# Supporting Information

## Supercritical $CO_2$-modulated defect dynamic equilibrium for magnetic-proton dual-functional $CaZrO_3$

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# Contents

## Experimental

Commercial - grade $CaZrO_3$ powder (purity 99.2% by mass fraction) provided by Yuanye Biotech is used in the experiment and can be directly used without further purification; high - purity carbon dioxide (purity 99.99% by volume fraction) provided by Zhengzhou Yuanzheng Gas Company, analytically pure ethanol from China Pharmaceutical Reagent Co., Ltd., and deionized water prepared by double distillation are used in the experiment. The SC $CO_2$ reaction system in the experiment is a 316L stainless - steel high - pressure reactor (volume 50 mL) equipped with a heating jacket and a temperature controller. Take 30 mg of $CaZrO_3$ powder and disperse it in 30 mL of ethanol - water (volume ratio 1:1) solution, and perform ultrasonication for 4 hours until fully dispersed to obtain a "ultrasonically treated $CaZrO_3$" suspension. When processing the sample, heat the high - pressure reactor to 80°C and maintain a constant temperature. Then quickly transfer the ultrasonically treated $CaZrO_3$ suspension to the preheated high - pressure reactor, start magnetic stirring, charge carbon dioxide to the target pressure (14 MPa, 16 MPa, or 18 MPa), and maintain a constant temperature. React at 80°C and the set pressure for 4 hours, and keep the parameters stable through the temperature and pressure control system. After the reaction ends, wait for the system to cool naturally to room temperature, then slowly release the pressure and collect the reaction liquid. First, centrifuge at 3000 r/min for 10 minutes to remove large aggregates, take the supernatant, and then centrifuge at 10000 r/min for 15 minutes to collect the precipitate. Dry the precipitate in an 80°C oven until constant weight. The characterization methods are as follows:

TEM images are collected by a FEI Tecnai G2 - F20 transmission electron microscope (acceleration voltage 200 kV); XRD patterns are collected by a Bruker D8 Focus diffractometer (Cu Kα radiation source) from Bruker AXS, Germany; XPS testing is completed with the aid of a Thermo Fisher Scientific K - Alpha+ system; Raman spectra are collected by a LabRAM HR Evolution spectrometer (excitation light 830 nm); EPR spectra are determined using a German Bruker EMXplus - 6/1 electron paramagnetic resonance spectrometer; magnetic properties are tested with the aid of an American LakeShore 7404/8604 vibrating - sample magnetometer (VSM), and a hysteresis loop is obtained in the magnetic - field range of - 30 kOe to 30 kOe at room temperature; FT - IR testing is carried out by an instrument (infrared light source) equipped with a DTGS KBr detector and a KBr beam - splitter, with a testing range of 4000.00 - 400.00 $cm^{-1}$. Thermogravimetric analysis (TGA) was performed using a Netzsch STA 449 F3 instrument (Netzsch, Germany) under a nitrogen atmosphere over the temperature range of 30–1100 °C. Electrochemical impedance spectroscopy (EIS) measurements were conducted on an electrochemical workstation within the same voltage range. X-ray fluorescence (XRF) spectroscopy was carried out using a Rigaku ZSX Primus IV spectrometer (Rigaku, Japan) in oxide analysis mode.

