Supporting Information

Sulfur-antisite induced intrinsic high-temperature ferromagnetism in Ag_2S:Y nanocrystals

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1. EDS analysis of monoclinic Ag_2S:Y nanocrystals

As we can see from Figure S1-4 and Table S1-4 of energy-dispersive X-ray spectroscopy (EDS) analysis, Y contents are about 0.41 atom%, 0.55 atom%, 0.64 atom%, and 0.88 atom% for the 0.12, 0.16, 0.18, and 0.20 of the molar ratio of Y^{3+} and Ag^+ in the reaction solution, respectively, respectively.

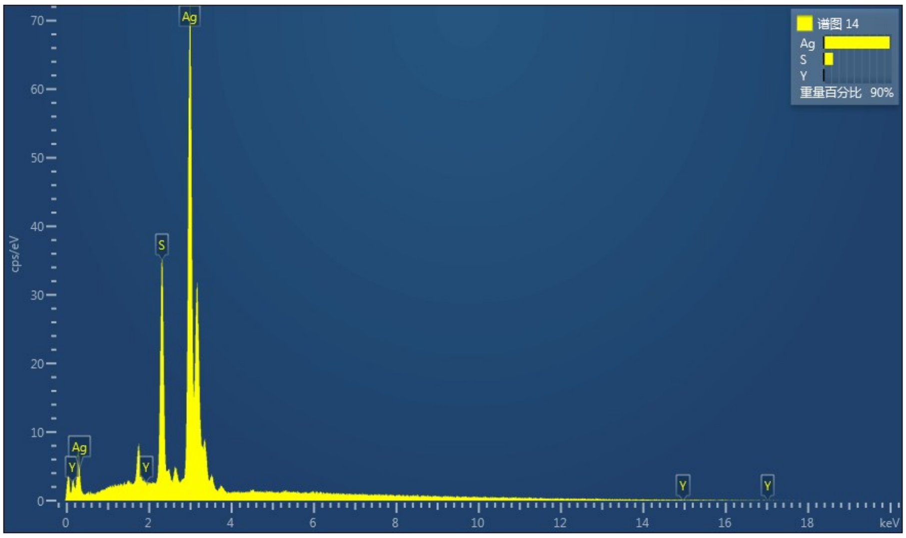

Figure S1. EDS spectrum of the monoclinic Ag_2S:Y nanocrystals for the 0.12 molar ratio of Y^{3+} and Ag^+ in the reaction solution.

Table S1. Element content percentage of the monoclinic Ag_2S:Y nanocrystals for the 0.12 molar ratio of Y^{3+} and Ag^{+} in the reaction solution.

Element	Weight (%)	Atom (%)
S	12.36	32.15
Y	0.43	0.41
Ag	87.21	67.44
Total	100.00	100.00

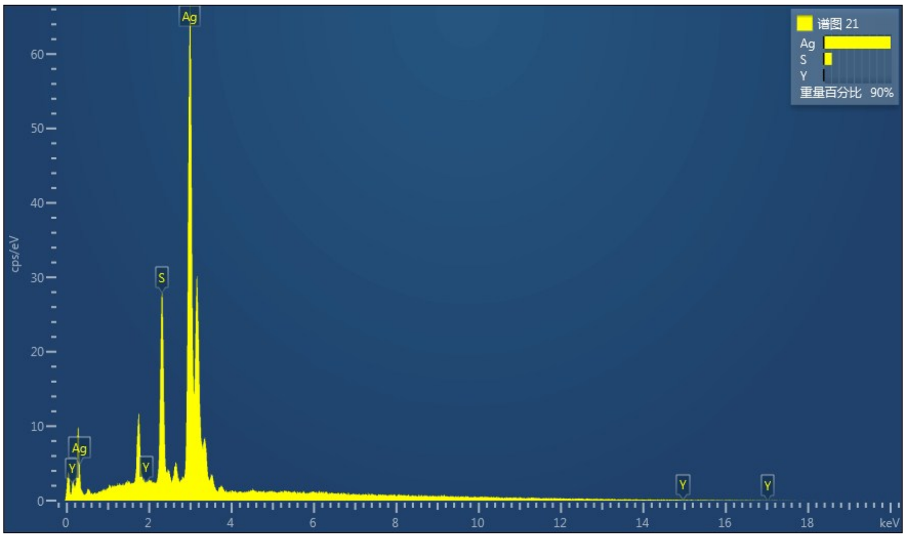

Figure S2. EDS spectrum of the monoclinic Ag_2S:Y nanocrystals for the 0.16 molar ratio of Y^{3+} and Ag^{+} in the reaction solution.

