Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supplementary Information

Ligand effect on the synthesis of emission-tunable near-infrared Ag_2S quantum dots

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When the metal ions coordinated by ligand, its standard redox potential (φ^{θ}) will change (eqs 1-3). It can be calculated according to Nernst equation (eq 4):

$$M^{n+} + ne \rightarrow M \qquad \varphi_1^{\theta} \qquad (1)$$

$$M^{n+} + pX^{q-} \leftrightarrow MX_p^{(n-pq)} \qquad K_f \qquad (2)$$

$$MX_p^{(n-pq)} + ne \rightarrow M + pX^{q-} \qquad \varphi_2^{\theta} \qquad (3)$$

$$\varphi_2^{\theta} = \varphi_1^{\theta} - \frac{RT}{nF} lnK_f \qquad (4)$$

where φ_2^{θ} and φ_1^{θ} are representative of the standard redox potential of metal ions and the metal-ligand complex, respectively, R is the ideal gas constant, T is the thermodynamic temperature, n is the number of the transferred electrons, F is the Faraday constant, and K_f is stability constant of metal-ligand complex. It can be inferred from eq 4 that the φ^{θ} of metal ions is lower when K_f is higher, and the metal ions will be more difficult to be reduced. Therefore, the addition of 1-octanethiol will suppress the reduction of Ag^+ ions to Ag nanocrystals.

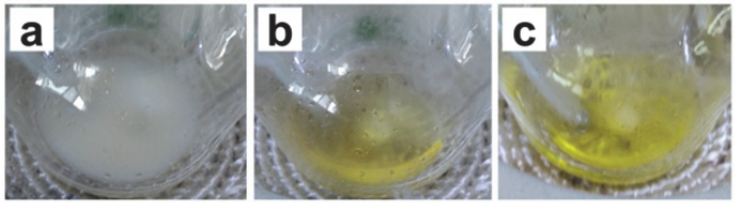

Fig. S1 Photographs of the reaction solution (a) after adding 1-octanethiol into the Ag(I) solution at (a) 80 °C, (b) further heated to 110 °C and (c) heated to 160 °C. After the addition of 1-octanethiol, the colorless Ag(I) solution became white turbid due to the formation of Ag(I)-thiolate complex and further changed to yellow clear at above 110 °C, which was similar to the reported thiol-based synthesis of Ag_2S QDs.[1] Different from the reaction without 1-octanethiol, the Ag(I) solution containing 1-octanethiol did not turn brown even at 160 °C.

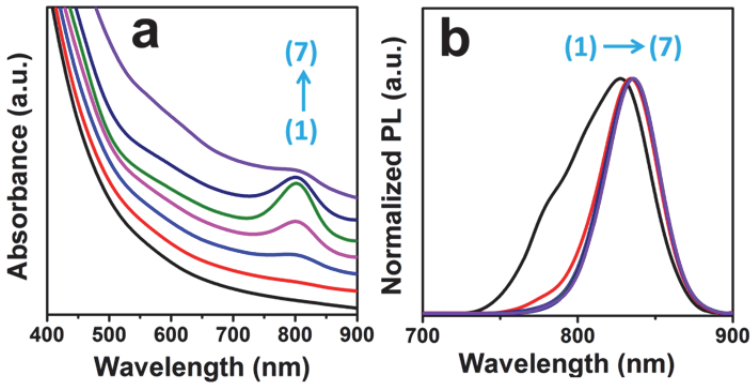

Fig. S2 Temporal evolution of absorption spectra and PL spectra of Ag_2S QDs. The growth time: (1) 5 s, (2) 30 s, (3) 1 min, (4) 5 min, (5) 15 min, (6) 30 min, (7) 60 min. Ligand composition: 0.5 M of OAc, 0.5 M of OAm and 0.04 M of RSH. Injection temperature: 160 °C.

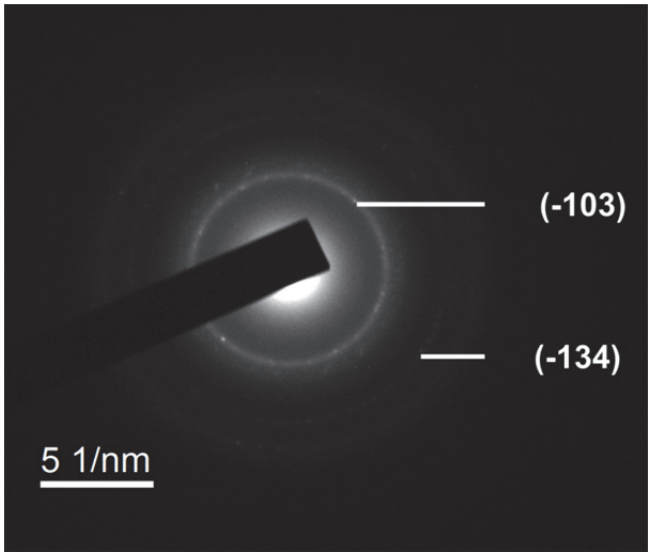

Fig. S3 Selected area electron diffraction (SAED) image of the as-prepared Ag_2S QDs.

