

Supporting Information for:

**Synthesis of Normal and Flatten Rhombic
Dodecahedral Ag₂S Particles**

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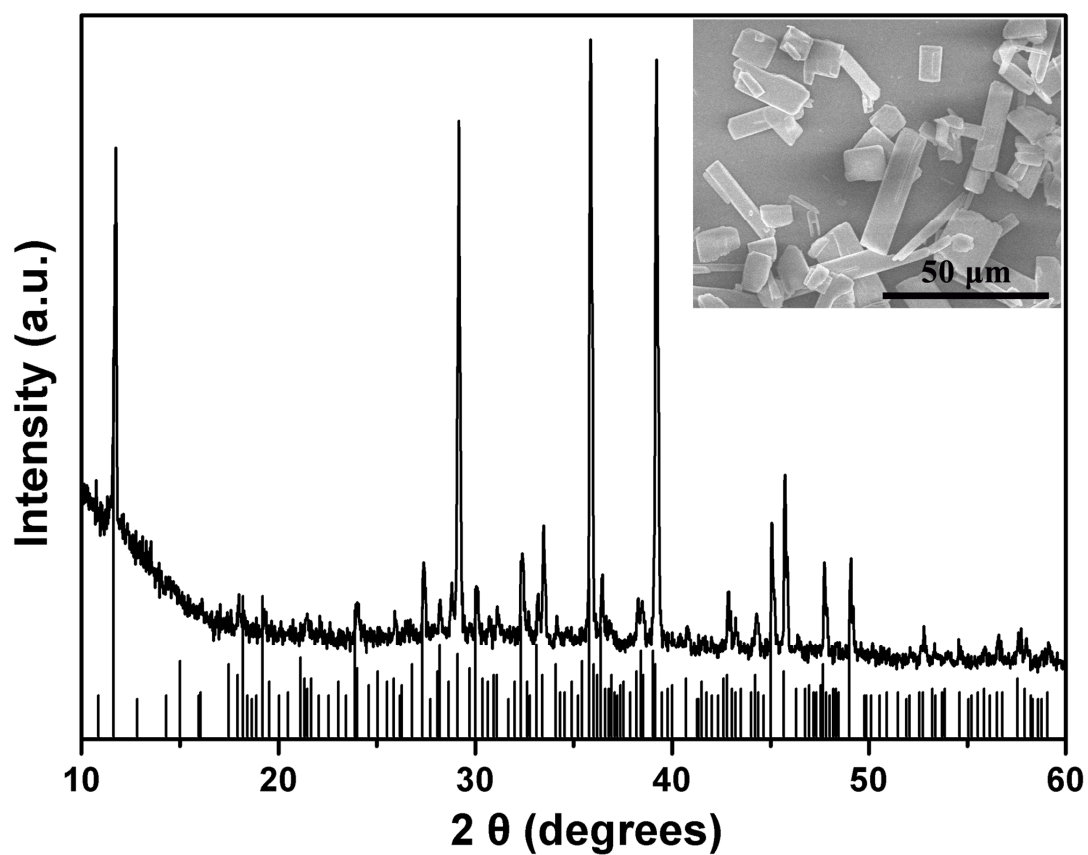


Figure S1: XRD pattern of the white precipitate in the reactive solution before heated. The column lines at the bottom are the standard JCPDS (No: 52-0589) data for $\text{Ag}(\text{Tu})_2\text{Cl}$. The inset is the SEM image of as-precipitated $\text{Ag}(\text{Tu})_2\text{Cl}$.