Table S2. Element content percentage of the monoclinic Ag_2S:Y nanocrystals for the 0.16 molar ratio of Y^{3+} and Ag^{+} in the reaction solution.

Element	Weight (%)	Atom (%)
S	10.82	28.95
Y	0.57	0.55
Ag	88.61	70.50
Total	100.00	100.00

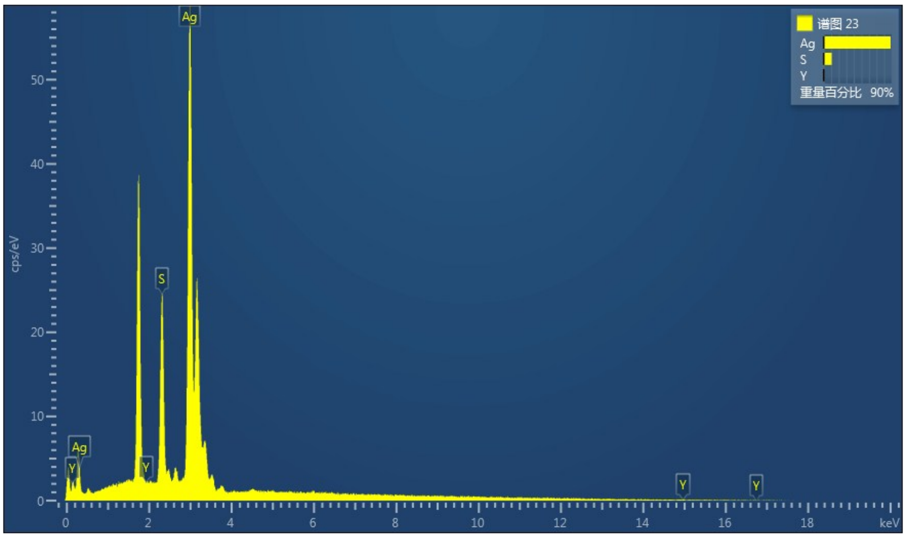

Figure S3. EDS spectrum of the monoclinic Ag_2S:Y nanocrystals for the 0.18 molar ratio of Y^{3+} and Ag^+ in the reaction solution.

Table S3. Element content percentage of the monoclinic Ag_2S:Y nanocrystals for the 0.18 molar ratio of Y^{3+} and Ag^+ in the reaction solution.

Element	Weight (%)	Atom (%)
S	10.77	28.84
Y	0.67	0.64
Ag	88.57	70.52
Total	100.00	100.00

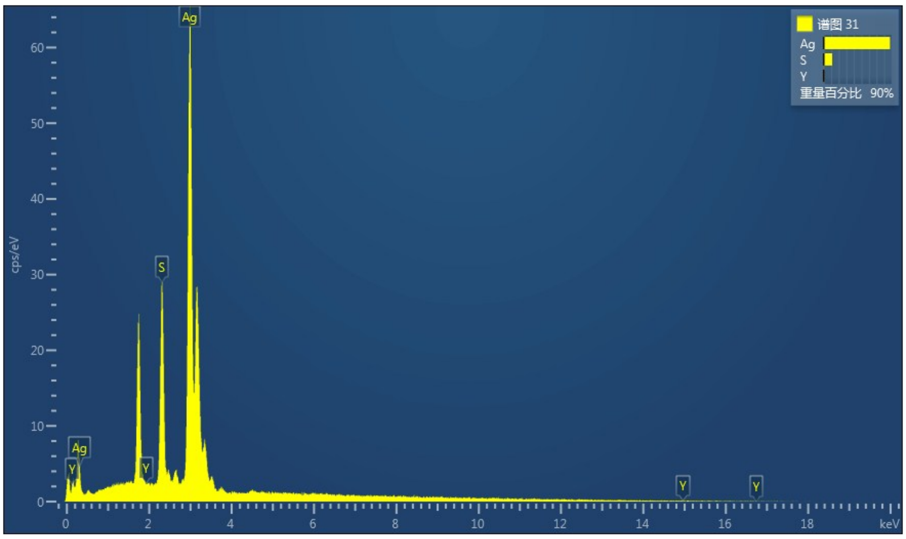

Figure S4. EDS spectrum of the monoclinic Ag_2S:Y nanocrystals for the 0.20 molar ratio of Y^{3+} and Ag^+ in the reaction solution.

