Supporting information

Near-infrared light-responsive nanocomposite for photothermal release of H₂S and suppression of cell viability

Haifeng Li, a Yu Yao, a Hui Shi, a Yanli Lei, b Yan Huang, a Kemin Wang , a Xiaoxiao He a,* and Jianbo Liu a,*

a State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Biology, College of Chemistry and Chemical Engineering, Key Laboratory for Bio-Nanotechnology and Molecular Engineering of Hunan Province, Hunan University, Changsha 410082 (China)
b School of Chemistry and Food Engineering, Changsha University of Science and Technology, Changsha 410114, China.

*Address correspondence to these authors at: State Key Laboratory for Chemo/Biosensing and Chemometrics, College of Biology, College of Chemistry and Chemical Engineering, Hunan University, Changsha, 410082, P. R. China. E-mail: xiaoxiaohe@hnu.edu.cn, liujianbo@hnu.edu.cn; Fax/Tel: +86 731 88821566.
Figure S1. FTIR spectra of PEI and PEI-DTC powders. In comparison with polymer PEI, new FTIR peaks at 1389 cm$^{-1}$ and 974 cm$^{-1}$ can be noticed for PEI-DTC, which are attributed to the asymmetric stretching vibration of CS-NH and the symmetric stretching vibration of C-S in dithiocarbamate, respectively.

Figure S2. $^{13}$C NMR spectra of PEI and PEI-DTC. The structure of the polymer PEI and the newly synthesized PEI-DTC was characterized by $^{13}$C NMR. A new peak at 211.0 ppm emerged for polymer PEI-DTC, which might be caused by carbon in the dithiocarbamate ester of PEI-DTC, generated from the condensation reaction of dithiocarbamate between CS$_2$ and the amine group in the PEI polymer. This further confirms the successful synthesis of the polymer PEI-DTC.
Figure S3. (A) UV-vis adsorption, and (B) standard curve for colorimetric assay of H₂S generated from thermal degradation of PEI-DTC. The qualification of PEI-DTC was based on the characteristic adsorption peak at 290 nm.

Figure S4. (A) The mechanism illustration of the methylene blue colorimetric assay for H₂S determination. (B) UV-vis adsorption spectra, and (C) standard curve for colorimetric assay of H₂S made from different concentrations of H₂S. The qualification of H₂S was based on the characteristic adsorption peak at 670 nm.
**Figure S5.** Time dependent thermogravimetric analysis of rGO-PEI-DTC nanocomposites (0.25 mg·mL⁻¹) under 50°C.

**Figure S6.** Time-dependent H₂S generation from different nanocomposites (100-250 μg·mL⁻¹) under NIR light irradiation. Laser power: 3.0 W·cm⁻² at 780 nm.
Figure S7. Time-dependent H$_2$S generation from rGO-PEI-DTC nanocomposites (250 μg·mL$^{-1}$) and PEI-DTC (158 μg·mL$^{-1}$) under laser illumination (3.0 W·cm$^{-2}$ at 780 nm).

Figure S8. Relative cell viabilities of MCF-7 cells treatment with rGO-PEI-DTC nanocomposites at different concentrations. The cell viabilities were determined through MTS experiments.
Figure S9. The MTS cell viability assay. Cells were treated under NIR irradiation (780 nm at 2.0 W·cm⁻², for 10 min).

Figure S10. The CLSM images of cells treated with different nanocomposite sample, NIR laser irradiation (780 nm at 2.0 W·cm⁻², 10 min). Scale bar: 50 μm. H₂S fluorescence probe (WSP-5) was used to determine the intracellular production of H₂S by NIR irradiation of rGO-PEI-DTC nanocomposite. The polymer donor PEI-DTC, rGO nanosheets and NIR illumination are three necessary conditions for the photothermal generation of H₂S. The absence of any of the three conditions will result in the failure or inefficiency production of H₂S. rGO nanosheets nanocomplex loaded with the polymer PEI-DTC can generate H₂S by NIR irradiation, which is
much higher than the case with the polymer PEI-DTC alone.

Figure S11. The CLSM images of MCF-7 cells treatment with rGO-PEI-DTC (0.10 mg·mL\(^{-1}\)) and NIR light irradiation for 0-6 min at different laser irradiation (1.0-3.0 W·cm\(^{-2}\)). Scale bar: 20 μm. H\(_2\)S fluorescence probe (WSP-5) was used to determine the intracellular production of H\(_2\)S by NIR light irradiation of rGO-PEI-DTC nanocomposites. The illumination time and laser power of rGO-PEI-DTC nanocomposites are the determinants of H\(_2\)S production.

Figure S12. The microscopic images of cells before (A) and after (B) incubation with rGO-PEI-DTC nanocomposites for 4 h.