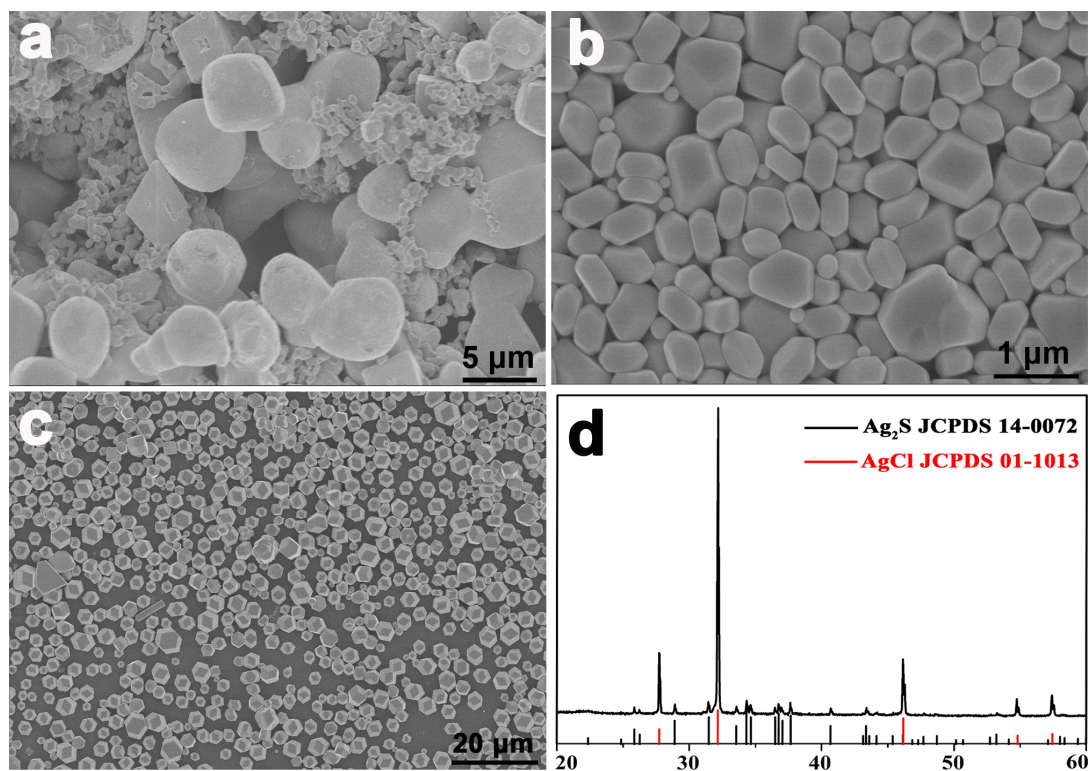


Figure S2: SEM images of Ag_2S sub-micrometer particles obtained with $R_{\text{S/Ag}}$ at 1 (a), 3 (b) and 12 (c) respectively, XRD pattern of as-prepared Ag_2S with $R_{\text{S/Ag}} = 1$.