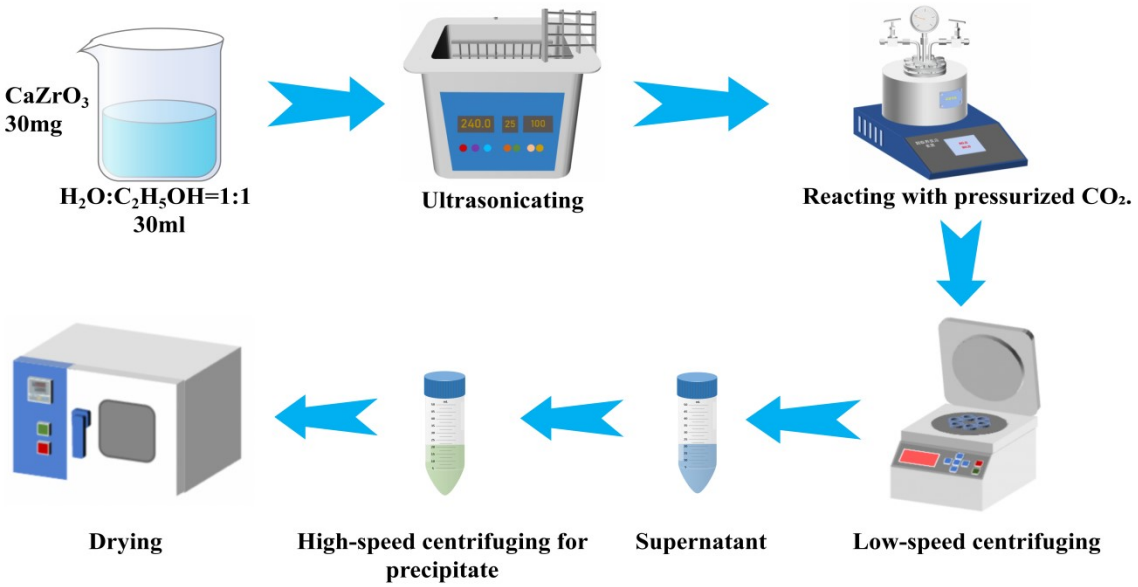


**Figure S1**. Experimental flow chart of $CaZrO_3$ treatment by SC $CO_2$

## Characterization

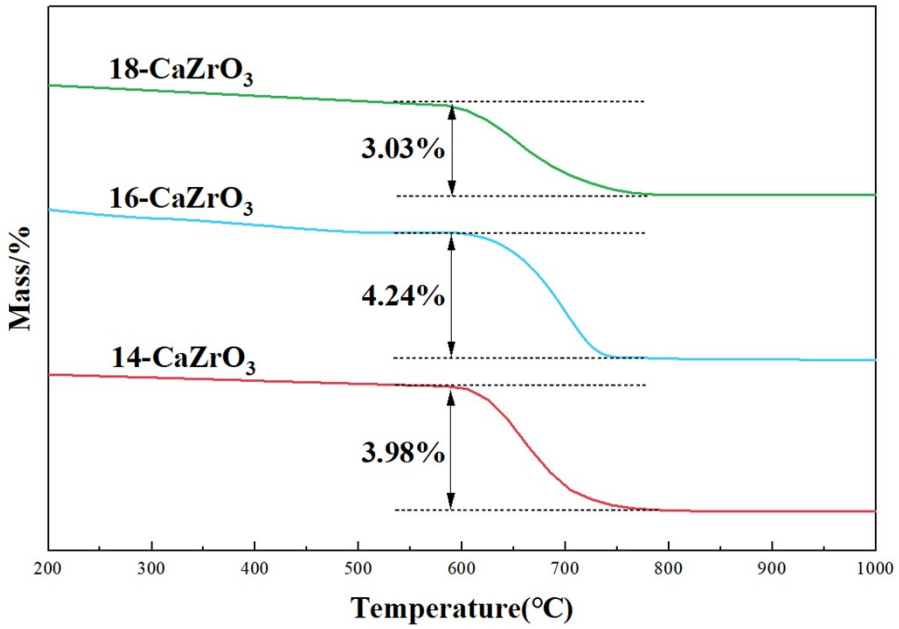


**Figure S2.** Thermogravimetric Analysis (TGA) curves of $CaZrO_3$ samples treated at SC $CO_2$

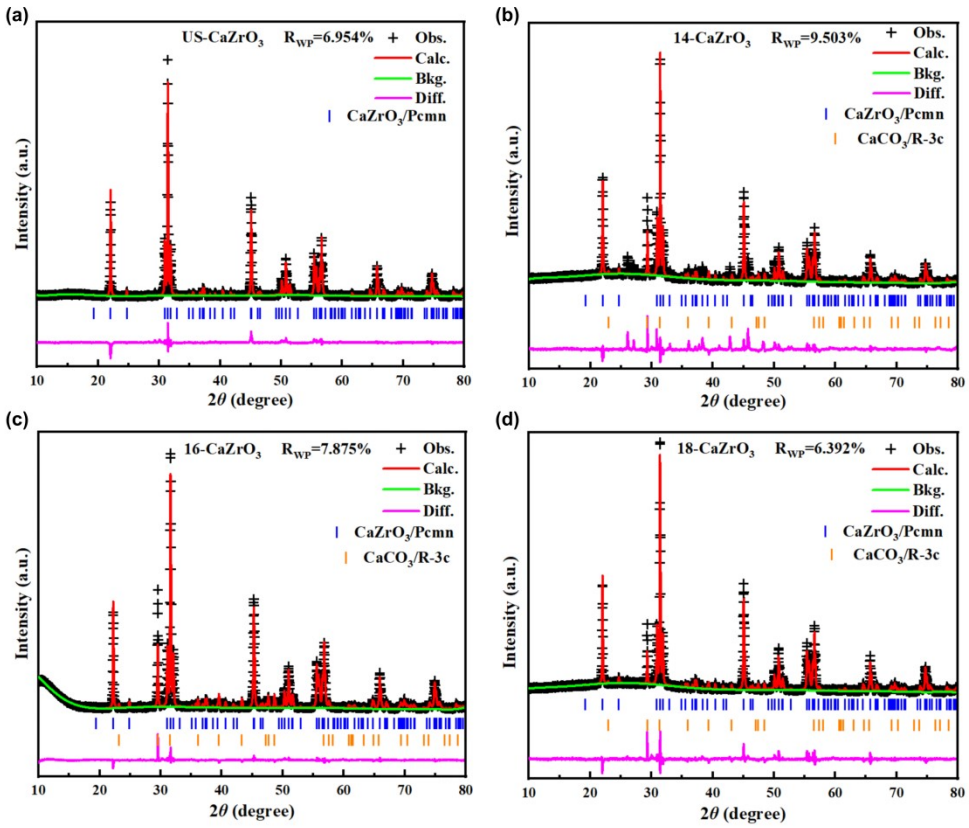


**Figure S3.** Rietveld refinement XRD patterns of $CaZrO_3$ under different pressure treatments.

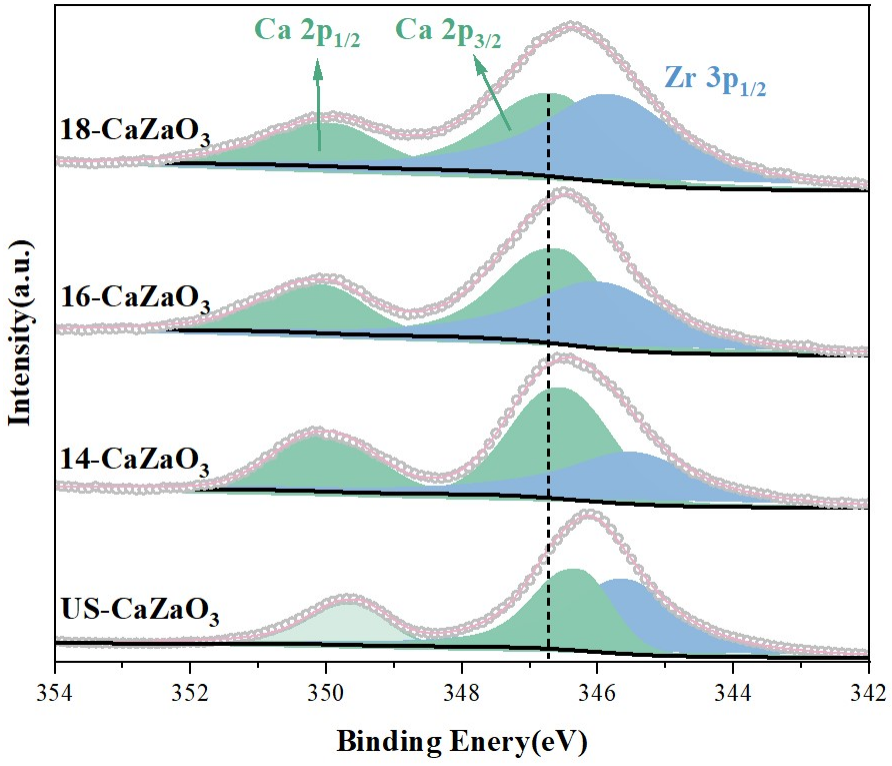

**Figure S4**. The Ca 2p XPS characterization of $CaZrO_3$ samples under different pressure treatments.

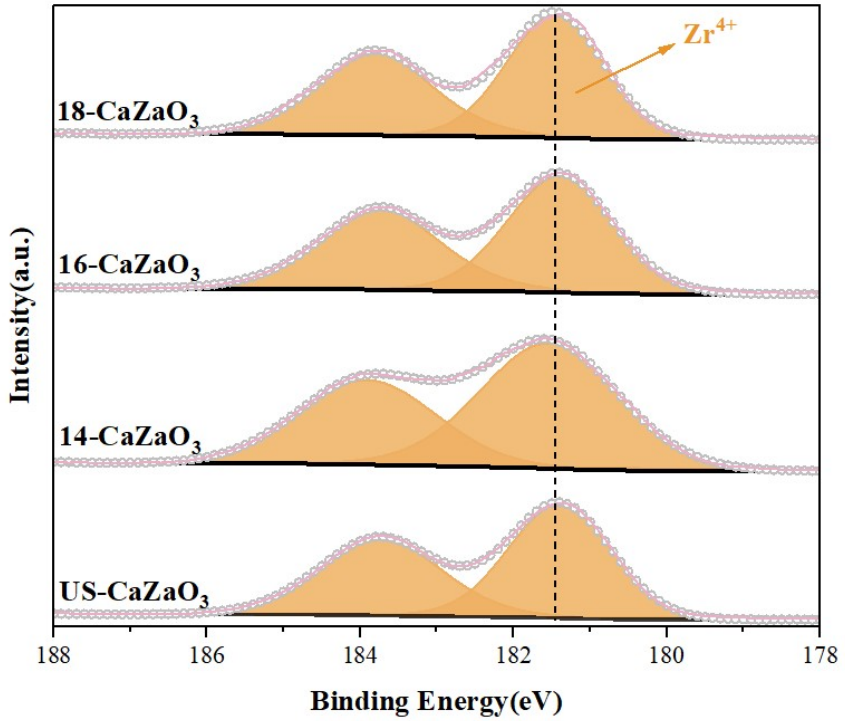


