Supplementary Information

Low temperature synthesis of crystalline pyrite FeS_2 for high energy density supercapacitors

Experimental Section

Materials

Ferric chloride ($FeCl_3 \cdot 6H_2O$), carboxymethyl cellulose (CMC) sodium salt and glass-fibre separators were purchased from Sigma-Aldrich. Ethanol (purity 99.9%) was purchased from CSCPL, India. Super P conducting carbon and Ni foam were obtained from local vendors. All the solutions were prepared using deionized (DI) water. The chemicals procured were used as such and no further purification was performed.

Preparation of FeOOH

$FeCl_3 \cdot 6H_2O$ (1.6 g) was dissolved in 150 mL of DI water. The solution was maintained under constant stirring for 15 h at 80 °C. The suspension obtained was centrifuged, washed three times with DI water and dried at 60 °C for 6 h.

Preparation of pyrite-FeS_2

The FeOOH precursor is taken in a boat and placed in a tube furnace. Sulfidation occurs under the influence of N_2/H_2S gas in a solid-gas interphase reaction to yield FeS_2. Parameters such as sulfidation temperature, gas composition and time were tuned to obtain pure-phase pyrite-FeS_2.

Characterization

X-ray diffraction (XRD) was carried out using a Rigaku SmartLab diffractometer from 10–80°. Raman spectra were recorded using a green laser (532 nm) on a Horiba XploRA PLUS V1.2 Multiline confocal Raman microscope. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) micrographs were obtained using a TALOS F200S G2. The

grid for TEM analysis was prepared by dispersing the sample in ethanol and drop-casting onto a grid. Contact angle measurements were carried out with a KYOWA DM501 contact angle meter.

Electrochemical characterization

The cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) measurements were performed using a Metrohm Autolab PGSTAT302N electrochemical workstation. For three-electrode studies, 6 M KOH was used as the electrolyte. Hg/HgO was employed as the reference while Pt coil acted as the counter electrode. The active materials are dispersed in IPA with 10 wt% Super P carbon and 10 wt% Nafion binder and subsequently coated onto carbon cloth. The mass loading was maintained at 10 mg cm^{-2}. The electrodes for the Swagelok cell were prepared by dispersing the active material (80 wt%) in IPA with 10 wt% Super P carbon and 10 wt% Nafion binder and subsequently coated onto Ni foam. The mass loading was maintained at 8.85 mg cm^{-2}.

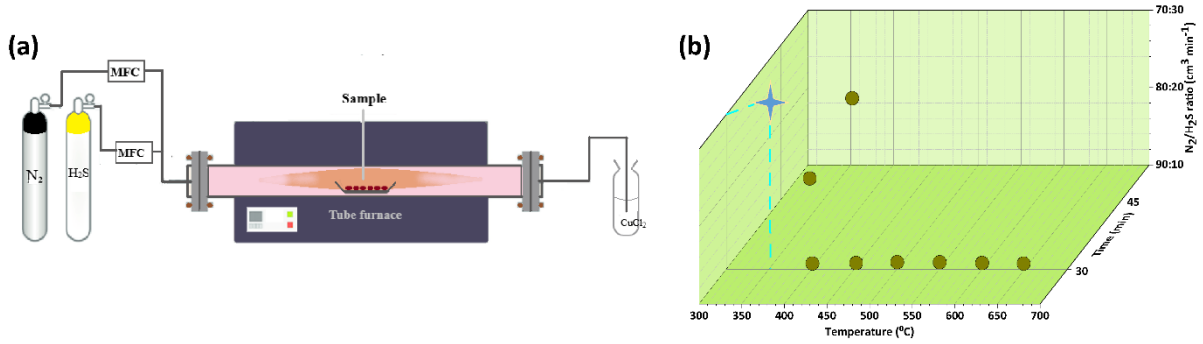

Figure S1(a) Schematic of sulfidation of β-FeOOH, (b) optimization of sulfidation parameters

