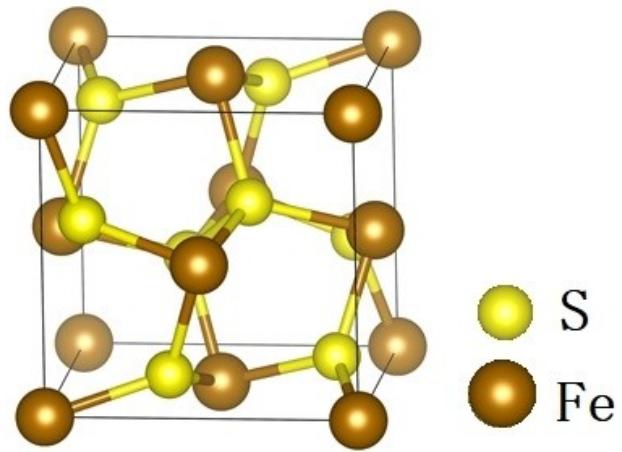
**Fig. S1** single crystals of FeS<sub>2</sub>(100) and FeS<sub>2</sub>(210)



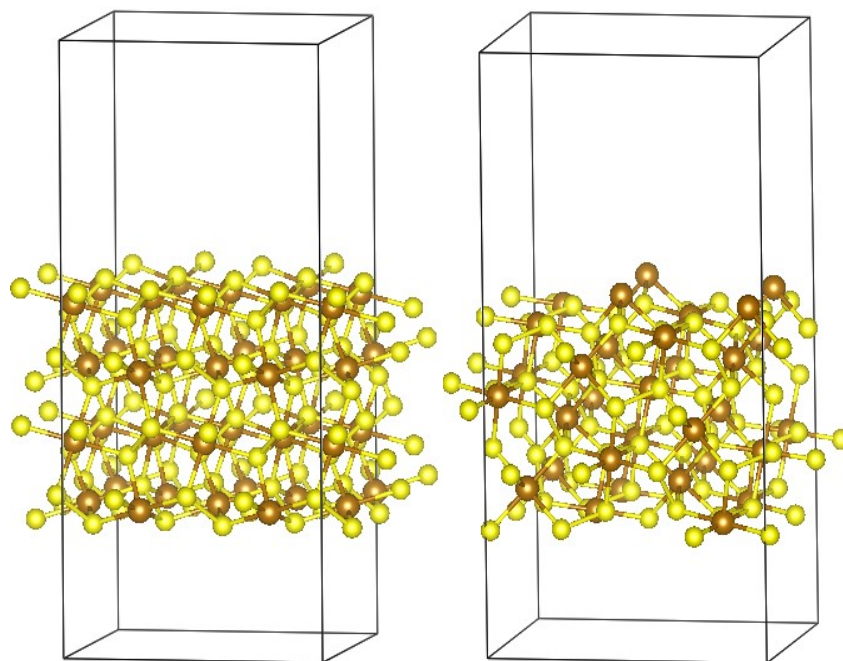
**Fig. S2** The pore size distributions of FeS<sub>2</sub>(100)



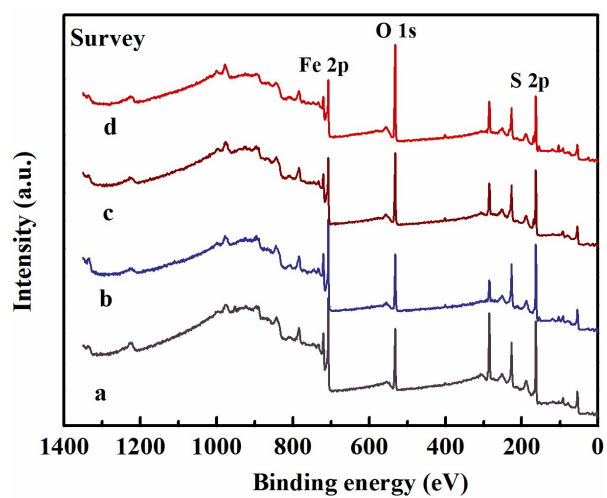
**Fig. S3** (a-b) The Mott-Schottky plots of FeS<sub>2</sub>(100) and FeS<sub>2</sub>(210) at different frequency ranges.



**Fig. S4** Bulk structure of pyrite



**Fig. S5** Structure of pyrite with FeS<sub>2</sub>(100) and FeS<sub>2</sub>(210) facets



**Fig. S6** XPS spectra of (a) FeS<sub>2</sub>(100) before oxidation; (b) FeS<sub>2</sub>(210) before oxidation; (c) FeS<sub>2</sub>(100) after oxidation; (d) FeS<sub>2</sub>(210) after oxidation.

