Supplementary Information for：

Mechanistic insights into hydrogen-enhanced sulfidation of smithsonite via fluidization roasting

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Materials and methods

Materials and reagents

High-purity smithsonite and pyrite ores were sourced from Yunnan Province and Hubei Province, China, respectively. The raw ore photographs and and SEM images are presented in **Fig. 1**a, b. The smithsonite and pyrite ores were subjected to crushing, grinding, and sieving to achieve target particle sizes of −74+38 μm for smithsonite and −74 μm for pyrite, which were subsequently used in roasting and flotation experiments. SEM images of the mixed ore with a pyrite/smithsonite molar ratio of 0.2 revealing that pyrite particles are significantly smaller than smithsonite particles and readily adhere to the smithsonite surface. XRD analysis and elemental analysis were conducted on the smithsonite and pyrite, with results shown in **Fig. 1**c, d. The diffraction peaks of smithsonite and pyrite closely matched PDF#99-0095 and PDF#99-0087, respectively, with negligible impurity peaks observed. The zinc grade of the smithsonite was determined to be 49.42%, with primary impurities including CaO, Fe, Al_2O_3, and SiO_2. The sulfur grade of pyrite reaches 53.45%, with a purity approaching nearly 100%.

The chemical reagent BX utilized in the experiments was industrial grade (purity >90%). Copper sulfate ($CuSO_4$), methyl isobutyl carbinol (MIBC), sodium hydroxide (NaOH), and hydrochloric acid (HCl) were all of analytical-grade reagent. Deionized water was produced using a laboratory ultrapure water system (XJG1-20-B, Xin Jie, China), with resistivity maintained at 10–18.25 MΩ·cm.

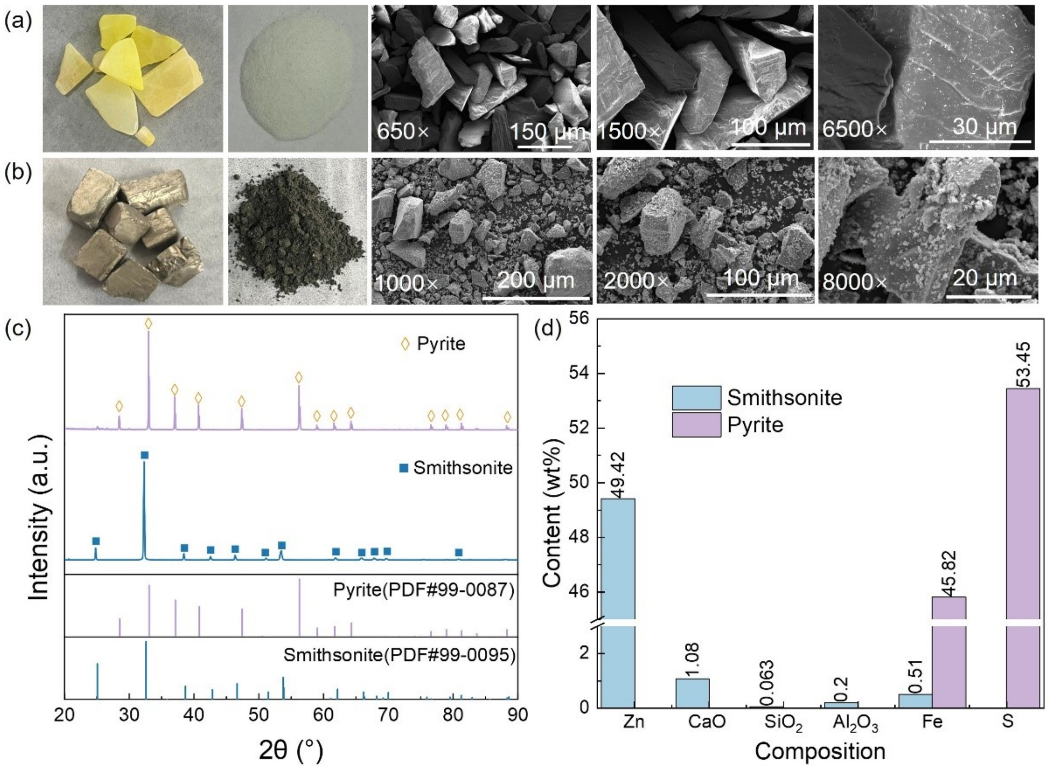

Fig. S1 Photographs and SEM images of (a)smithsonite and (b)pyrite; (c) XRD patterns of zinc smithsonite and pyrite; (d) Elemental analyses of smithsonite and pyrite.