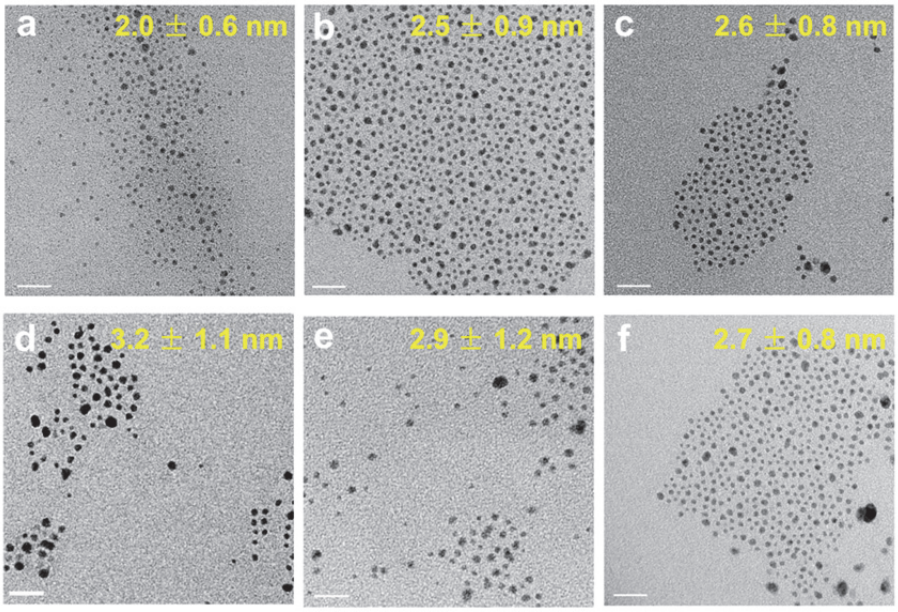

Fig. S4 TEM images (scale bar: 20 nm) of Ag_2S QDs grown with different ligands: (a, d) 0.5 M OAc and 0.04 M RSH, (b, e) 0.5 M OAm and 0.04 M RSH, (c, f) 0.5 M OAm, 0.5 M OAc and 0.04 M RSH. The growth time (a-c): 5 s, (d-f): 60 min. The RSH refers to 1-octanethiol.

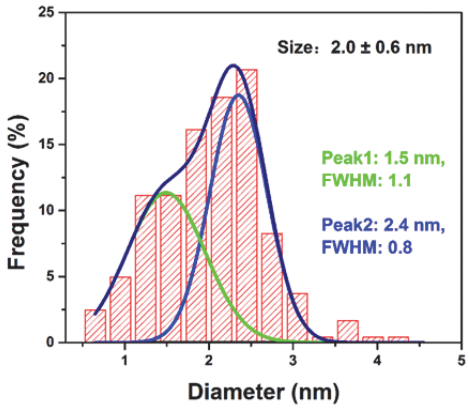

Fig. S5 Size distribution of Ag_2S QDs corresponded to the sample a in Fig. S4. The size distribution could be fitted to two peaks at 1.5 nm and 2.4 nm.

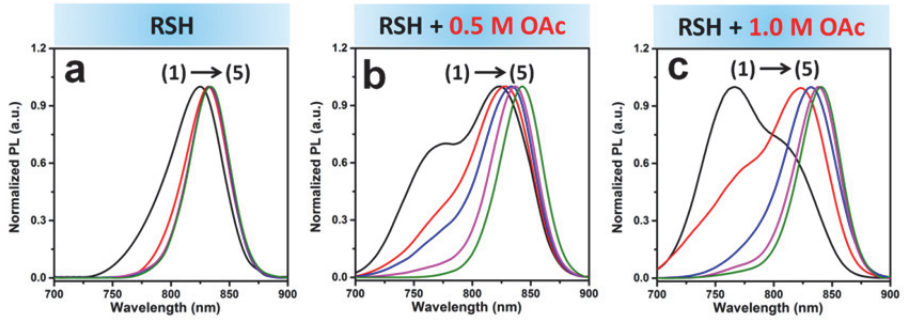

Fig. S6 Temporal evolution of PL spectra of Ag_2S QDs grown with identical 1-octanethiol concentration (0.04 M) and different OAc concentration (0.0 M, 0.5 M and 1.0 M). The growth time (1-5): 5 s, 5 min, 15 min, 30 min and 60 min.

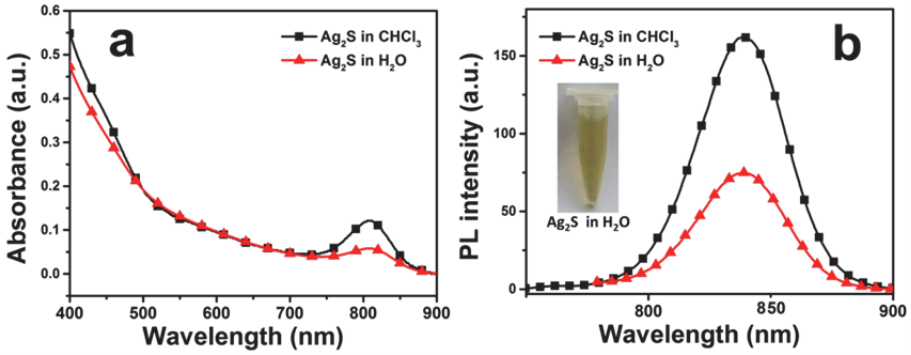

Fig. S7 (a) Absorption and (b) PL spectra of the Ag_2S QDs before and after transferred from chloroform to water and the photograph of the water-soluble Ag_2S QDs (b, inset).

References

[1] Jiang P, Wang R and Chen Z L 2015 *RSC Adv.* **5** 56789