**Table. S1** The Outlier Detection Method for each element in FeS<sub>2</sub>(100)  
and FeS<sub>2</sub>(210)

Elements	FeS <sub>2</sub> (100)			FeS <sub>2</sub> (210)		
	<i>PI</i>	<i>P2</i>	<i>P3</i>	<i>PI</i>	<i>P2</i>	<i>P3</i>
Na	0.299	1.047	1.347	/	/	/
Mg	0.579	0.828	1.407	1	-1	/
Al	1.400	0.528	0.872	1.412	0.779	0.632
Si	1.402	0.543	0.859	1.406	0.838	0.568
P	1.336	0.267	1.069	/	/	/
S	1.364	0.358	1.005	1.214	1.235	0.020
Cl	/	/	/	/	/	/
K	1.298	0.162	1.135	1.191	1.256	0.064
Ca	0.8167	1.408	0.594	1.406	0.575	0.831
Ti	0.405	1.377	0.971	1	1	/
Cr	0.097	1.174564	1.269	1.225	0	1.225
Mn	1.412	0.767	0.646	0.683	1.414	0.731
Fe	1.372	0.984	0.387	1.117	0.192	1.309
Ni	0.843	1.405	0.562	/	/	/
Zr	1.225	1.225	0	/	/	/
W	/	/	/	/	/	/

**Table. S2** Properties of FeS<sub>2</sub>(100) and FeS<sub>2</sub>(210)

Samples	SSA (m <sup>2</sup> /g)
FeS <sub>2</sub> (100)	0.265
FeS <sub>2</sub> (210)	0.121

**Table. S3** Surface energies and coordinated numbers of FeS<sub>2</sub>(100) and FeS<sub>2</sub>(210) facets

Facet	Surface Fe coordination	Surface S coordination	Surface energy (J/m <sup>2</sup> )	
			Unrelaxed	Relaxed
(100)	5	2,3	1.08	0.88
(210)	4,5	2,3	1.37	1.27

**Table. S4** The adsorption energies of different O<sub>2</sub> adsorption sites on FeS<sub>2</sub>(100) and FeS<sub>2</sub>(210) facets

Crystal facets	FeS <sub>2</sub> (100)					
Adsorption Sites	Fe <sub>5</sub> -Fe <sub>5</sub>	Fe <sub>5</sub> -S <sub>3</sub>	Fe <sub>5</sub> -S <sub>2</sub>	S <sub>2</sub> -S <sub>3</sub>		
Adsorption Energy (eV)	-0.7962	0.85594	0.5348	4.3934		
Crystal facets	FeS <sub>2</sub> (210)					
Adsorption Sites	Fe <sub>5</sub> -Fe <sub>4</sub>	Fe <sub>5</sub> -S <sub>3</sub>	Fe <sub>5</sub> -S <sub>2</sub>	Fe <sub>4</sub> -S <sub>3</sub>	Fe <sub>4</sub> -S <sub>2</sub>	S <sub>2</sub> -S <sub>3</sub>
Adsorption Energy (eV)	-3.865	1.1602	-2.06	2.614	-2.217	-1.022

**Table. S5** The composition of Fe, S, and O elements of FeS<sub>2</sub> before and after reaction

	Sample	Element (%)		
		Fe	S	O
Before reaction	FeS <sub>2</sub> (100)	17.51	48.53	33.96
	FeS <sub>2</sub> (210)	14.55	47.97	37.48
After reaction	FeS <sub>2</sub> (100)	14.39	46.22	39.39
	FeS <sub>2</sub> (210)	11.68	44.65	43.67



**Table. S6** The composition of Fe, S, and O elements of FeS<sub>2</sub> before and after reaction

Species	Before reaction		After reaction		FWHM	L-G
	FeS <sub>2</sub> (100)	FeS <sub>2</sub> (210)	FeS <sub>2</sub> (100)	FeS <sub>2</sub> (210)		
Fe(II)	0.726	0.721	0.696	0.582	0.9	0.8
Fe(III)	0.216	0.219	0.221	0.305	2.2	0.8
Fe(hydro)oxides	0.058	0.060	0.083	0.113	2.2	0.8
S <sub>2</sub> <sup>2-</sup>	0.773	0.791	0.738	0.760	0.8	0.8
S <sup>2-</sup>	0.124	0.093	0.109	0.055	1.2	0.8
S <sub>n</sub> <sup>2-</sup>	0.059	0.078	0.069	0.073	1.2	0.8
SO <sub>4</sub> <sup>2-</sup>	0.044	0.038	0.084	0.112	1.5	0.8