Experimental apparatus and procedure

The sulfidation roasting of smithsonite was conducted in a roasting system equipped with an open-type vertical tube furnace (OTF-1200X-S-VT, Kejing, China) and a four-channel proton flow control system (GSL-LCD-SW, Kejing, China), as shown in **Fig. 2**. For each experiment, 10 g of the sample was loaded into a quartz tube and sealed using flanges. A N_2-H_2 gas mixture with predetermined composition and flow rate was introduced into the system. Once the furnace temperature stabilized at 450°C, the quartz tube was transferred into the roasting zone. Following completion of the roasting process, the tube was withdrawn and cooled under a N_2 atmosphere.

Flotation experiments were conducted using a hanging trough flotation machine

(XFG II, Jitan, China). For each experiment, 2 g of the roasted product was weighed and subjected to flotation. Hydrochloric acid (HCl) or sodium hydroxide (NaOH) is first added to adjust the pH, followed by sequential addition of $CuSO_4$ (2×10^{-4} mol/L), BX collector (1×10^{-4} mol/L), and MIBC frother (1×10^{-4} mol/L) at 2 min intervals. The flotation pH is maintained at 7.0±0.2. The mineral-laden froth floating on the surface was then skimmed and dried for yield calculation. Given that pure mineral flotation tests were performed in this study, yield was used as a proxy for recovery.

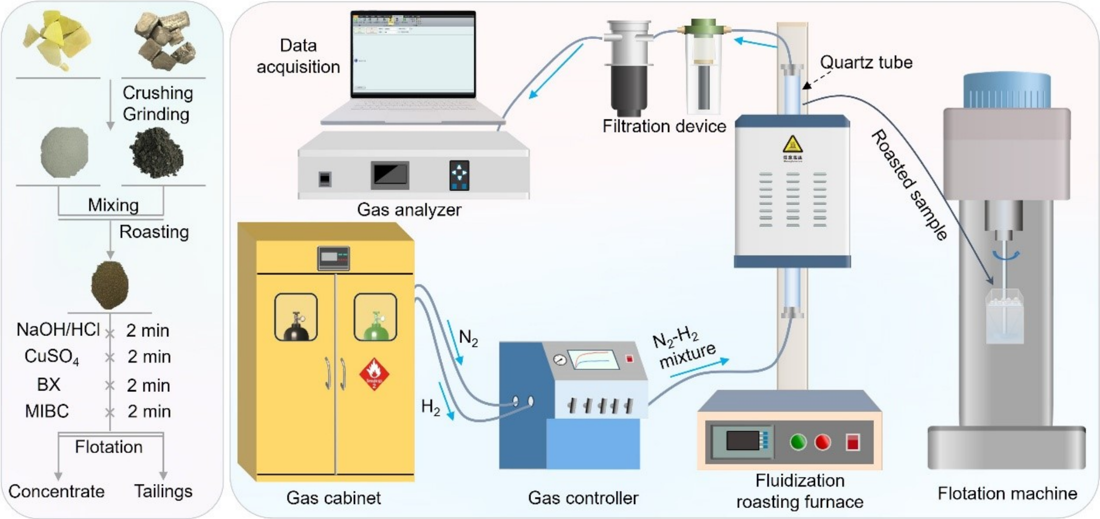

Fig. S2 Schematic diagrams of experimental and process experimental equipment.

