Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Impact of reaction variables and PEI/l-cysteine ratio on optical properties and cytocompatibility of cationic Ag_2S quantum dots as NIR bio-imaging probes

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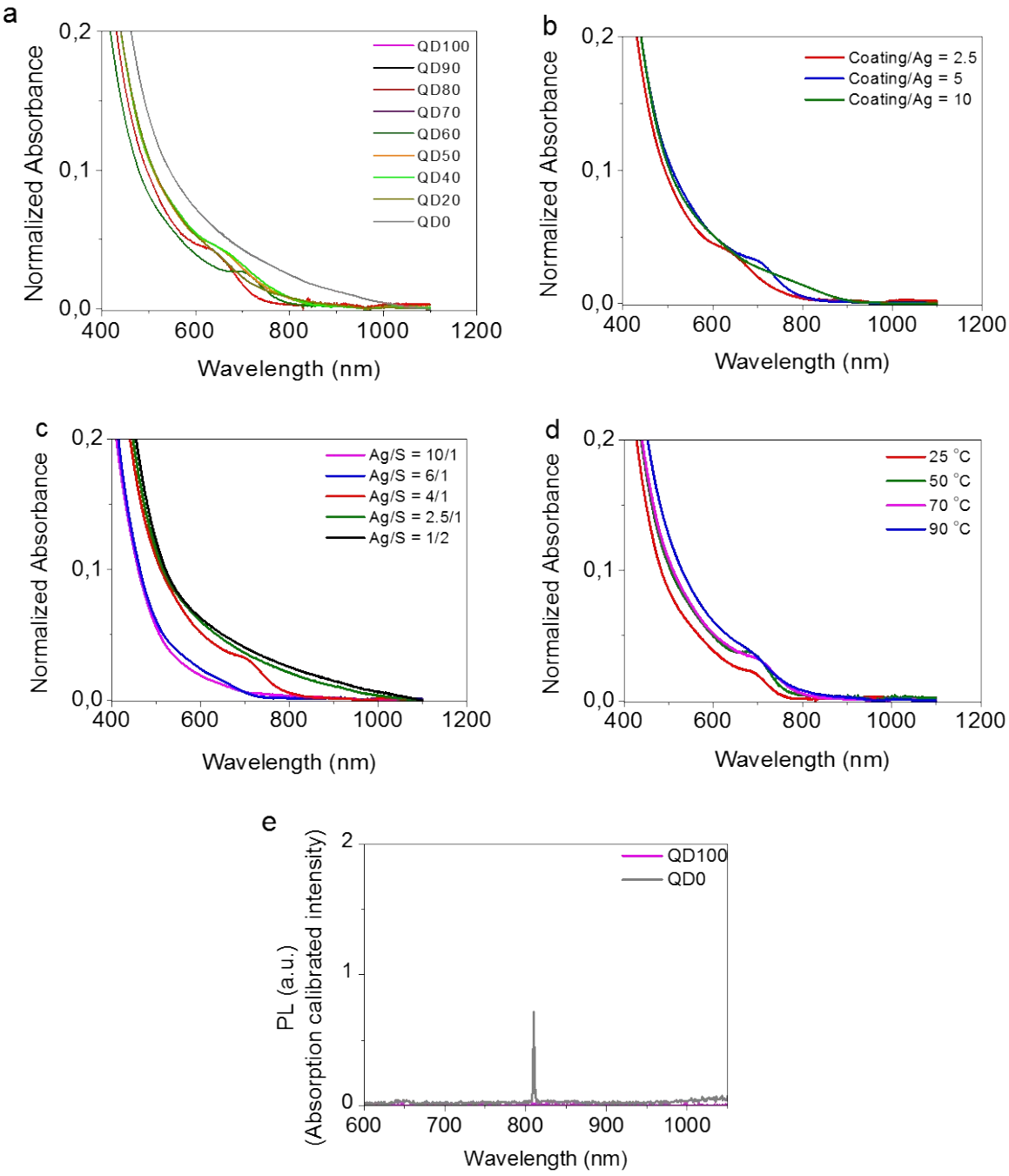

Fig. S1 Absorbance spectra of PEI/Cys coated Ag_2S QDs synthesized at different PEI/Cys (a), Ag/coating (PEI and Cys) (b) Ag/S mole ratios (c), temperature (d) and Photoluminescence spectra of QD100 and QD0 (e).

