Supporting information

Facile synthesis of water-soluble Zn-doped $AgIn_5S_8$/ZnS core/shell fluorescent nanocrystals and their biological application

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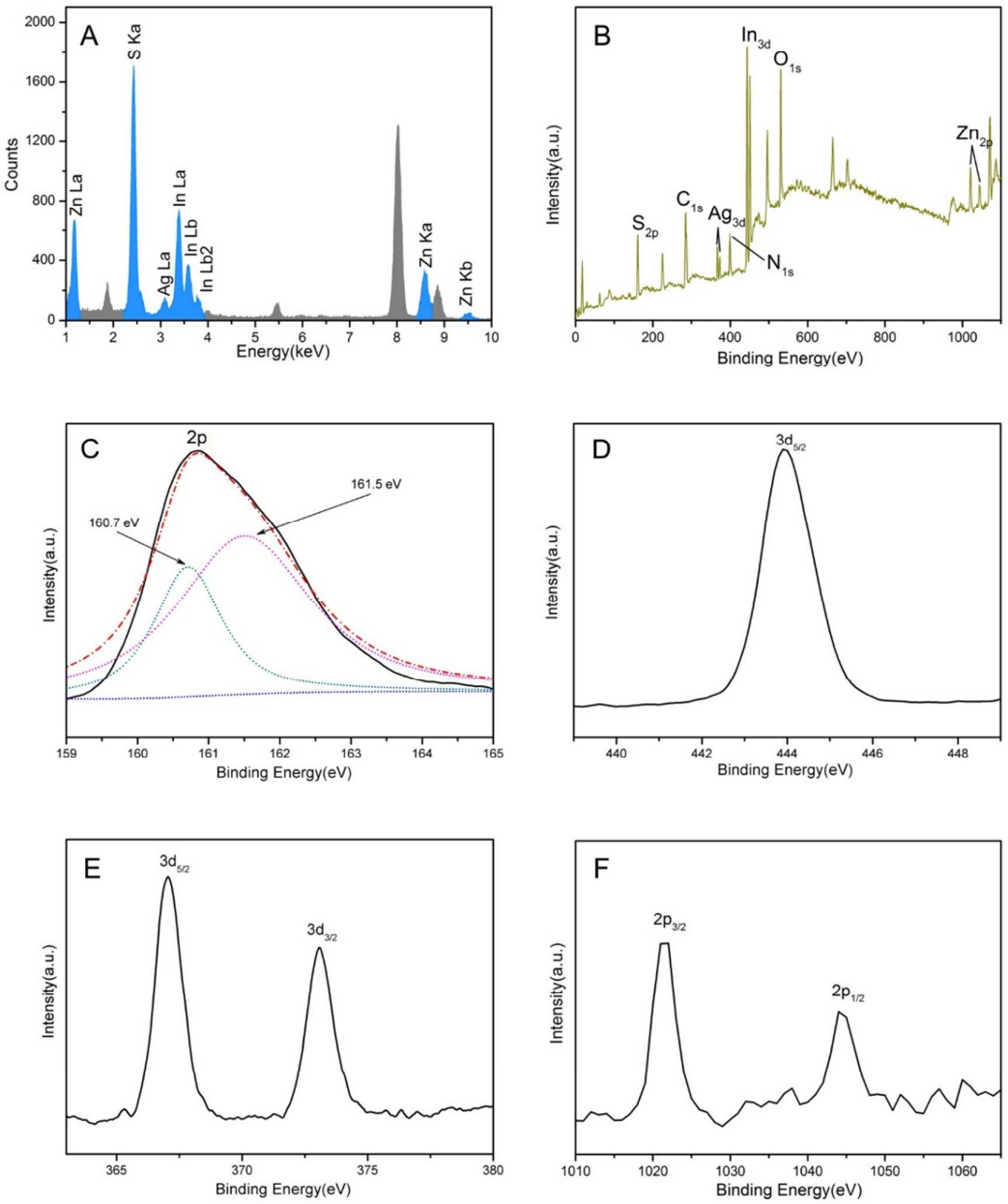

Figure S1. EDS spectrum (A), XPS surveys (B) and the corresponding XPS spectra of S 2p (C), In 3d (D), Ag 3d (E) and Zn 2p (F) of ZAIS QDs with [Ag]/[Zn]=1/5.