**Figure S5**. The Zr 3d XPS characterization of $CaZrO_3$ samples under different pressure treatments.

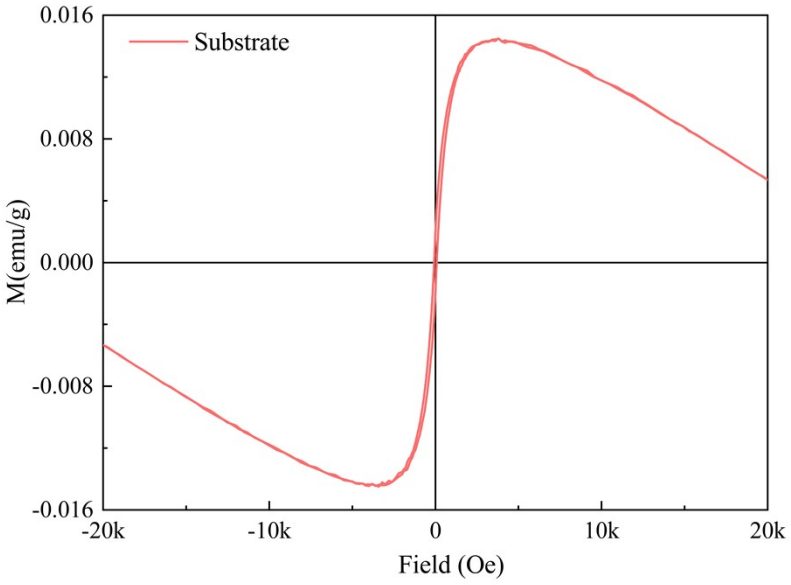

**Figure S6**. M-H curve of calcium $CaZrO_3$ substrate samples after low-speed centrifugation

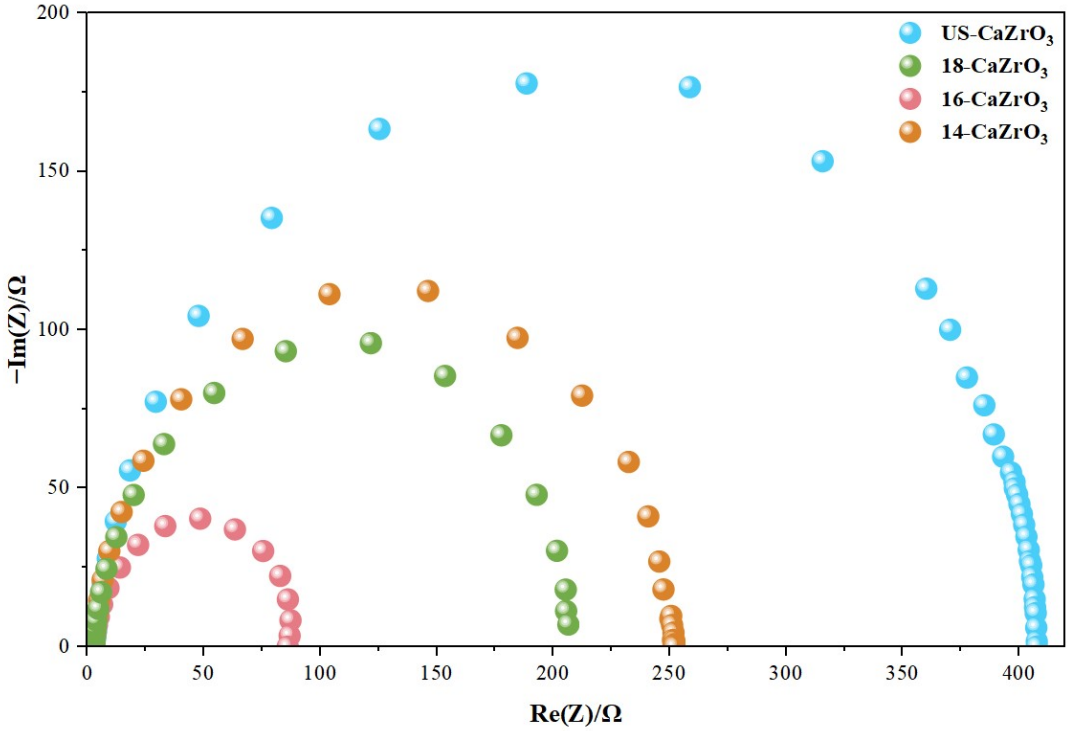


**Figure S7**. Electrochemical impedance spectroscopy Nyquist plots of $CaZrO_3$ under different pressure treatments.

## Additional data

**Table S1.** Crystal structure data of $CaZrO_3$ under different conditions.

