Electronic Supplementary Information

Large-scaled star-shaped α-MnS nanocrystals with novel magnetic properties

Qiwei Tian[a], Minghua Tang[a], Feiran Jiang[a], Yiwei Liu[b], Jianghong Wu[a], Rujia Zou[a], Yangang Sun[a], Zhigang Chen[a], Runwei Li[b], and Junqing Hu[*,a]

[a] *State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, China. E-mail: hu.junqing@dhu.edu.cn (Junqing Hu), Tel/Fax: 86-21-6779-2947.*

[b] *Key Laboratory of Magnetic Materials and Devices, Ningbo Institute of Material Technology and Engineering (NIMTE), Chinese Academy of Sciences (CAS), Ningbo, Zhejiang 315201, China.*

Synthesis of manganese-oleate complex

(All of the chemical are bought from Sinopharm Chemical Reagent Co. China, analytical pure and used as received without further purification). Manganese-oleate complex was prepared by reacting manganese chloride and sodium oleate[1]. A solution of tetrahydrate manganese chloride (10 mmol) in 5 ml distilled water was added into another solution containing sodium oleate (20 mmol), ethanol (30 mL), distilled water (10 mL) and hexane (35 mL), under magnetic stirring, forming a red-brown solution. Then, the red-brown solution was heated to 70 °C and kept at this temperature for 4 hrs. When the reaction was finished, an upper organic layer containing the Mn-oleate complex was collected and washed with distilled water and dried over $MgSO_4$ for 12 hrs night. When the $MgSO_4$ was removed by a filtration, the resulting solution was evaporated under a low pressure to afford the product as a light-pink foamy solid.

Synthesis of α-MnS Nanocrystals

α-MnS NCs were prepared as follows: 1 mmol manganese-oleate complex and 2 mol sulfur were dissolved at room temperature in 20 mL of a solvent, which was

consisted of pure 1-octadecene or the mixture of oleylamine, oleic acid and 1-octadecene with different volume ratios, in a flask. The solution was slowly heated to 120 °C under vacuum with magnetic stirring for 30 min to remove residual water and oxygen during which time the flask was purged periodically with dry nitrogen gas. The resulting transparent solution was then heated to 250-320 °C at a rate of 10 °C/min under dry nitrogen gas and kept at this temperature for 2-30 min, and then the mixture was allowed to cool to room temperature, naturally. The products were precipitated by an addition of ethanol and isolated via centrifugation at 10000 rpm, and were then washed twice with ethanol, and further purified by dispersing in 1 mL of chloroform and precipitated again with excess ethanol. The final products were dried under vacuum for 24 hr. (Note: The resulting nanocrystals' samples can be dispersed in non-polar solvents, e.g., hexane, toluene, dichloromethane.).

Characterization:

Size and morphology of α-MnS were determined using a JEOL JEM-2010F high-resolution transmission electron microscope (HR-TEM) at 200 kV. A TEM sample was prepared by conventional dispersing followed by carbon film fishing, i.e., a small amount of the sample (~ 1 mg) was dispersed in 1 g of hexane to give an approximate 0.1 wt% solution, and then one drop of the resulting solution was evaporated on a carbon film supported on a copper grid. X-ray diffraction measurements were performed on a D/max-2550 PC X-ray diffractometer using Cu Kα radiation. For the measurement of magnetic properties of α-MnS nanocrystals, a weighted amount of MnS nanocrystals was placed in a gel capsule (sample). The sample was first cooled to 2 K in a zero field and the ZFC magnetization was measured by applying a 500 Oe field and heating the sample to 300 K, and then the sample was cooled to 2 K in a 500 Oe field and the FC magnetization was measured as before. Hysteresis loops were measured at 2 K after field cooling at 50 KOe. Magnetic measurements were carried out by a Quantum Design

MPMS-5 SQUID magnetometer.