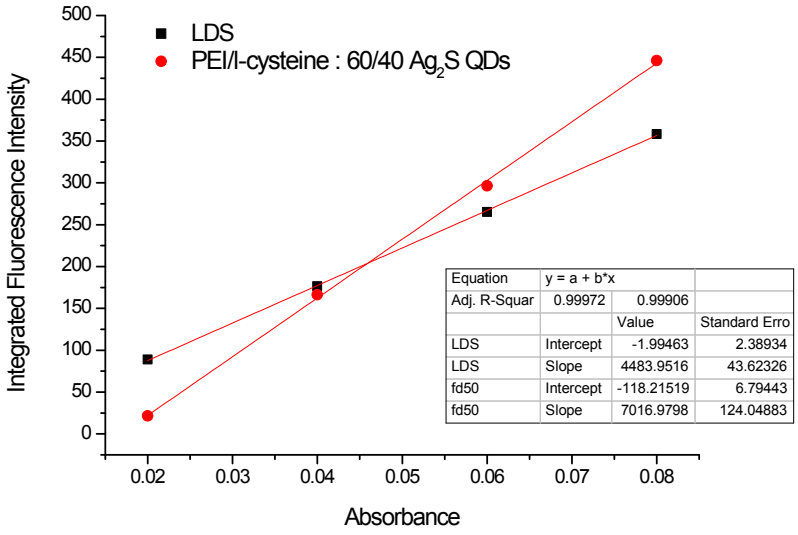

Fig. S2 Plot of the the integrated luminesence intensities of the reference dye and Ag_2S QDs against the absorbance. Inset shows the slope of each line corresponding to Ag_2S and dye samples.

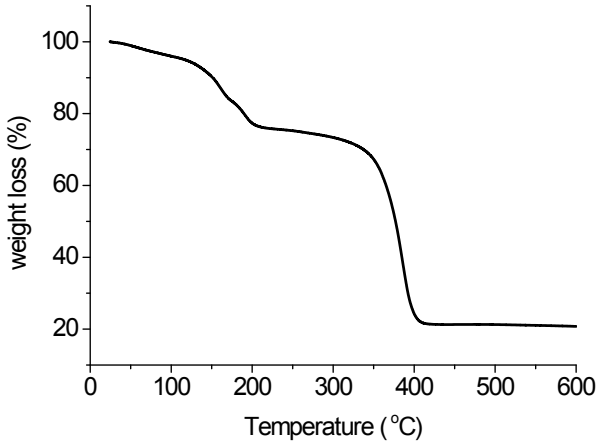

Fig. S3 Thermogravimetric analysis of PEI/Cys coated Ag_2S (QD60-RT).

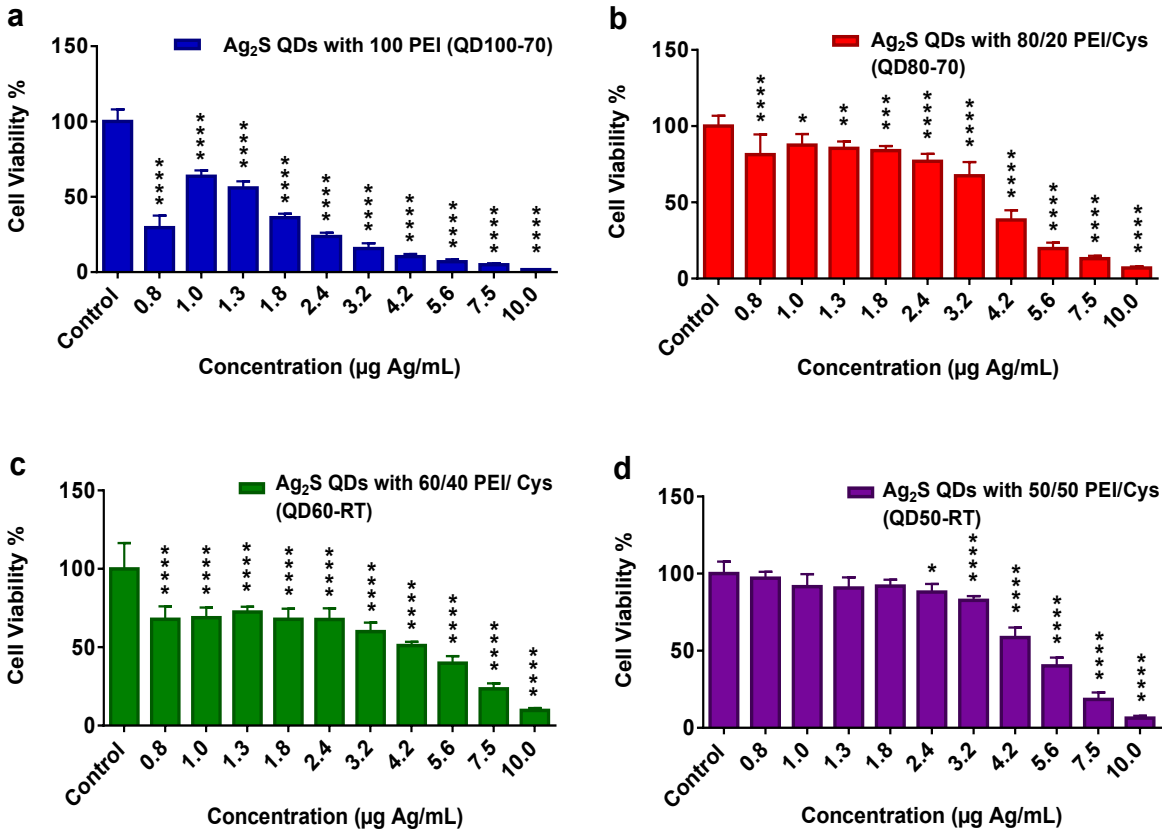

Fig. S4 Viability of HeLa cells treated with QD100-70 (QD100) (a), QD80-70 (b), QD60-RT (c) and QD50-RT (d) after 24 hours incubation measured by MTT assay compared to untreated HeLa cells. The data are expressed as mean ± S.D. (n = 8). ($p<0.05$).