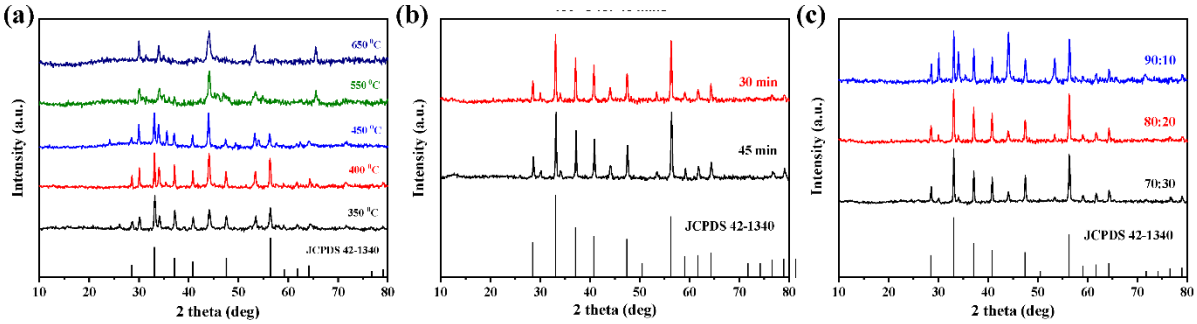

Figure S2. XRD patterns of sulfidation products of β-FeOOH (a) at different temperatures, (b) at 400 ^{0}C with different gas compositions, and (c) at 400 ^{0}C for different sulfidation times.

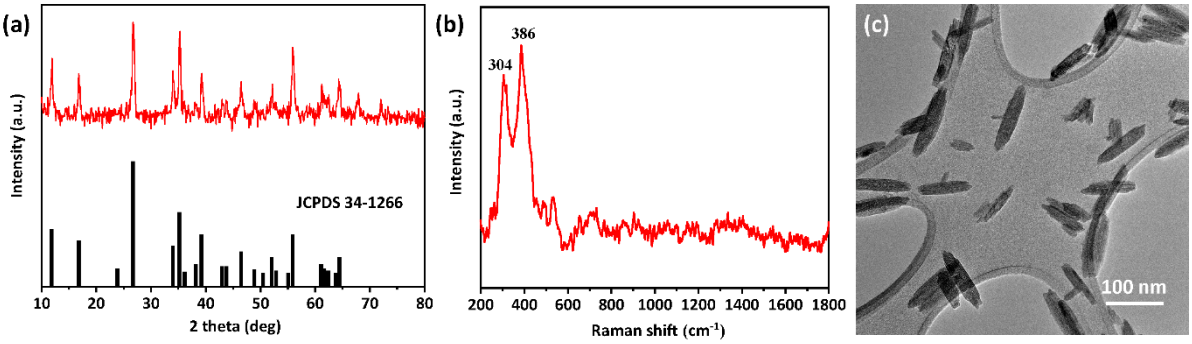

Figure S3. (a) XRD pattern, (b) Raman spectra and (c) TEM image of β-FeOOH.