EDS was worked to determine the elements and their molar ratio of the samples. As is presented in Figure S1A, we can find the characteristic peaks of Zn, Ag, In, S, respectively, which indicate that the formation of our quaternary ZAIS QDs. The determined atom percentage of AIS (without Zn) were 7.1%, 34.8%, 58.1%, corresponding to Ag, In and S respectively. Their atom ratio is [Ag]:[In]:[S]=1:4.9:8.2, in accordance with the ratio of 1:5:8 of $AgIn_5S_8$. So we determine the stiochiometric of the obtained AIS as $AgIn_5S_8$. Table S1 demonstrates the atom percentage of Ag and

Zn of ZAIS and their calculated ratio of Ag/Zn=1/4.96, 1/2.92 and 1/0.96, well in agreement with [Ag]/[Zn]=1/5, [Ag]/[Zn]=1/3 and [Ag]/[Zn]=1/1, respectively. For comparison, the atom percentage of Ag and Zn with [Ag]/[Zn]=1 are also listed. The element content of Zn in ZAIS@ZnS NCs is more than that in ZAIS QDs, which elucidated that ZnS is definitely coated outside the ZAIS core.

Table S1. The content of Ag and Zn and percentage of Ag/Zn

element	ZAIS ([Ag]/[Zn]=1/5)	ZAIS ([Ag]/[Zn]=1/3)	ZAIS ([Ag]/[Zn]=1)	ZAIS/ZnS ([Ag]/[Zn]=1)
Ag (at. %)	3.15	4.18	6.31	5.58
Zn (at. %)	15.65	12.21	6.55	8.91
Atom ratio of Ag/Zn	1/4.96	1/2.92	1/0.96	--

X-ray photoelectron spectroscopy (XPS) was used to study the chemical compositions and their valence state of ZAIS core/shell structure. Figure S1B shows the XPS survey of the ZAIS QDs of [Ag]/[Zn]=1/3. The characteristic peak of S 2p (160.7 and 161.5 eV), In 3d (443.9 eV), Ag 3d (367.1 and 374.7 eV), Zn 2p (1021.4 and 1045.0 eV) are presented in Figure S1C-S1F, respectively, which illustrate that the valence state of the ions are S^{2-}, In^{3+}, Ag^{+} and Zn^{2+}, certifying the formation of ZAIS in our production. Besides, C 1s (284.65 eV), O 1s (531.0 eV) and N 1s (399.9 eV) peaks also emerge in the spectrum (Figure S1B), giving the potential existence of L-cysteine.

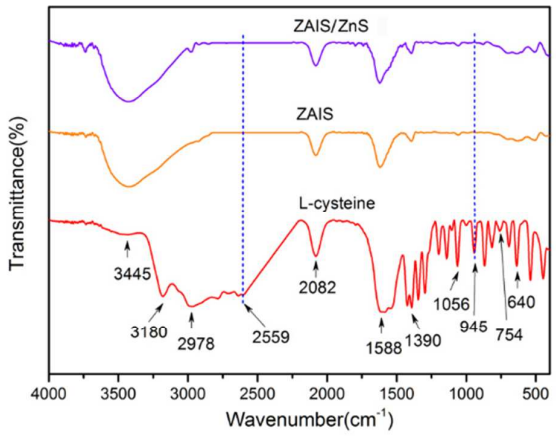

Figure S2. FTIR spectra of ZAIS/ZnS NCs, ZAIS QDs and L-cysteine.

To further certify the presence of L-cysteine on the surface of ZAIS QDs and ZAIS/ZnS NCs, FTIR spectra were examined on the samples prepared with different [Ag]/[Zn]. Figure S2 show the

FTIR spectra of ZAIS QDs, corresponding ZAIS/ZnS NCs ([Ag]/[Zn]=1/6) and L-cysteine. As for L-cysteine, the bands 3445 and 3180 cm^{-1} originate from the O-H stretching vibration. The bands 2978 and 2082 cm^{-1} refer to the vibration of N-H stretching. The symmetric and asymmetric vibration bands of COO^- are around 1588 and 1390 cm^{-1}.The band at 1056 cm^{-1} is due to C-N stretching.[1,2] These peaks are also observed both in ZAIS and ZAIS/ZnS. However, the most significant change is the band around 2559 and 945 cm^{-1} which attribute to the S-H stretching and bend mode. Generally, the amino acid cysteine is water soluble and can readily bind to the metal atom via the thiolate linkage.[3] As is seen in Figure S2, the bands around 2559 and 945 cm^{-1} are almost disappeared, which provides strong evidence for the surface binding of L-cysteine to ZAIS particles by S-Zn linkage. The broadened and weak bands around 750 and 640 cm^{-1}, correspond to the bend vibrations of C-S, giving the same interpretation of the binding between S and Zn.[4] These observations demonstrated the presence of L-cysteine and they are successfully bound to the surface of ZAIS QDs and ZAIS/ZnS NCs.

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