**Ag$_2$S-catalyzed Growth of Quaternary AgInZn$_7$S$_9$ Semiconductor Nanowires in Solution**

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**Figure S1.** EDS spectrum of AgInZn$_7$S$_9$ nanowire (taken in the TEM) shown in Figure 1b. The Cu and C elements are attributed to copper grids and carbon film, respectively.

**Figure S2.** EDS spectrum of tips of AgInZn$_7$S$_9$ nanowire (taken in the TEM) shown in Figure 1b. The Cu and C elements are attributed to copper grids and carbon film, respectively.
Figure S3. XPS survey spectra of AgInZn$_7$S$_9$ nanowire. The peaks assignable to core levels of Ag 3d, In 3d, Zn 2p, S 2p, O 1s, N 1s and C 1s are identified. The Si element is attributed to silicon wafer substrate.

Figure S4. High-resolution of XPS analysis of AgInZn$_7$S$_9$ nanowire. In high-resolution spectrum of silver 3d, two peaks at 367.6 and 373.5 eV appear, indicative of Ag(I) with a splitting of 5.9 eV, which is close consistent with standard separation of 6.0 eV. The In(III) is confirmed by a peak splitting of 7.6 eV, two peaks located at 444.8 and 452.4 eV, respectively. The zinc 2p peaks located at 1021.4 and 1044.4 eV, and a peak splitting of 23.0 eV indicates Zn(II). The two peaks of sulfur 2p are located at 161.6 and 162.8 eV, respectively, showing a peak separation of 1.2 eV, which are also consistent with the literature value in metal sulfide.
Figure S5. XRD pattern of Ag$_2$S nanocrystals derived from Ag(dedc) precursor. The standard pattern of Ag$_2$S is also shown.

Figure S6. XPS spectra of as-synthesized Ag$_2$S nanocrystals. (a) XPS survey spectrum of Ag$_2$S; (b) High-resolution XPS of Ag 3d in Ag$_2$S; (c) High-resolution XPS of S 2p in Ag$_2$S.
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Figure S7. Typical TEM image of AgInZn$_7$S$_9$ nanowires at early stage of nanowire growth (1 min). The initial nanowires appeared as short matchstick with nanoparticles on the tip, as the typical morphologies in nanowire synthesis by SLS growth.

Figure S8. (a) Typical TEM image of ZnS nanowire with Ag$_2$S nanoparticles at the tip. (b-d) HRTEM images of tips of ZnS nanowires. The tips are polycrystalline.

Typical TEM image shows the samples are matchstick-like nanowires with a typical length of 150 nm and width of 12 nm (Figure S8a). The nanowires have nanoparticles at the tip, which are confirmed as Ag$_2$S by EDS, XRD and XPS in control experiment (Figure S2, S5, and S6). Ag$_2$S nanocrystals were also found to play catalytic roles in the synthesis of ZnS nanowires. We also noticed that the tips of nanowires are polycrystalline rather than single crystal (Figure S8, b-d). It was deduced that the catalysts in this process were quasi-liquid state, only the surface regions of the Ag$_2$S NPs were melted and the inner retained solid state.