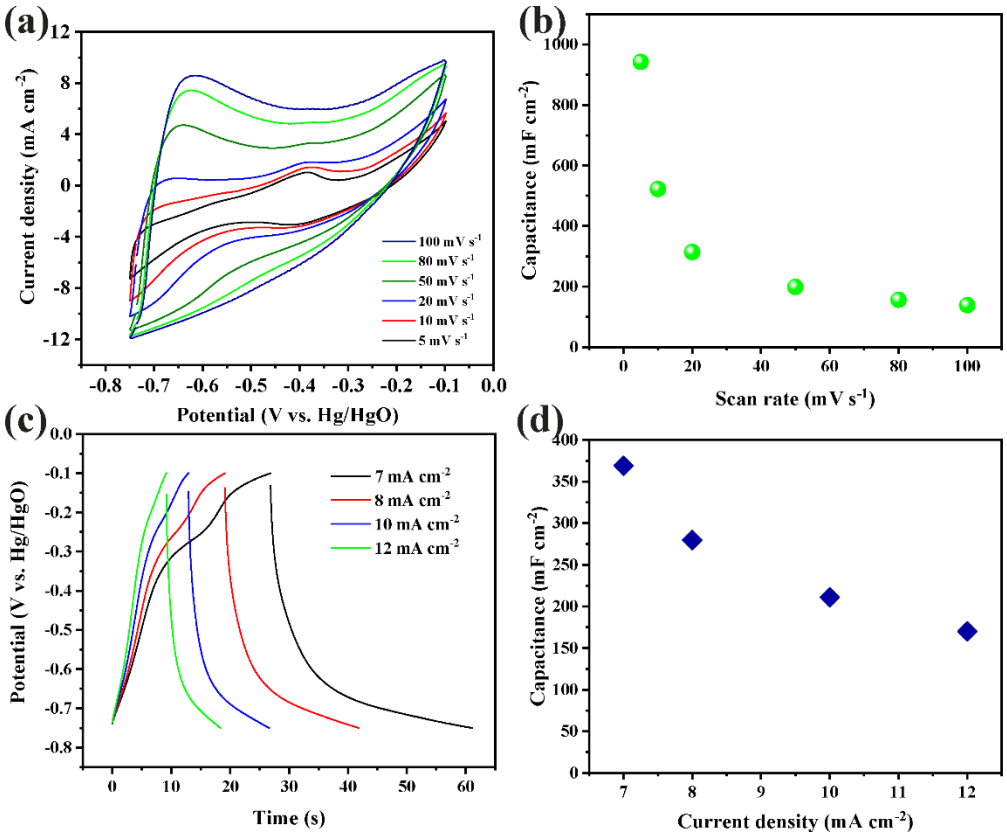

Figure S4. (a) CV at different scan rates for FeS_2 electrode in 6 M KOH, (b) variation of specific capacitance with scan rate, (c) GCD of FeS_2 electrode in 6 M KOH, (d) variation of specific capacitance with current density.

Table S1. Comparison of SC performance of FeS_2 SCs with literature

Electrode material	**Specific capacitance**	**Voltage window (V)**	**Electrolyte**	**Ref**
CoS_2/ MoS_2 NSs	4.32 F cm^{-3} at 1 mA cm^{-2}	1.8	$NaMoO_4$/ Na_2SO_4 PVA gel	1
MoS_2@ CNT/RGO	20.4 mF cm^{-2} at 10 mA cm^{-2} 27 mF cm^{-2} at 50 mV s^{-1}	1	H_2SO_4/PVA	2
MoS_2/rGO with NiO NPs	7.38 mF cm^{-2} at 25 mV s^{-1}	1	1 M KCl	3
MnO_2/ Graphene NSs	56 mF cm^{-2} at 0.5 mA cm^{-2}	1	PVA/Na_2SO_4	4
$Ti_3C_2T_x$// $NiCo_2S_4$ ASC	48.6 mF cm^{-2} at 2 mA cm^{-2}	1.4	0.5 M K_2SO_4	5
Ti_3C_2/ Polypyrrole	40 mF cm^{-2} at 3.5 mA cm^{-2}	0.5	PVA/H_2SO_4	6
$Ti_3C_2T_x$// LDH	28.5 mF cm^{-2} at 0.75 mA cm^{-2}	1	PVA/KOH	7
Ionic liquid intercalated MXene	24 mF cm^{-2} at 1 mA cm^{-2}	3	$EMIMBF_4$/ PVDF-HFP	8
$Ti_3C_2T_x$//MnO_2 ASC	24.7 mF cm^{-2} at 5 mV s^{-1}	2.5	$EMIMBF_4$/ PVA	9

FeS_2 NSs	**30 mF cm^{-2} at 0.4 mA cm^{-2}** **35 mF cm^{-2} at 0.6 mA cm^{-2}**	**2.5** **2.5**	**1 M $TEABF_4$ in PC** **$EMIMBF_4$ in DMC**	**Our work**