Table S4. Element content percentage of the monoclinic Ag_2S:Y nanocrystals for the 0.20 molar ratio of Y^{3+} and Ag^+ in the reaction solution.

Element	Weight (%)	Atom (%)
S	11.37	30.10
Y	0.92	0.88
Ag	87.71	69.02
Total	100.00	100.00

2. TEM analysis of the monoclinic Ag_2S:Y nanocrystals

As shown in high-resolution transmission electron microscopy (HRTEM) image (Figure S5a) of the undoped Ag_2S nanocrystals, the measured interplanar spacings of 0.308 nm and 0.258 nm are consistent with (111) and (022) lattice planes of the monoclinic Ag_2S structutre, respectively. The particle size of the pure Ag_2S sample (Figure S5a) can be clearly distinguished and the average size is 30-32 nm. Moreover, there are some defects (denoted by white dotted circles) in the Ag_2S nanocrystals, as shown in Figure S5a. The measured interplanar spacings (Figure S5(b-e)) for 0.41 atom%, 0.55 stom%, 0.64 atom% and 0.88 atom% Ag_2S:Y nanocrystals are consistent with the corresponding lattice planes of the monoclinic Ag_2S structutre, and the observed particle sizes are also about 30-32 nm. As displayed in Figure S5, there are more defects in these Ag_2S:Y nanocrystals in comparision to the pure Ag_2S samples.

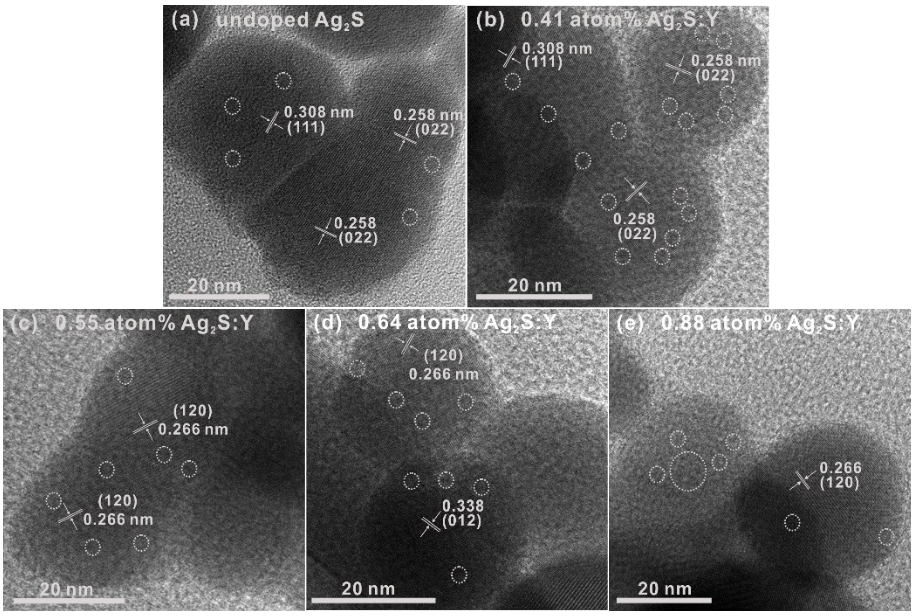

Figure S5. HRTEM image (a) undoped, (b) 0.41 atom%, (c) 0.55 stom%, (d) 0.64 atom% and (e) 0.88 atom Y^{3+} doped monoclinic Ag_2S nanocrystals (the white dotted circles denoted as the defect regions), respectively.

