Supplementary information

Rapid tumor bioimaging and photothermal treatment based on

GSH-capped red fluorescent gold nanoclusters

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Synthesis and purification of GSH stabilized Au NCs:

The red-emitting Au NCs were synthesized by a CO-reduction method¹. In a typical synthesis, aqueous solutions of HAuCl₄ (12.5 mL, 20 mM) and GSH (7.5 mL, 50 mM) were added to a 500-mL flask containing 230 mL of ultrapure water. After 2 min of vigorous stirring, the pH value of the reaction solution was brought to 11.0 with 1 M NaOH. Thereafter, CO was bubbled through the reaction solution for 2 min, and the reaction solution was sealed airtight and stirred at 500 rpm at room temperature. After 0.5 h, the remaining CO was released and the solution pH value was adjusted to 2.5 with 1 M HCl. The reaction solution was then sealed airtight and aged for 24 h. An aqueous solution of strong red-emitting Au NCs was formed.

The synthesized Au NCs can be separated from the reaction solution by ultrafiltration and ethanol precipitation. The solution was filtered by 0.22 μ m filter and further centrifuged by ultrafilter (Pall Corporation, formula weight cutoff 10 kDa) to cut down the large-sized nanoparticles. To avoid the interference from the free GSH, the supernatant was further purified by adding an amount of ethanol into the aqueous solution (the ratio between water and ethanol is 1:1) and centrifuged at 12000 rpm for 10 min. Under such condition, the fluorescent Au NCs were precipitated out of the solution while the free GSH remained in the solution. The precipitates were then resuspended in an aqueous solution to get the final solution containing Au NCs. The final solution was stored at 4 °C when not in use.

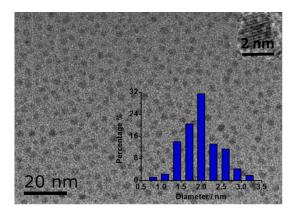


Fig. S1 Typical TEM image of Au NCs. Inset: high resolution image with the crystallinity of the metallic structure and the size distribution histogram of Au NCs by counting 263 particles.

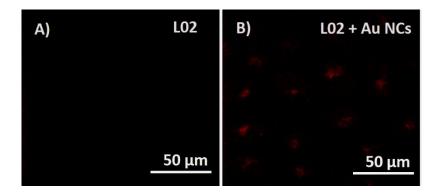


Fig. S2 Laser confocal fluorescence micrographs of L02 cells after incubation for 24 h in the absence of Au NCs (A) and in the presence of 300 μ M Au NCs (B). The micrographs of cells were acquired by 40 × IR coated objective. The excitation wavelength was at 532 nm.

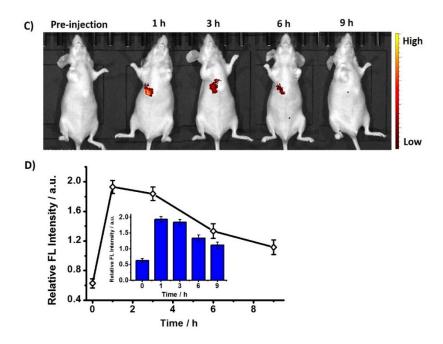


Fig. S3 Representative xenograft tumor nude mice models of U87 cells by *in vivo* NIR fluorescence imaging. (A) *In vivo* fluorescence imaging pre injection and after a subcutaneous injection 5 mM Au NCs for 1, 3, 6, and 9 h. The excitation wavelength was 520 nm. (B) Statistical analysis of the fluorescence intensity corresponded to the fluorescence images of bearing U87 tumor mice.

References

1 Y. Yu, Z. Luo, D. M. Chevrier, D. T. Leong, P. Zhang, D. E. Jiang and J. Xie, *J. Am. Chem. Soc.*, 2014, **136**, 1246-1249.