## **Supporting Information**

# Ultrasensitive Colorimetric Detection of Heparin Based on Self-assembly of Gold Nanoparticles on Graphene Oxide

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**Fig. S1.** TEM image (A) and UV-Vis absorption (B) of AuNPs. Inset of (B) shows the photographic image of AuNPs.



Fig. S2. UV-Vis absorption of AuNPs at different conditions: (a) GO/protamine+AuNPs,
(b) GO/protamine+heparin+AuNPs, (c) AuNPs, (d) GO+AuNPs, (e) GO+heparin+AuNPs.



**Fig. S3.** Plots of  $A_{520}/A_{655}$  versus the concentrations of heparin for AuNPs in different concentrations of GO/protamin mixed solutions in 10 mM HEPES solution (pH 7.4).



Fig. S4. (A) Plots of  $A_{520}/A_{655}$  versus the concentrations of heparin in 10 mM HEPES solution; (B) Polts of the value of  $A_{520}/A_{655}$ -blank versus pH values in the presence of 0.02 and 0.04 µg/mL of heparin.



Fig. S5. Plots of  $A_{520}/A_{655}$  versus the concentrations of heparin using different sizes of AuNPs in 1 µg/mL of GO/protamin mixed solutions in 10 mM HEPES buffer solution (pH 7.4).

Table S1. Comparisons of analytical performances of various typical methods for heparin detection.

Methods	Technique in detail	Linear range	Detection limit	Test media	Applications	Ref.
Colorimetry	Self-assembly of AuNPs on the	0.06–0.36 µg/mL	3.0 ng/mL	HEPES (10 mM, pH	Fetal bovine serum	Present work
	surface of GO		(0.000555 U/mL)	7.4)	(detection limit 1.7	
					ng/mL)	
Colorimetry	Color quenching of gold nanorods by	0.02–0.28 µg/mL	5 ng/mL (0.0009	HEPES (10 mM, pH	NA	1
	GO		U/mL)	7.4)		
Colorimetry	Electrostatic interaction leading to	0.09–3.12 µg/mL	0.03 µg/mL	Britton-Robinson ( pH	Human serum	2
	the aggregation of positively-charged AuNPs			3.6)	samples	
Colorimetry	Electrostatic interaction leads to the	0–6.7 U/mL	0.01 U/mL	Methanol–water (3:2,	Fetal bovine serum	3
	absorbance change of a water-soluble			v/v)	(detection limit:	
	polymer and color change				0.15 U/mL)	
Colorimetry	Reversible aggregation and	0.6–10 µg/mL	0.6 µg/mL	PBS (2 mM, pH 7.2)	NA	4
	de-aggregation of nano-sized AuNPs					
Fluorometry	Ratiometric fluorescence detection	1.0–15 μM	20 nM	HEPES (5 mM, pH 7.4,	Horse serum matrix	5
	based on aggregation-induced			containing 2‰ DMSO)		
	fluorescence quenching and					
	enhancement		20.14			-
Fluorometry	Fluorescent detection using a cationic	0–0.7 μM	30 nM	HEPES (2 mM, pH	NA	6
	conjugated polyfluorene probe			7.4)		
	containing aggregation-induced					
	emission units		NT A		F (11 )	7
Fluorometry	Turn-on fluorescent detection using	UFH: 0-0.56 IU	NA	HEPES (5 mM, pH	Foetal bovine serum	/
	NIK-emissive alkynylplatinum (II)	mL <sup>-</sup> ;		/.4)		

	terpyridyl complex by induced	LMWH: 0-0.36				
	helical self-assembly behaviour	$IU mL^{-1}$				
Fluorometry	Coupled using of butterfly-shaped	0–1.76 U/mL	0.046 U/mL	PBS (10 mM, pH 7.4)	NA	8
	conjugated oligoelectrolyte and GO					
	for light-up fluorescence detection					
Fluorometry	Ratiometric fluorescence sensor	5–30 µM	0.157 μΜ	HEPES (10 mM,	Fetal bovine serum	9
	based on a pyrene derivative			water/ethanol, 85/15,	medium	
				v/v, pH 7.4)	(detection limit:	
					0.53 μM)	
Light	Turn-on room temperature	Tunable	$0.014 \ \mu M$ (the	Tris-HCl (10 mM, pH	Human serum	10
scattering	phosphorescence assay based on		highest sensitivity)	7.4)	samples (detection	
	target induced self-assembly of (PEI)				limit: 0.15 µM)	
	capped Mn-doped ZnS QDs					
Electrochemist	Reversible potentiolmetric detection	1-20 U/mL	NA	PBS (10 mM, pH 7.4)	NA	11
ry	using pulsed chronopotentiometric					
	polymer membrane electrode					
Electrochemist	Cyclic voltammetry detection using a	4.0–22.0 µg/mL	0.28 µg/mL	HClO <sub>4</sub> (0.1 M)	Heparin sodium	12
ry	poly(thionine) modified glassy				injection	
	carbon electrode					

PEI: polyethyleneimine; QDs: quantum dots; UFH: unfractionated heparin; LMWH: low molecular weight heparin; NA: not available.

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