

Hierarchical-like multipod MnS microcrystals: solvothermal synthesis, characterization and growth mechanism

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1. Experimental Section

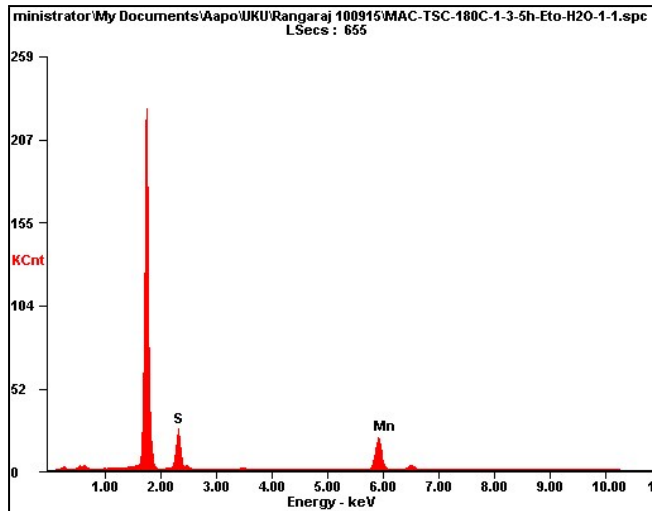
1.1 Preparation of hierarchical multipod MnS microcrystals.

The MnS multipods were synthesized using analytical grade manganese acetate [$C_4H_6MnO_4 \cdot 4H_2O$] and thiosemicarbazide [CSN_3H_5], without further purification. In a typical synthesis, 4.080 mmol of $C_4H_6MnO_4 \cdot 4H_2O$ and 12.24 mmol of CSN_3H_5 were dissolved in 70 mL of ethanol/water (1:1, v/v) and continuously stirred for 30 min to form a clear solution. The solution was then transferred to an autoclave, maintained at 180 °C for 0-10 h, and then cooled to room temperature naturally. The precipitate was harvested by centrifugation, washed several times with deionized water and ethanol, then dried in an oven at 70 °C for 24 h.

1.2 Characterization of MnS microcrystals.

The structural analysis of the samples was performed using a Bruker (D5005) X-ray diffractometer equipped with graphite monochromatized Cu $K\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). An accelerating voltage of 40 kV and emission current of 30 mA were adopted for the measurements. The morphology and microstructure were characterized by field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800). For the high-resolution transmission electron microscopy (HR-TEM) study, the samples were dispersed onto a Cu grid with holey carbon supporting films and studied at room temperature in a JEOL JEM-3010 microscope operated at 200 kV. The ratio between Mn and S within the sample was analyzed using an energy-dispersive X-ray spectrophotometer installed in the scanning electron microscope. X-ray photoelectron spectroscopy (XPS) was conducted with a Sigma Probe

(ThermoVG, U.K.) X-ray photoelectron spectrometer, of which the source is Al $K\alpha$ radiation (1.486 eV). The charging effect was evaluated using the main component of the C 1s peak, associated with adventitious hydrocarbons with a binding energy of 284.6 eV as reference for calibration. The photoemitted electrons from the sample were analysed in a hemispherical energy analyzer at a pass energy of $E_p = 20$ eV. All spectra were obtained with an energy step of 0.1 eV and a dwell time of 50 ms. A software package (Avantage Thermo VG) has been used to analyze the XPS data. The absorption spectrum of the samples in the diffused reflectance spectrum mode was recorded in the wavelength range between 200 and 1000 nm using a spectrophotometer (V-670, JASCO), with $BaSO_4$ as a reference. From the absorption edge, the band gap values were calculated by the extrapolation method.



<i>Element</i>	<i>Wt%</i>	<i>At%</i>
<i>SK</i>	41.64	54.96
<i>MnK</i>	58.39	45.01
<i>Matrix</i>	Correction	ZAF

Fig. S1. EDS survey spectrum of the γ -MnS tripods.