| Sample | *a* (Å) | *b* (Å) | *c* (Å) | *V* (Å$^3$) | Bond Zr-$O_1$(Å) | Bond Zr-$O_2$(Å) | *V* $ZrO_6$(Å$^3$) | $R_{wp}$(%) |
|---|---|---|---|---|---|---|---|---|
| PDF | 5.591 | 8.017 | 5.761 | 258.260 | 2.097 | 2.091 | 12.278 | —— |
| US-$CaZrO_3$ | 5.591 | 8.016 | 5.760 | 258.170 | 2.099 | 2.094 | 12.290 | 6.954 |
| 14-$CaZrO_3$ | 5.582 | 8.001 | 5.752 | 257.041 | 2.097 | 2.090 | 12.244 | 9.503 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 16-$CaZrO_3$ | 5.564 | 7.979 | 5.734 | 254.635 | 2.090 | 2.083 | 12.112 | 7.875 |
| 18-$CaZrO_3$ | 5.566 | 7.982 | 5.736 | 254.879 | 2.090 | 2.085 | 12.144 | 6.392 |

**Table S2**. The proportion of components obtained by XPS.

| Sample | $O_v$(%) | -OH(%) | $O_v$+-OH(%) |
|---|---|---|---|
| Ultrasonic | 47.5 | 0 | 47.5 |
| 14MPa | 42.9 | 6.6 | 49.5 |
| 16MPa | 29.8 | 16.5 | 46.3 |
| 18MPa | 40.4 | 7.5 | 47.9 |

**Table S3**. Mass Fractions of Various Oxides in $CaZrO_3$ treated at SC $CO_2$

| Component | $Al_2O_3$ | $SiO_2$ | Cl | CaO | SrO | $ZrO_2$ | $HfO_2$ | $CO_2$ |
|---|---|---|---|---|---|---|---|---|
| Mass fraction(%) | 0.0102 | 0.0338 | 0.0368 | 30.1142 | 0.0407 | 65.0085 | 1.0234 | 3.7324 |