

Supporting Information:

Colloidal synthesis of marcasite FeS₂ nanoparticles with improved electrochemical performance

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I. Experimental Section

1. Materials and reagents

Ferric acetylacetonate ($\text{Fe}(\text{acac})_3$, 99.9%) was purchased from Aldrich. Dodecanethiol (DT, 98%), diphenyl ether (DE, 99%), and N-methyl-2-pyrrolidione (NMP, 99%) were obtained from Aladdin. The electrolyte, composed of 1.0 M LiPF_6 in 1:1 v/v ethylene carbonate (EC)/dimethyl carbonate (DMC), was purchased from Beijing Institute of Chemical Reagent. Sulfur powder (S), polyvinylidene fluoride (PVDF), acetone, chloroform, and acetylene black were all commercially available products and used as received without further purification.

2. Synthesis and purification

For the synthesis of marcasite FeS_2 nanoparticles (NPs), 176 mg $\text{Fe}(\text{acac})_3$ (0.5 mmol), 7 mL DE, and 3 mL DT were mixed in a four-necked flask at 100 °C and degassed under vacuum for 30 min to produce the Fe solution. In another three-necked flask, 96 mg sulfur powder was dissolved into 5 mL DE and degassed at 50 °C for 30 min to produce the S solution. After the Fe solution was heated to 220 °C under nitrogen atmosphere, the S solution was rapidly injected and maintained at 220 °C for 1 h. The reaction system was naturally cooled down to room temperature. Then the black solution was washed with chloroform/acetone (1:2 v/v) for two times. After centrifugation, the precipitates were collected and re-dispersed in 15 mL chloroform.

3. Characterization

UV-visible absorption spectra were measured using a Shimadzu 3600 UV-VIS-NIR spectrophotometer. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were recorded using a Hitachi H-800 electron microscope at an acceleration voltage of 200 kV with a CCD camera. High-resolution TEM (HRTEM) images were implemented by a JEM-2100F electron microscope at 200 kV. An energy-dispersive X-

ray spectroscopy (EDS) detector coupled with scanning electron microscope (XL 30 ESEM FEG Scanning Electron Microscope, FEI Company) was used for elemental analysis. Inductively coupled plasma (ICP) was performed with PerkinElmer OPTIMA 3300DV analyzer. X-ray diffraction (XRD) was carried out on a Rigaku X-ray diffractometer using Cu K radiation ($\lambda=1.5418 \text{ \AA}$). Thermogravimetric analysis (TGA) was measured on an American TA Q500 analyzer under N_2 atmosphere with the flow rate of 60 mL/min.

4. Electrochemical measurement

The marcasite powders used for electrochemical measurement were treated by annealing the freshly synthesized marcasite NPs in a tube furnace at 300 °C for 2 h under argon atmosphere. The acetylene black and PVDF were added into the marcasite powders with a weight ratio of 80/10/10 in NMP to fabricate the anode of a coin cell battery. After drying for 12 h at 120 °C, the obtained slurry was coated on copper foil. It was punched into a round plate with diameter of 13.0 mm for forming an anode electrode. In an argon-filled glove box (H_2O and $\text{O}_2 < 1 \text{ ppm}$), the marcasite NPs-based anode, a glass microfiber filters (16.0 mm in diameter), a lithium cathode, and an electrolyte solution of 1 M LiPF_6 in 1:1 v/v EC/DMC were assembled to an coin cell (CR2032). Galvanostatic cycling measurements were made using a Land battery test system from 0.01 to 3.0 V. The electrochemical impedance spectroscopy (EIS) measurement was carried out in two-electrode cells on Princeton Applied Research (PARSTAT 4000) with a $\pm 5 \text{ mV}$ AC signal amplitude and frequency ranged from 10 kHz to 10 mHz. Cyclic voltammetry (CV) was measured using an Autolab PGSTAT30 electrochemical workstation.