Table S1 Effect of coating/Ag ratio on the properties of Ag_2S QD (QD60)*

Coating/Ag (mol/mol)	$\lambda_{em\ (max)}$ (nm)	Size[a] (nm)	Band gap (eV)	$\lambda_{abs(cutoff)}$[b] (nm)	FWHM (nm)	Dh[c] (nm)	Zeta pot. (mV)
2.5	-	2.59	1.55	799	-	48.1 ± 11.1	49.3 ± 2.5
5	775	2.64	1.52	816	105	49.3 ± 14.1	63.6 ± 4.9
10	-	2.87	1.40	886	-	13.2 ± 1.8	46.7 ± 4.0

* Formulation: PEI/Cys=60/40 mol/mol, Ag:S = 4, reaction pH = 10.5, 1h reaction. [a]Calculated by Brus equation. [b] Absorbance onset. [c] Hydrodynamic diameter measured by DLS and reported as the number average.

Table S2 Effect of the Ag/S on the properties of Ag_2S QDs (QD60)*

Ag	S	$\lambda_{em\ (max)}$ (nm)	Size[a] (nm)	Band gap (eV)	$\lambda_{abs(cutoff)}$[b] (nm)	FWHM (nm)	Dh[c] (nm)	Zeta pot. (mV)
10	1	716	2.30	1.78	698	104	54.0 ± 15.4	68.1 ± 1.5
6	1	724	2.40	1.69	736	108	23.2 ± 3.1	54.3 ± 5.2
4	1	775	2.64	1.52	816	105	49.3 ± 14.1	63.6 ± 4.9
2.5	1	-	3.04	1.33	932	-	13.3 ± 0.8	47.7 ± 3.9
1	2	-	3.13	1.30	955	-	26.2 ± 10.2	41.7 ± 5.1

* Formulation: PEI/Cys=60/40 mol/mol, Ag:S = 4, reaction pH = 10.5, 1h reaction. [a]Calculated by Brus equation. [b] Absorbance onset. [c] Hydrodynamic diameter measured by DLS and reported as the number average.

Table S3 Properties of QD50-RT Ag_2S QDs *

Rxn Code	T (°C)	Rxn Time	λ_{em} (max) (nm)	Size[a] (nm)	Band gap (eV)	$\lambda_{abs(cutoff)}$ [b] (nm)	FWHM (nm)	Dh[c] (nm)	Zeta pot. (mV)
QD50-RT	25	3h	749	2.73	1.47	843	110	28.2 ± 11.7	48.8 ± 0.2

* Formulation: PEI/Cys=50/50 mol/mol, Ag:S = 4, reaction pH = 10.5. [a]Calculated by Brus equation. [b] Absorbance onset. [c] Hydrodynamic diameter measured by DLS and reported as the number average.

Table S4 Fluoresence lifetime analysis of QD60-RT*

T1 (ns)	T2 (ns)	T3 (ns)	T4 (ns)	B1 (%)	B2 (%)	B3 (%)	B4 (%)	Weight Average (ns)
11.66	42.17	154.79	1.55	17.54	45.69	35.17	1.60	75.78

*Components of PL decay of Ag_2S QDs were identified to be multiexponential in the form of;

$$A + B1\exp(-i/\tau 1) + B2exp(-i/\tau 2) + B3\exp(-i/\tau 3) + B4exp(-i/\tau 4)$$

where τ_1, τ_2, τ_3, τ_4 are decay components and B1, B2, B3 and B4 are percentage of related decay component.

Table S5 Composition analysis of Ag_2S QDs

PEI/Cys (mol/mol)[a]	Ag (wt %)[b]	N/S (mol/mol) [c] (Experimental)[d]	N/S (mol/mol) [c] (Theoretical)[e]
80/20	21.5	7.24	7.30
60/40	28.4	5.29	3.39
50/50	24.6	4.71	2.58

[a] Mol ratio was originally calculated as the total number of moles of primary and secondary amines of the branched PEI (25kDa) / moles of thiol coming from Cys. [b] Measured by ICP OES. [c] N = (moles of N coming from PEI) + (moles of N coming from Cys). S = moles of S coming from Cys. [d] Measured by CHNS/O Analyzer. [e] Based on feed ratio provided in first column.