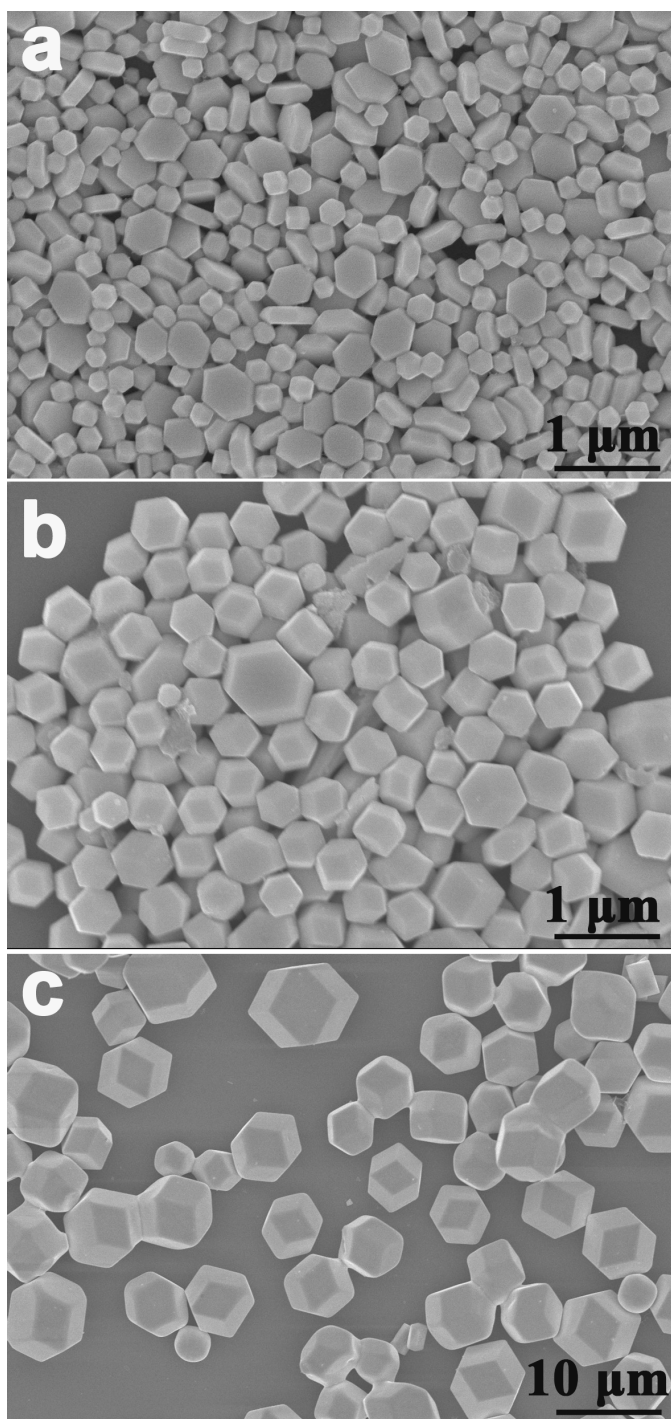


Figure S3: SEM images of RD sub-micrometer Ag_2S particles obtained with different amounts of HCl: 0 mL (a), 0.05 mL (b), and 0.1 mL (c).