II. Supporting Figures

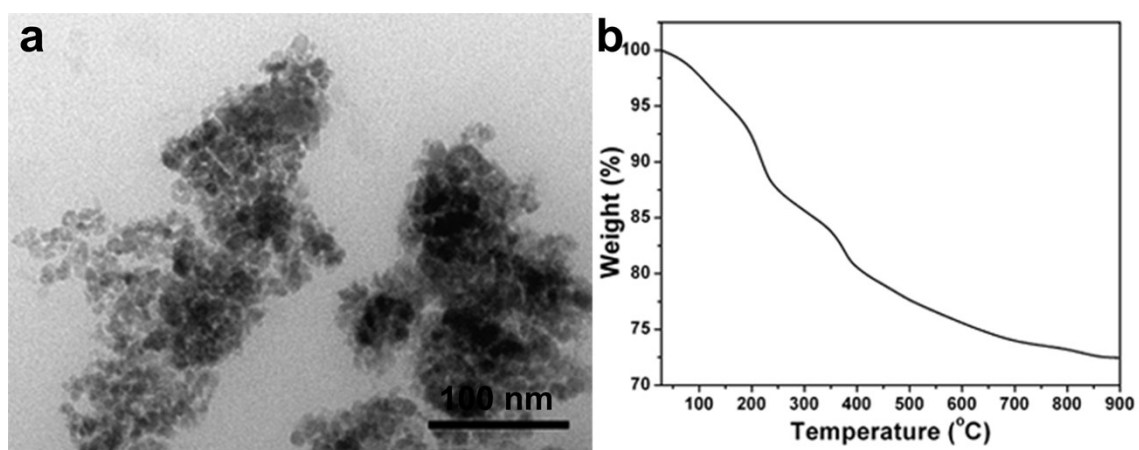


Figure S1. (a) TEM image of the marcassite FeS₂ NPs after annealing at 300 °C for 2 h. (b) TGA profile of the marcassite FeS₂ NPs heated in N₂ atmosphere from room temperature to 900 °C.

