Solution-solid-solid growth of metastable wurtzite $\gamma$-MnS nanowires with controlled length

Y. L. Zhang$^{a,b}$, R. Xu$^a$, W. M. Chen$^a$, O. Zhuo$^b$, Q. Wu$^b$, J. Cai*$^a$, X. Z. Wang*$^b$ and Z. Hu*$^b$

Experiments

Synthesis of $\left[\left(C_4H_9\right)_2NCS\right]Ag$, $\left[\left(C_4H_9\right)_2NCS\right]_2Mn$ precursors and $Ag_2S$ nanoparticles. The metal dibutylthiocarbamate complexes precursors were synthesized via the method reported in our previous work$^1$. The $Ag_2S$ nanoparticles was synthesized similar to our previous work$^1$ except few modification of reaction time for 7 min at atmosphere ambience.

Synthesis of MnS nanowires. In a typical synthesis, $Ag_2S$ nanoparticles suspension in cyclohexane was added into the mixed solution of 1-dodecylamine and 1-dodecanethiol with the volume ratio of 1:1 in a round bottom flask, and $\left[\left(C_4H_9\right)_2NCS\right]_2Mn$ precursor 1-dodecanethiol suspension was dropped into it at 40 °C. Then, the mixture solution was quickly heated to 140 °C and kept for 8 min. After that, the products were washed by methanol for several times and re-dispersed in cyclohexane for further characterization. To regulate the length of nanowires, different volumes of $\left[\left(C_4H_9\right)_2NCS\right]_2Mn$ precursor suspension in 1-dodecanethiol (2, 4, 6 to 8 mL) were used while keeping the same amount of $Ag_2S$ nanoparticles and other reaction conditions unchanged.

Fig. S1. (a) TEM image of typical $Ag_2S$ nanoparticles. (b) The corresponding diameter distribution of the $Ag_2S$ particles in (a). The fitted Gaussian plot (dark line) shows the average diameter is $13.4 \pm 1.8$ nm.

Fig. S2. The diameter distribution of the $\gamma$-MnS nanowires corresponding to Fig. 1a. The fitted Gaussian plot (dark line) shows the peak center of $9.7 \pm 1.7$ nm.
Fig. S3. XRD pattern of Ag$_2$S-(γ-)MnS heteronanostructures synthesized using high amount ratio of Ag$_2$S nanoparticles to [(C$_4$H$_9$)$_2$NCS]$_2$Mn precursors.

Fig. S4. EDS spectrum of the typical product. To prepare the sample for EDS analysis, the product was first dispersed in ethanol, then dropped on Si wafer and dried before Au sputter coating. EDS analysis confirmed the presence of Ag, Mn and S elements in the product in agreement with the XRD results. Besides, the C and O signals could come from the residual ethanol during the sample preparation or organic capping ligand on surface of the product.

Fig. S5. (a) TEM and (b) HRTEM images corresponding to Fig. 2c at low magnification.
The survey spectrum (Fig. S6a) of the Ag$_2$S-(\')MnS heteronanostructures reveals the existence of Mn, Ag, S, N, C and O elements. The peak at 641.1 eV (Fig. S6b) are assigned to the binding energy of Mn 2p$_{3/2}$ matching well the reported value of $\gamma$-MnS$^{[ref.2]}$. The peak at 367.9 eV (Fig. S6c) are assigned to the binding energy of Ag 3d$_{5/2}$ matching well with the reported value of Ag$_2$S quantum dots$^3$. The XPS spectrum of S region (Fig. S6d) provides rich information of the product. The peak around 161.0 eV (indicated by ‘\*’) can be assigned to the overlap of S 2p$_{3/2}$ from Ag$_2$S (reported value of 160.6 eV$^{[ref.3]}$) and $\gamma$-MnS (reported value of 161.2 eV$^{[ref.2]}$), similar to the case reported in Ag$_2$S-CdS heteronanostructures$^4$. The peak around 163.3 eV (indicated by ‘\*’) could be assigned to the dialkyl sulfides (reported value of 163.3 eV$^{[ref.5]}$), and such S species could be formed by irradiation during XPS experiment$^5$ or formed during reaction, which is still under investigation, anyhow, this character indicates the organic sulfide agents could cap on the surface of the heteronanostructures. The broad peak centered at 168.0 eV could come from the oxidation state of S (S=O) on the surface of the heteronanostructures$^4$. 

Fig. S6. XPS spectra of typical Ag$_2$S-(\')MnS heteronanostructures. (a) Survey spectrum; (b) Mn region. (c) Ag region. (d) S region. The binding energy were calibrated with the standard C 1s peak of 284.8 eV.
**Fig. S7(a-d).** TEM images corresponding to the 1(a), 2(b), 3(c), 4(d) samples at low magnification in Fig. 3.

**Fig. S8.** TG (red)-DTA (dark) curves of [(C₄H₉)₂NCS₂]₂Mn in Ar/8%O₂ gas flow with the heating rate of 10 °C/min.
Fig. S9. (a) TEM image of the product sample obtained in pure 1-dodecanethiol solvent. (b) TEM image of the product sample obtained in pure 1-dodecylamine solvent.

Fig. S10. Raman spectrums of the typical product (red) and the Ag₃S nanoparticles (dark).

References