

## Electronic Supplementary Information

### Ultrasensitive chemiluminescent biosensor for tracing glutathione in human serum using BSA@AuNCs as peroxidase-mimetic nanozyme on luminol/ artesunate system

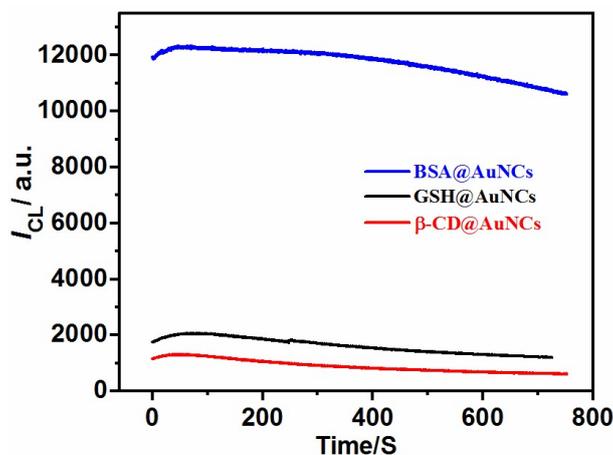
Mohamed Ibrahim Halawa,<sup>a,b,c\*</sup> Qing Xia,<sup>a</sup> Bing Shi Li<sup>a\*</sup>

<sup>a</sup> College of Chemistry and Environmental Engineering, Shenzhen University, Shenzhen 518060, China.

<sup>b</sup> College of Physics and optoelectronic engineering, Shenzhen University, Shenzhen 518060, China.

<sup>c</sup>Department of Pharmaceutical Analytical Chemistry, Faculty of Pharmacy, Mansoura University, Mansoura 35516, Egypt.

\* **Corresponding Author:** E-mail: m\_halawa88@hotmail.com, phbingsl@szu.edu.cn; Fax: +86-755-26536141; Tel: +86-755-26558094



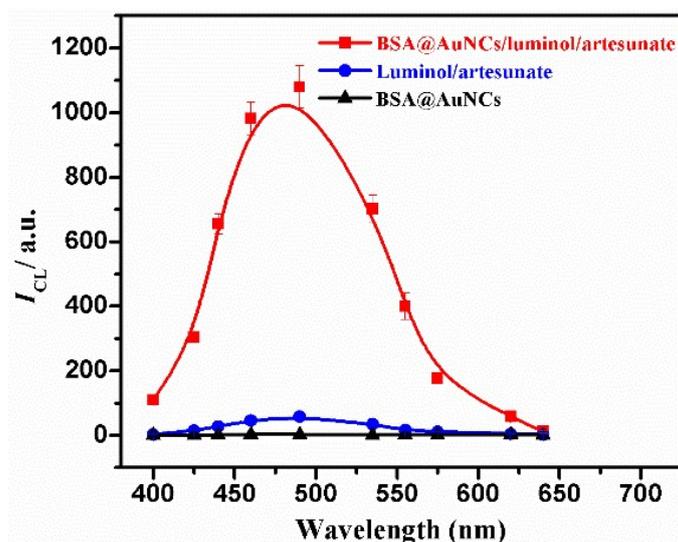
**Figure S1:** Effect of different AuNCs (BSA@AuNCs,  $\beta$ -CD@AuNCs, and GSH@AuNCs) on CL intensity of luminol/artesunate system. Carbonate buffer (0.2 M), pH 13; concentrations of luminol, artesunate and AuNCs are 200  $\mu$ M, 1.0 mM and 0.166 X; respectively.

#### Synthesis of the $\beta$ -CD@AuNCs<sup>1</sup>:

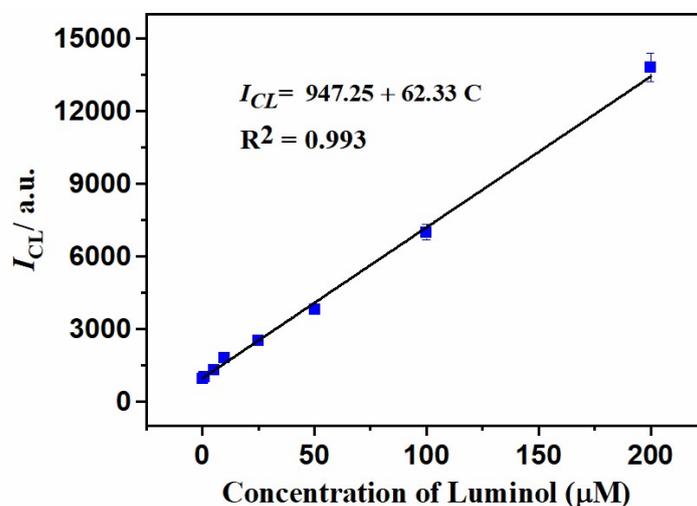
$\beta$ -CD stabilized AuNCs was synthesized as follows. After heating an aqueous solution of HAuCl<sub>4</sub> (1 mM, 5.0 mL) at 90° C for 10 minutes, 567.5 mg of  $\beta$ -CD was added under vigorous stirring so that the molar ratio between AuCl<sub>4</sub><sup>-</sup> and  $\beta$ -CD was at 1:100. Then, NaOH solution (2.5 mL, 1 M) was quickly added after 5 minutes into the mixture. The mixture was continuously heated at 90° C for 4 hours with vigorous stirring. The color of the solution immediately changed from pale yellow to light brown, then to dark brown revealing the successful formation of AuNCs. The synthesized  $\beta$ -CD@AuNCs was centrifuged, purified by dialysis and stored 4 °C.

#### Synthesis of GSH@AuNCs<sup>2</sup>:

Freshly prepared aqueous solutions of HAuCl<sub>4</sub> (20 mM, 0.50 mL) and GSH (100 mM, 0.15 mL) were mixed with 4.35 mL of ultrapure water at 25 °C. The reaction mixture was heated to 70 °C under gentle stirring (500 rpm) for 24 h. An aqueous solution of strongly orange-emitting Au NCs was formed. The synthesized GSH@AuNCs was purified by dialysis and stored 4 °C.



**Figure S2:** CL intensities of BSA@AuNCs/luminol/artesunate, BSA@AuNCs/luminol, and BSA@AuNCs *versus* the wavelength (400 - 640 nm). Carbonate buffer (0.2 M), pH 13; Concentrations of luminol, artesunate and BSA@AuNCs are 200  $\mu$ M, 0.5 mM and 0.1 X; respectively. PMT=800V.



**Figure S3:** Calibration plot shows the linear relationship between CL intensity and luminol concentrations through the concentration range from 0.1  $\mu$ M to 200.0  $\mu$ M. The CL intensities were measured at carbonate buffer solution (0.2 M, pH 13) using 0.166 X of BSA@AuNCs and 1.0 mM artesunate.

**Table S1.** Assay results for GSH detection in diluted human serum samples.

Target	Amount found (nM)	Amount spiked (nM)	Total found (nM)	Recovery (% , n= 3)	RSD (% , n= 3)
GSH	3.15	100.0	101.82	98.71	3.25
		250.0	261.20	103.18	4.42
		1000.0	1020.02	101.68	3.88

1. M. I. Halawa, F. Wu, T. H. Fereja, B. Lou and G. Xu, *Sensors Actuators B: Chem.*, 2018, **254**, 1017-1024.
2. Z. Luo, X. Yuan, Y. Yu, Q. Zhang, D. T. Leong, J. Y. Lee and J. Xie, *J. Am. Chem. Soc.*, 2012, **134**, 16662-16670.