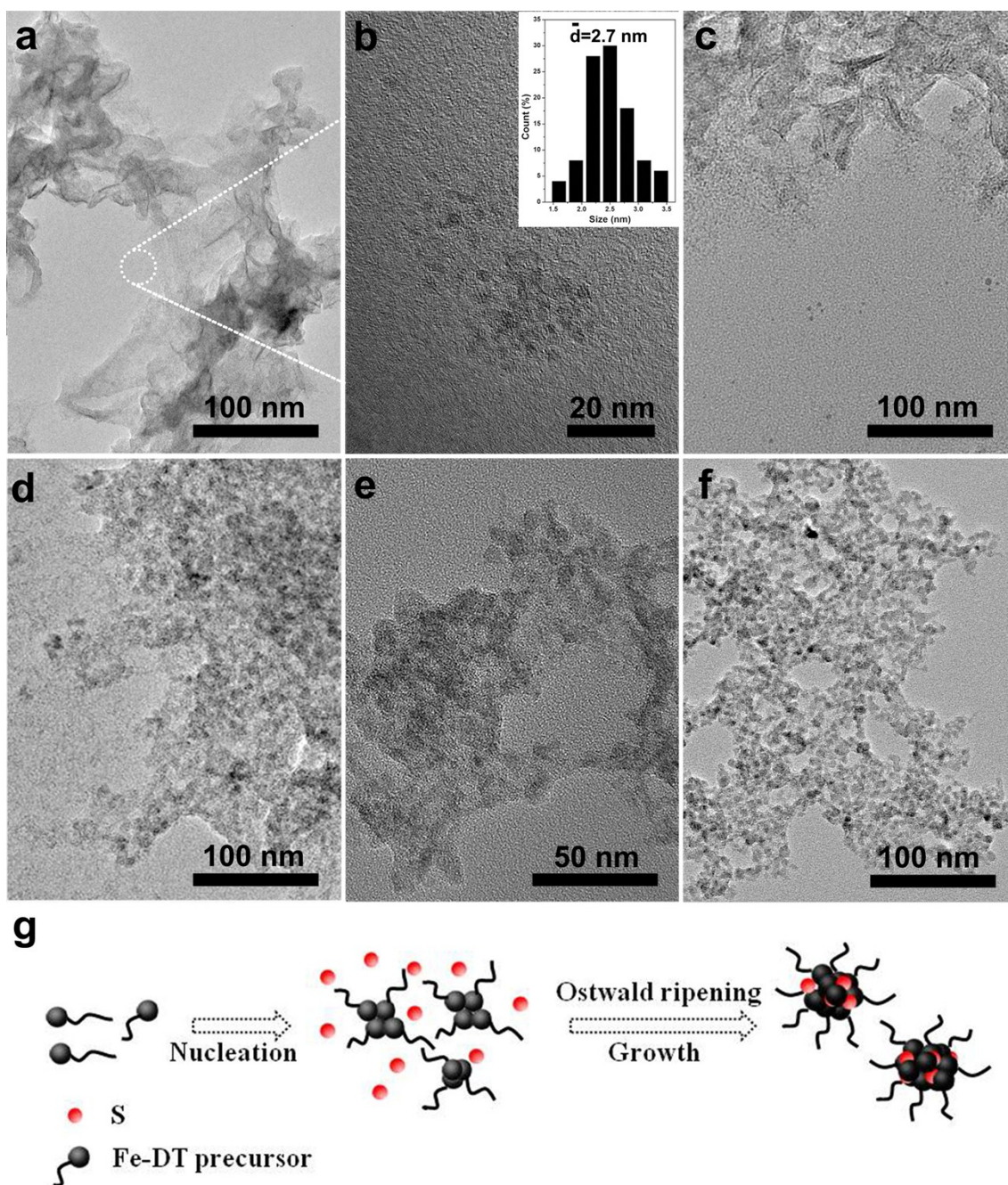


Figure S2. TEM temporal evolution of the marcasite FeS₂ NPs before injection at 217 °C (a, b), after injection at 217 °C for 0 min (c), 5 min (d), 10 min (e), and 60 min (f). (g) The schematic morphology evolution of marcasite FeS₂ NPs *via* OR process. Inset in (b): size distribution of the nucleus at nucleation stage.

