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Electronic Supplementary Information

Ultra-bright Near-infrared-Emitting HgS/ZnS core/shell Nanocrystals for *in vitro* and *in vivo* imaging

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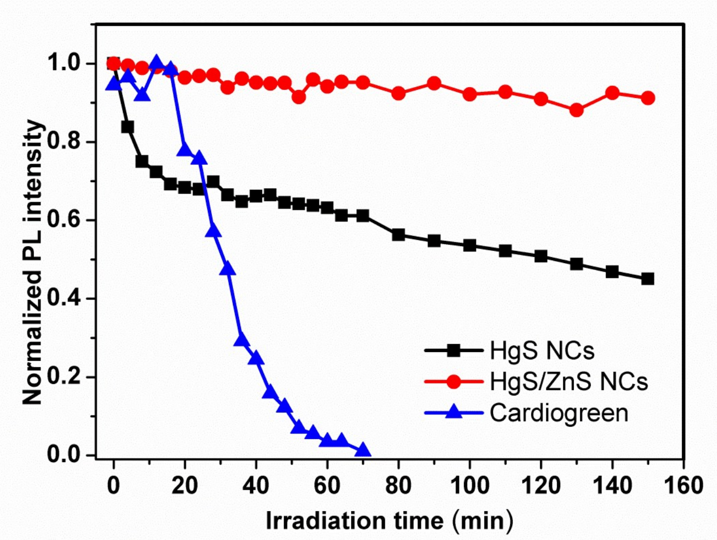

Fig. S1 The photo-stability studies of HgS/ZnS NCs, bare HgS NCs and cardiogreen when exposed to an 635 nm laser diode at a power density of 250 mW/cm^2 as a function of exposure time.

Fig. S1 illustrated the excellent photostability of the GSH-stabilized HgS/ZnS nanocrystals, which preserved more than 95% of its initial strong fluorescence intensity after 150 min of continuous irradiation of an 635 nm laser at a power density of 250 mW/cm^2. In contract, the bare HgS core barely retained 45% of its original PL intensity accompanied by the blue shift of PL emission due to photooxidation; while for indocyanine green (ICG), a classic NIR organic dye, loose completely its PL intensity within 70 min. This comparison indicated a superior photostability of the NIR-emitting NCs similar to conventional NCs which makes their use for long-term and real-time bioimaging applications possible.[1]

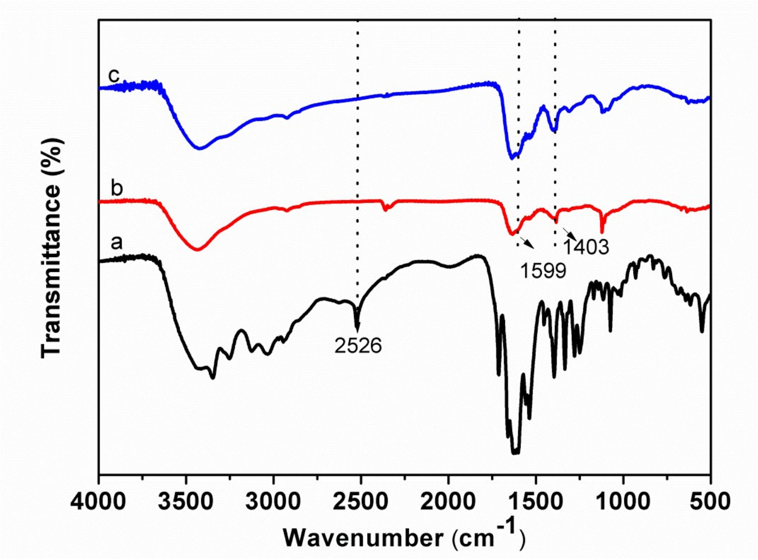

Fig. S2. Infrared spectra of (a) free GSH, (b) GSH-capped HgS NCs, and (c) GSH-capped HgS/ZnS NCs. The spectra are offset for clarity.

In the present work, GSH was used as a stabilizer to synthesize HgS/ZnS NCs. To study the role played by GSH, FT-IR spectra were taken for pure GSH, HgS NCs and HgS/ZnS NCs. As shown in Fig. S2, the IR spectra of the two types of NCs were very similar but were quite different from that of free GSH. Apparently, GSH binds in the same manner on the surfaces of the two NCs. The thiol group of GSH combines onto the surface of the NCs through the Hg-S bond in HgS NCs and Zn-S bond in HgS/ZnS NCs, as evidenced by the disappearance of S-H stretching frequency at 2526 cm^{-1}. The asymmetric (1599 cm^{-1}) and symmetric (1403 cm^{-1}) COO^- stretching band were observed in the spectra of two GSH-stabilized NCs, suggesting that the carboxylic groups of GSH deprotonated in the two NCs, which contributed to good water-solubility and colloidal stability to the NCs.