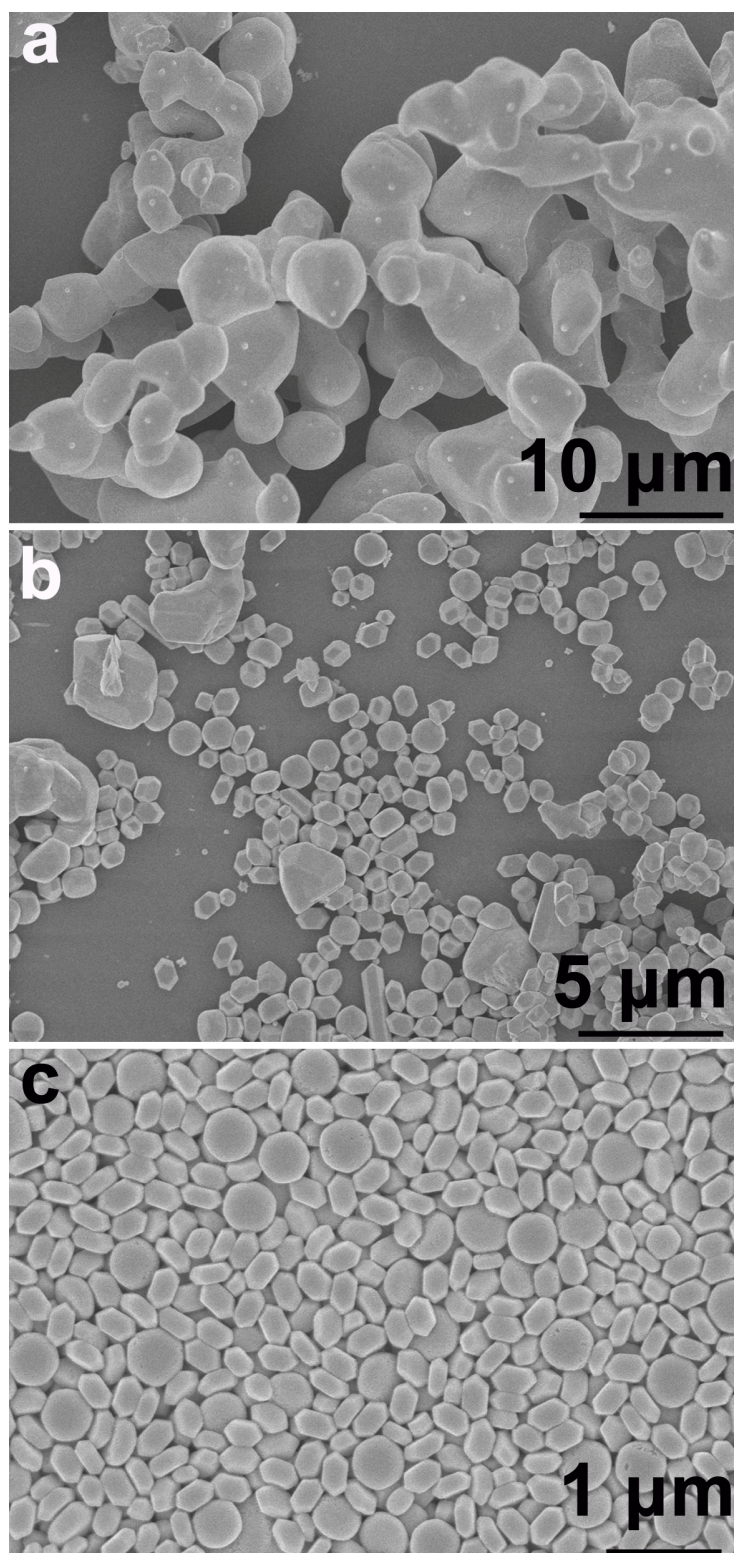


Figure S4: SEM images of FRD Ag₂S particles obtained with different amounts of PVP:
0 g (a), 0.1 g (b), and 0.8 g (c).

The reactions were terminated at different intervals to see reaction-time influence on FRD particles. The reactive solution remained transparent after 10 min heating in autoclave at 170°C, which might be due to the slow increase of reaction temperature inside the autoclave and no reaction could be initiated. If heated for 20 min, poorly developed FRD particles could be yielded and their surfaces were rough which suggested that the FRD aggregates were composed of small particles (Figure S5a). Prolonging the reaction time to 30 min would produce regular FRD Ag₂S products similar to those obtained under optimized conditions and the degree of surface roughness decreased (Figure S5b). Further increase the reaction time up to 12 h has barely effect on the product with smooth surfaces and sharp edges. These observations suggested that the nucleation and growth into small seeds occurred between 10 and 20 min. To minimize the overall energy of the system, the small particles tended to aggregate together and changed into FRD according to the ripening mechanism.

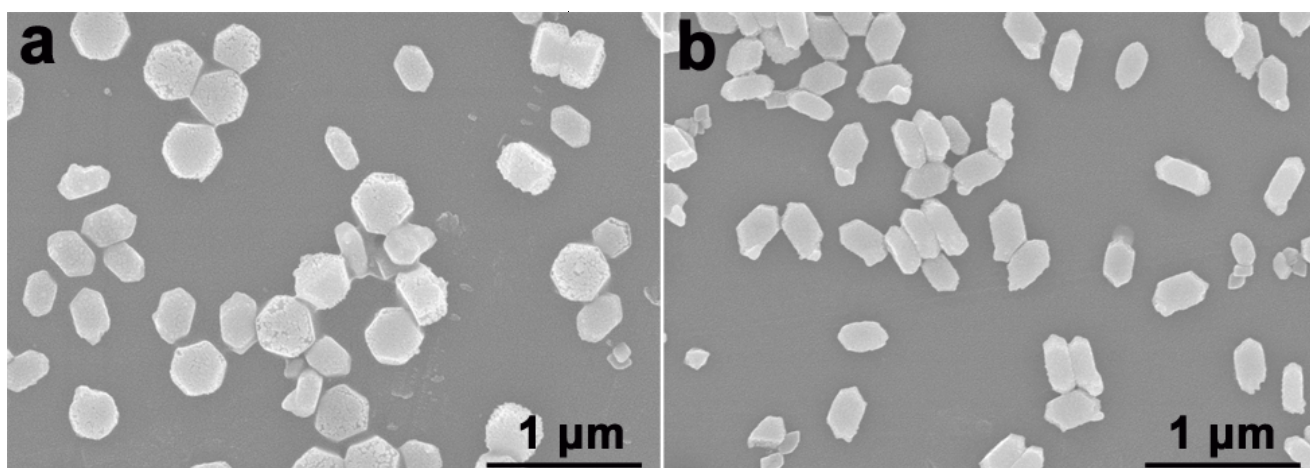


Figure S5. SEM images of FRD Ag₂S particles obtained at 170°C for 20 min (a), 30 min (b).