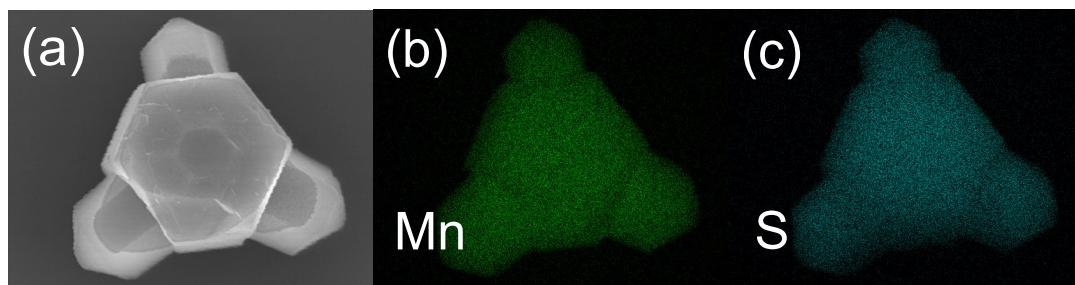


Fig. S2. (a) SEM image of the γ -MnS tripod; (b and c) the corresponding EDX elemental mapping images of Mn and S.

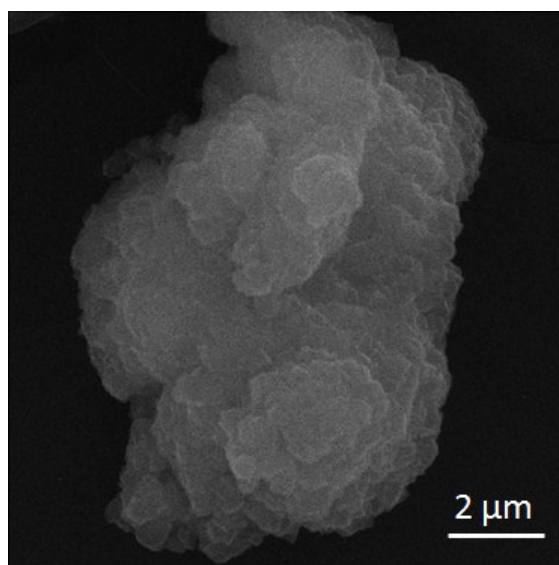


Fig. S3. Control experiments for the synthesis of MnS multipods by adding equimolar sulfur powder instead of thiosemicarbazide.

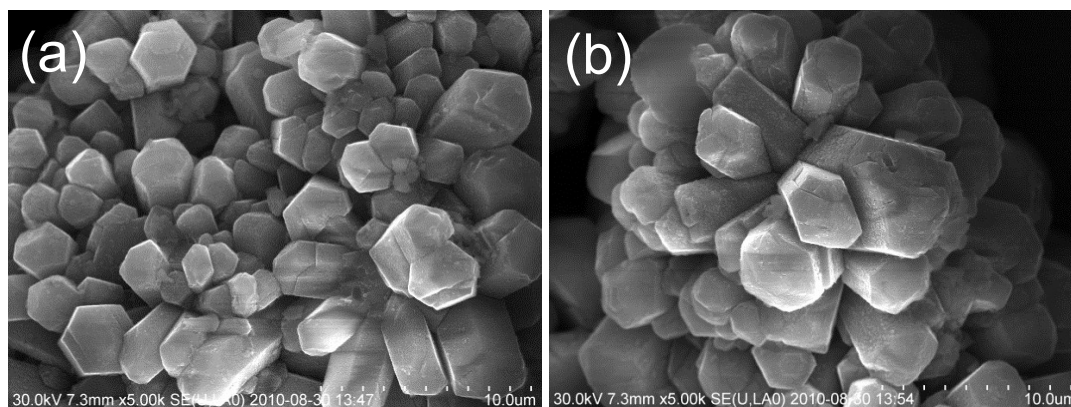


Fig. S4. (a) Low- and (b) high-magnification SEM images of the samples synthesized for 10 h.