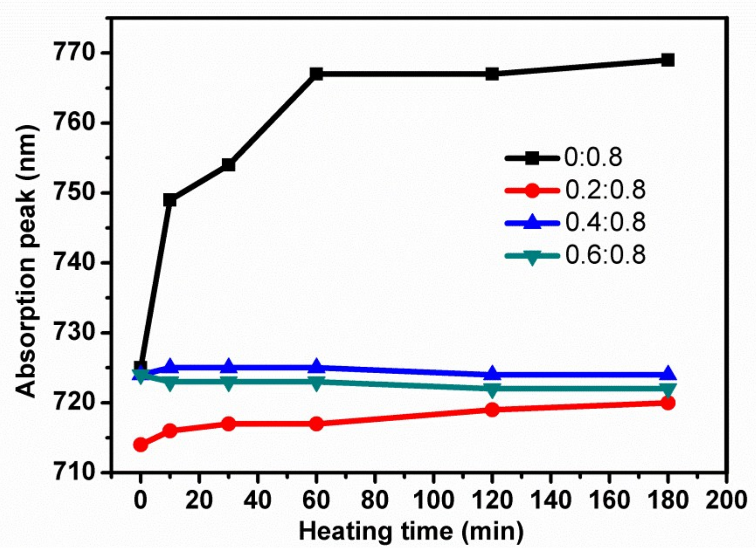

Fig. S3. Temporal evolution of absorption peaks of HgS/ZnS NCs obtained at different S-to-Zn molar ratios.

In our synthetic procedure, the molar ratio of S-to-Zn affected the controllable growth of HgS/ZnS NCs. When fixing the other experimental unchanged, the added amount of Na_2S was varied. Fig. S3 showed the evolution of PL spectra of HgS/ZnS core/shell nanostructure synthesized under different S-to-Zn molar ratio followed by heating at 95°C for 3h. When Zn-GSH complex was directly introduced intoto the freshly-prepared HgS core NCs solution and heating at 95°C, the colour of the Zn:HgS solution became darker and darker, and the absorption peak of solution continually vastly red-shifted from 725 to 769 nm, exhibiting the uncontrollable growth trends of HgS NCs. Correspondingly, the emission spectra red-shifted and became broadened and asymmetry. This indicated that the slow release of sulfur atoms from the organic sulfur supplier GSH at nearly neutral pH values leads to insufficient coating the surface of HgS NCs.[2] While additional introduction of a portion of Na_2S (S/Zn molar ratio at 0.2:0.8) to form a ZnS shell on the HgS NCs prior to heating, the uncontrollable growth of HgS NCs was drastically hindered. The absorption peak of the resultant HgS/ZnS NCs red-shifted a small shift of 8 nm with heating. In this step, the surface mercury site was pre-surrounded by a ZnS shell, and only a small portion of reactive Hg^{2+} were exposed on the surface, thus the uncontrollable growth of HgS NCs was hindered significantly. Continued to increase the molar ratio of S/Zn molar ratio to 0.4:0.8, the absorption peak and emission peak of HgS/ZnS NCs were not obviously dependent on the duration of heating, maintaining their PL peak at 785 nm (Fig. 1B), suggesting the uncontrollable growth of HgS NCs was completely hampered due to a compact ZnS shell with proper thickness being obtained in this state. If further increase the amount of introduced Na_2S to S/Zn of 0.6:0.8, the absorption peaks of HgS/ZnS NCs has not shifted appreciably, however, the profile of PL spectra became deteriorated, besides the major peak at 775 nm, two additional peaks at 909 nm and 1023 nm were observed, suggesting that excessive S^{2-} not benefit to form high-quality HgS/ZnS NCs. Experimental results showed the S/Zn molar ratio at 0.4:0.8 facilitated to form a proper ZnS shell passivated on HgS NCs, transferring the uncontrollable HgS NCs to be a controllable HgS/ZnS core/shell NCs.

References:

1. X. Michalet, F. F. Pinaud, L. A. Bentolila, J. M. Tsay, S. Doose, J. J. Li, G. Sundaresan, A. M. Wu, S. S. Gambhir and S. Weiss, *Science*, 2005, **307**, 538-544.

2. J. Zhang, J. Li, J. Zhang, R. Xie and W. Yang, *J. Phys. Chem. C*, 2010, **114**, 11087-11091.