3. XPS analysis of the monoclinic Ag_2S:Y nanocrystals

XPS analysis is to determin whether impurity elements such as N and magnetic impurities including Fe, Co, Ni are present and to determine the valence states of elements. For the pure and 0.64 atom% Y doped Ag_2S nanocrystals, it is obviously seen that no other impurities were detectable in the full XPS spectra of Fig. S6c and Fig. S6f, respectively. The two S 2p peaks (Figure S6a) correspond to S 2p3/2 and S 2p1/2 at 161.3 and 162.4 eV, respectively, manifesting that the S is in S^{2-} state.[1] In Ag 3d spectrum (Figure S6b), two peaks attributed to Ag $3d_{5/2}$ and Ag $3d_{3/2}$ at 368.2 and 374.2 eV indicate that Ag is in Ag^+ state, in agreement with the reported value of Ag_2S. [2] Area analysis of the peaks suggests that the Ag/S ratio reaches 1.8 smaller than the ideal theoretical value of 2. The above analysis reveals that S is in excess and Ag is relatively deficient in Ag_2S, probably because of the formation of sulfur antisite, Cd vacancy, and sulfur interstitial defects. For 0.64 atom% Y doped Ag_2S nanocrystals, there is some overlap in Figure S6d, due to the close binding energies of Y and S elements. The S $2p_{3/2}$ and S $2p_{1/2}$ peaks (Figure S6d) at 161.6 and 162.7 eV manifest that the S is in S^{2-} state. The fitted peak (Figure S6d) of Y $3d_{5/2}$ at 158.5 eV manifests that Y is in Y^{3+} state,[3] excluding the possibility of Y metal clusters. The Ag $3d_{5/2}$ and Ag $3d_{3/2}$ peaks (Fig. S6e) at 368.8 and 374.7 eV suggest that Ag is in Ag^+ state. The Ag/S ratio of 0.64 atom% Ag_2S:Y nanocrystals is 1.3 significantly smaller than that of the pure Ag_2S sample, which implies that the Y dopant is in favor of the sulfur antisite, Cd vacancy, and sulfur interstitial defects.

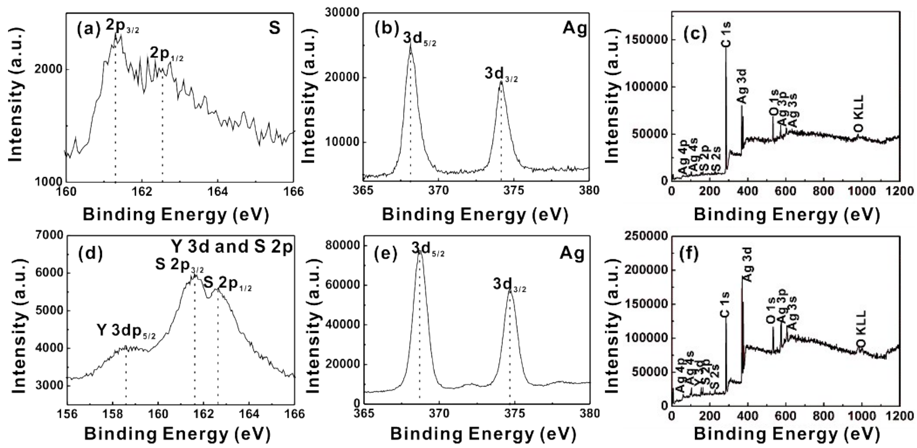

Fig. S6 XPS spectra of (a-c) undoped and (d-f) Y doped Ag_2S nanocrystals. (a, d) Binding energy of Y 3d and S 2p regions; (b, e) binding energies of Ag 3d regions; (c, f) full scan spectra, respectively.

Reference

1 X. Yang, H. T. Xue, J. Xu, X. Huang, J. Zhang, Y.-B. Tang, T.-W. Ng, H.-L. Kwong, X.-M. Meng and C.-S. Lee, *ACS Appl. Mater. Interfaces*, 2014, **6**, 9078-9084.

2 W. Jiang, Z. M. Wu, X. N. Yue, S. J. Yuan, H. F. Lu and B. Liang, *RSC Adv.*, 2015, **5**, 24064-24071.

3 I. Gonzalo-Juan, J. A. Escribano, Y. Castro, A. J. Sanchez-Herencia, J. L. G. Fierro and B. Ferrari, *Green Chem.*, 2014, **16**, 3286-3296.