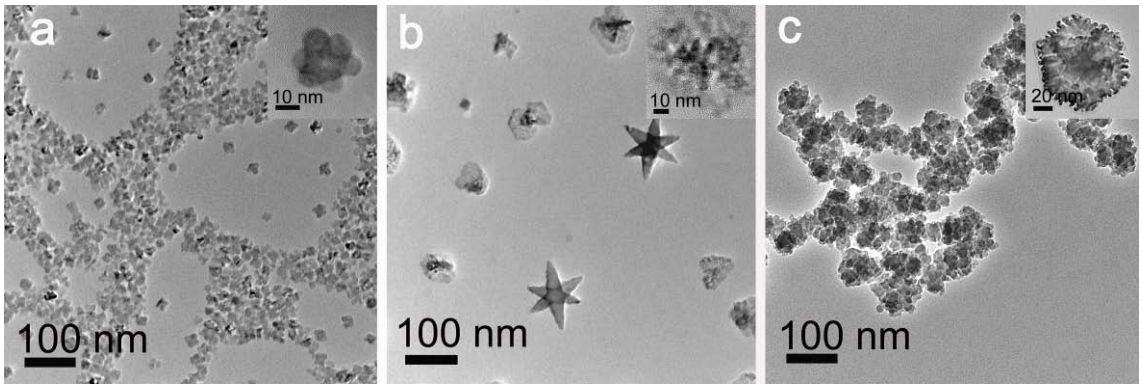

Fig. S1 TEM images show α-MnS products obtained at 250 °C for 2 min using different reaction solutions: (a) 1 mL OM and 19 mL ODE; (b) 5 mL OM, 5 mL OA and 10 mL ODE; (c) 10 mL OM and 10 mL OA.

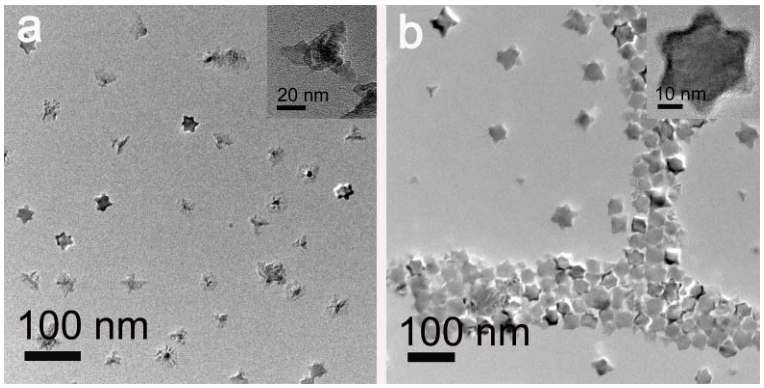

Fig. S2 TEM images show the morphology evolution at different treatment temperatures for 2 min: (a) 260 °C and (b) 280 °C. Inserts show their corresponding high magnification TEM images in a and b.

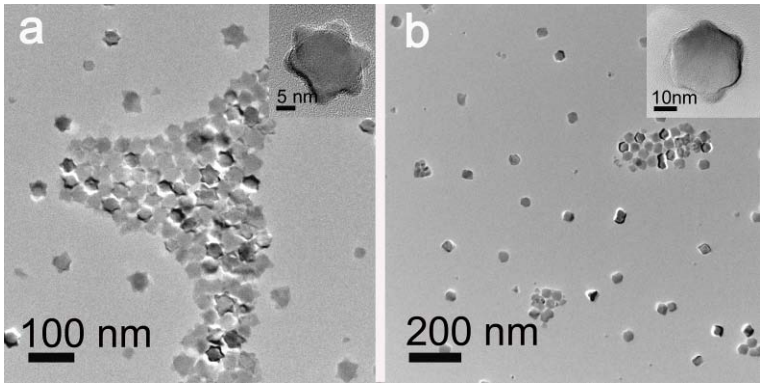

Fig. S3 TEM images show the morphology evolution at different treatment periods at 280 °C: (a) 2 min and (b) 15 min. Inserts show their corresponding high magnification TEM images in a and b.

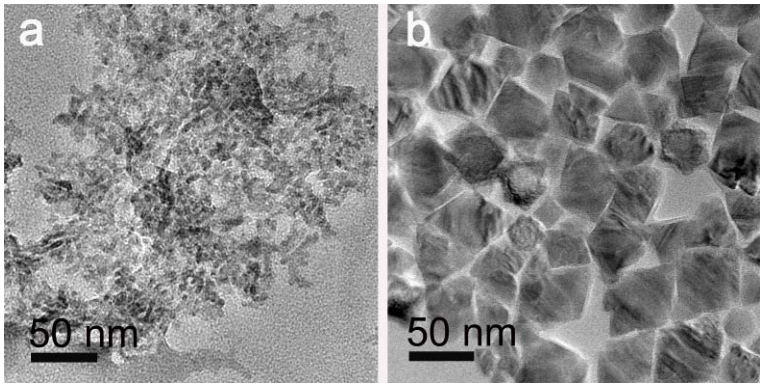

Fig. S4 TEM images show α-MnS obtained in a mixture of OM, OA and ODE with different a volume ratio: (a) OM:OA:ODE = 2:1:17, (b) OM:OA:ODE = 1:2:17.

Notes and references

1. J. Park, K. An, Y. Hwang, J.G. Park, H.J. Noh, J.Y. Kim, J.H. Park, N.M. Hwang and T. Hyeon, *Nat. Mater.*, 2004, **3**, 891.