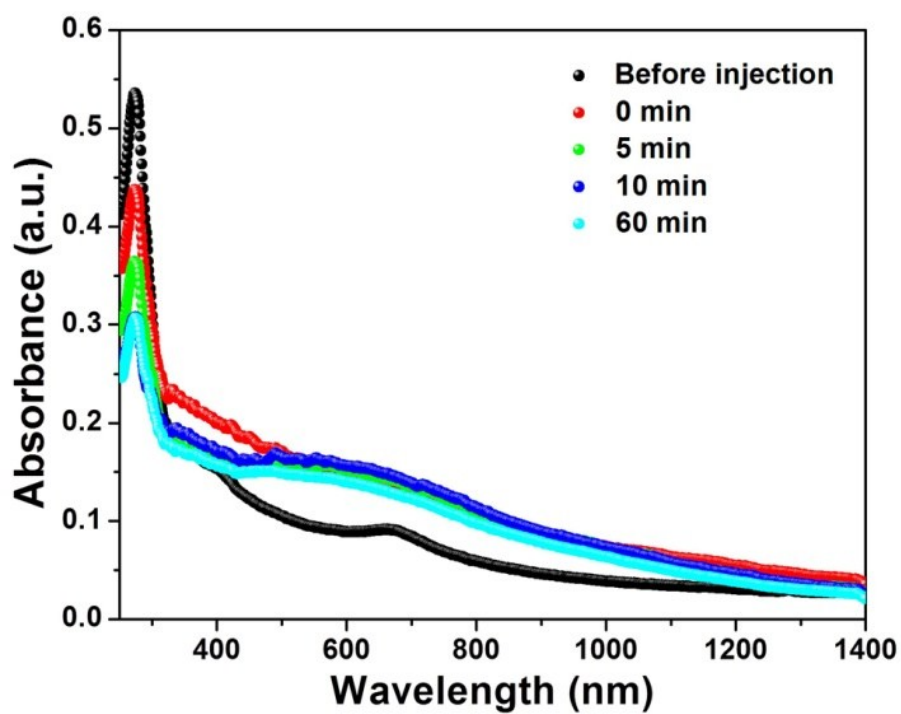


Figure S3. UV-vis absorption spectra of the marcasite FeS₂ NPs monitored at different time intervals during the nucleation and growth stage.

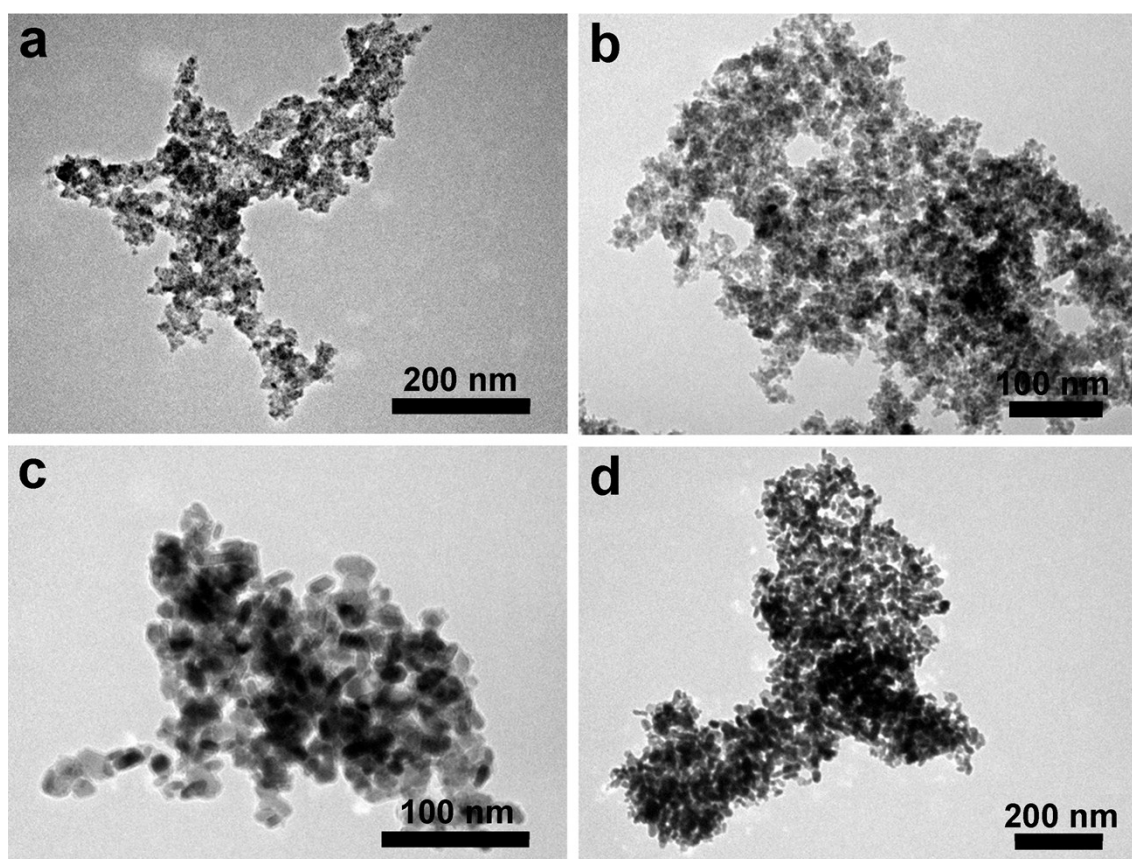


Figure S4. TEM images of the marcasite FeS₂ NPs synthesized at 180 °C (a), 200 °C (b), 240 °C (c), and 260 °C (d). The size of the NPs is 3.5, 5.0, 10.0, and 18.0 nm, respectively.