Materials characterization methods

Thermogravimetric analysis-differential thermal analysis (TG-DTA) was conducted to study the decomposition process of smithsonite using a simultaneous thermal analyzer equipped with a quadrupole mass spectrometer (STA 449 F5 Jupiter®, NETZSCH, Germany). For each test, a 20 mg sample was precisely weighed and loaded into the analyzer. Following sample loading, the chamber was evacuated twice to ensure complete removal of air. The heating rate during the test was maintained at

10°C/min over the temperature range of 50–800°C, with a gas flow rate of 200 mL/min (pure N_2 or 25vol% H_2–75vol% N_2 mixture). The X-ray diffraction (XRD) analysis of the samples was analyzed using an X-ray diffractometer (SmartLab, Rigaku, Japan). XRD was performed using Cu target, with a scanning rate of 5°/min. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were performed using a scanning electron microscope (Apreo 2 S, Thermoscientific, USA) equipped with an energy-dispersive spectrometer (Ultim Max 40, Oxford, UK). The working distance was maintained at 5–10 mm, and the acceleration voltage was set to 15 kV. To enhance electrical conductivity, the sample surface was sputter-coated with gold twice prior to analysis. Particle size analysis of the samples was performed using a laser diffraction particle size analyzer (MasterSizer 2000, Malvern, UK) via wet dispersion analysis. The contact angle measurement was conducted using a dynamic contact angle meter (XG-CAMC1, Shanghai Xuanzhun Instrument Co., Ltd., China), employing the hanging drop method. For the test, the powder sample was made into cake shape under a pressure of 6.0 MPa using a tablet press.

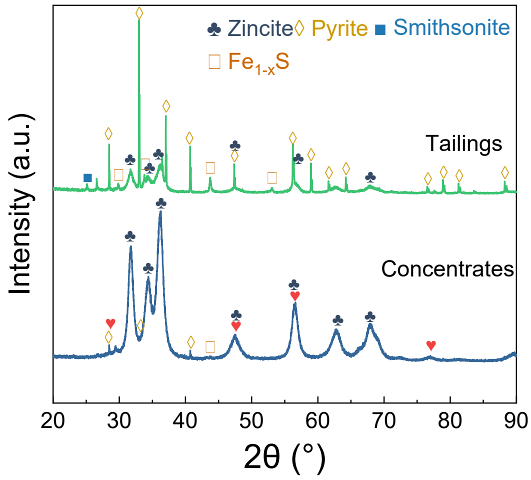

Fig. S3 XRD patterns of flotation concentrates and flotation tailings.

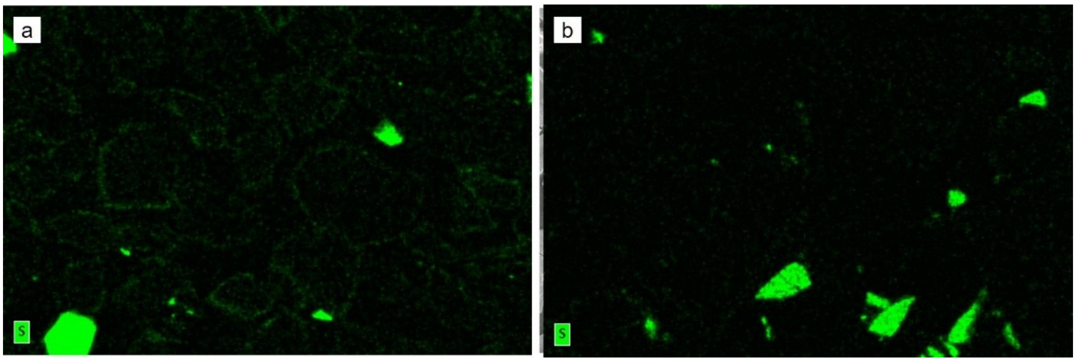

Fig. S4 SEM-EDS elemental mapping for S was performed on the areas indicated in **Fig. 4**a and 4h.

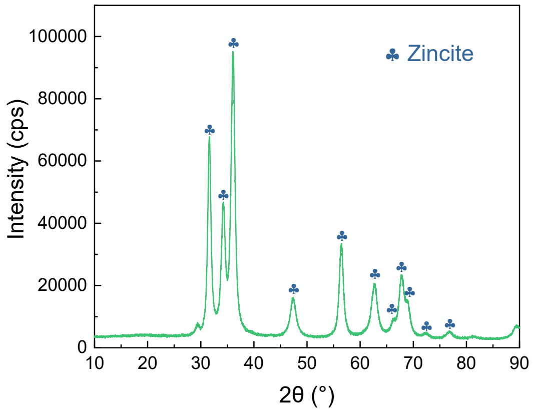

Fig. S5 XRD patterns of zincite.