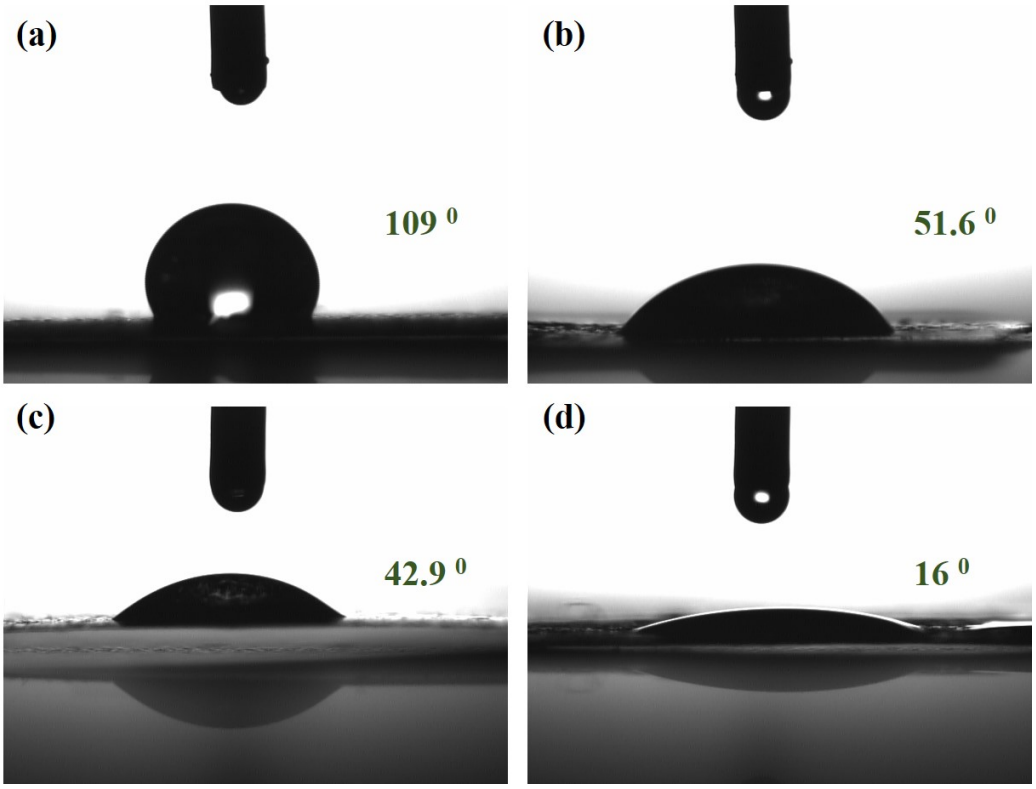

Figure S5. Contact angle measurements of (a, c) bare Ni foam and (b, d) FeS_2 coated Ni foam in the presence of $TEABF_4$ and EMIM-BF_4 electrolytes respectively.

References:

1. Y. Xie and Y. Wang, *Electrochim. Acta*, 2020, **364**, 137224.
2. S. Wang, J. Zhu, Y. Shao, W. Li, Y. Wu, L. Zhang and X. Hao, *Chem. Eur. J.*, 2017, **23**, 3438–3446.
3. F. Ghasemi, M. Jalali, A. Abdollahi, S. Mohammadi, Z. Sanaee and S. Mohajerzadeh, *RSC Adv.*, 2017, **7**, 52772–52781.
4. Y. Zhou, X. Cheng, F. Huang, Z. Sha, Z. Han, J. Chen, W. Yang, Y. Yu, J. Zhang, S. Peng, S. Wu, A. Rider, L. Dai and C. H. Wang, *Carbon N. Y.*, 2021, **172**, 272–282.
5. M. Pathak, S. R. Polaki and C. S. Rout, *RSC Adv.*, 2022, **12**, 10788–10799.
6. C. Zhang, S. Xu, D. Cai, J. Cao, L. Wang and W. Han, *Electrochim. Acta*, , DOI:10.1016/j.electacta.2019.135277.

7. S. Xu, Y. Dall'Agnese, G. Wei, C. Zhang, Y. Gogotsi and W. Han, *Nano Energy*, 2018, **50**, 479–488.
8. S. Zheng, C. Zhang, F. Zhou, Y. Dong, X. Shi, V. Nicolosi, Z. S. Wu and X. Bao, *J. Mater. Chem. A*, 2019, **7**, 9478–9485.
9. G. Cooksley, M. K. Dymond, X. Feng, J. Ning, M. Xia, H. Guo and Y. Zhou, *Nanotechnology*, 2021, **32**, 035402.