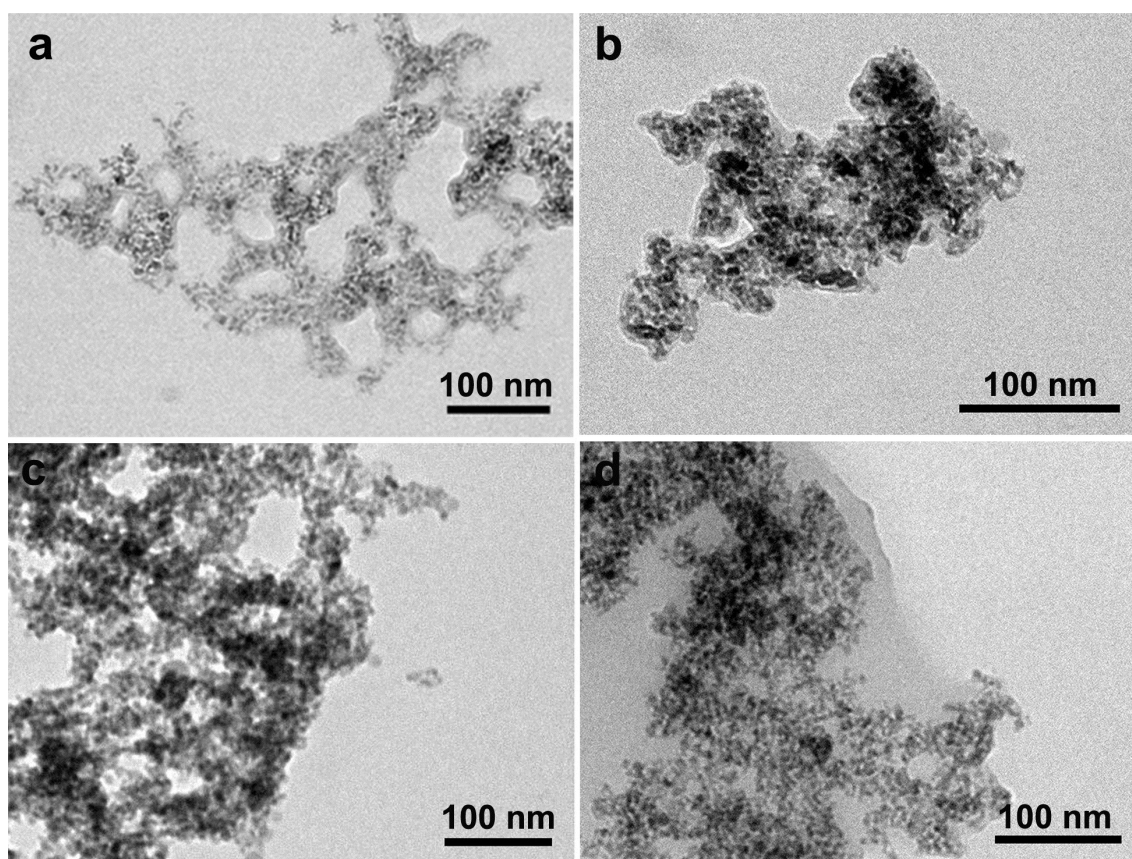


Figure S5. TEM images of the marcasite FeS₂ NPs synthesized with DT amount of 0.5 mL (a), 1.0 mL (b), 2.0 mL (c), and 5.0 mL (d). The size of the NPs is 3.4, 4.8, 6.0, and 8.1 nm, respectively.