In the process of nucleation, precursors decompose to form a supersaturation of monomers to set up a burst of nucleation. Although it is impossible to observe the two processes of nucleation and growth separately in this system, the synthesis still should be carried out at various temperatures to facilitate the decomposition of Tu and $\text{Ag}(\text{Tu})^{3+}$ complex and the reaction rate to the final products. No products could be obtained below 120°C which was probable the too low reactive temperature to offer enough energy to decompose the $\text{Ag}(\text{Tu})_3^{+}$ complex, so we elevated our temperature from 120°C , and nearly FRD Ag_2S particles with wide size distributions were produced (Figure S6a). Such situation could be improved by increasing the temperature to 150°C (Figure S6b) along with the dramatic improvement of crystallinity. This could be explained that the low reaction temperature resulting in the low reaction rate and the effect of Ostwald-ripening broadened the size distribution. However, the final products obtained at different reaction temperatures had the same monoclinic structure of Ag_2S which could be confirmed by the XRD patterns in Figure S6c and d.

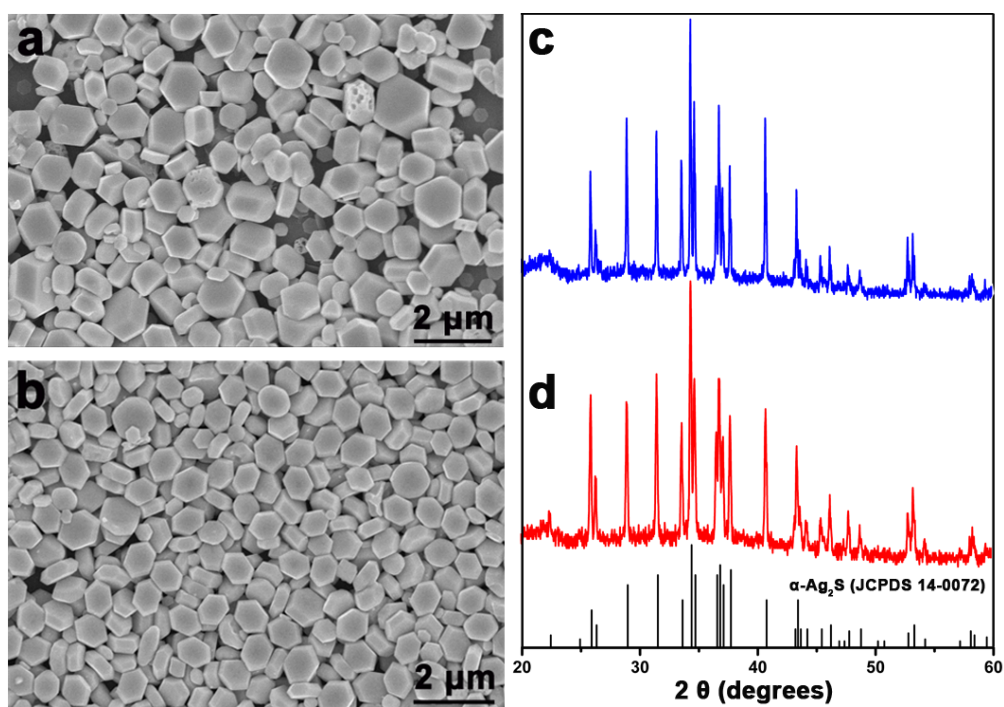


Figure S6: SEM images and XRD patterns of FRD Ag_2S particles obtained at 120°C for (a and c) and 150°C (b and d) for 12 h.