

## Supporting Information

### Glucose Oxidase-Catalyzed Growth of Gold Nanoparticles Enables Quantitative Detection of Attomolar Cancer Biomarkers

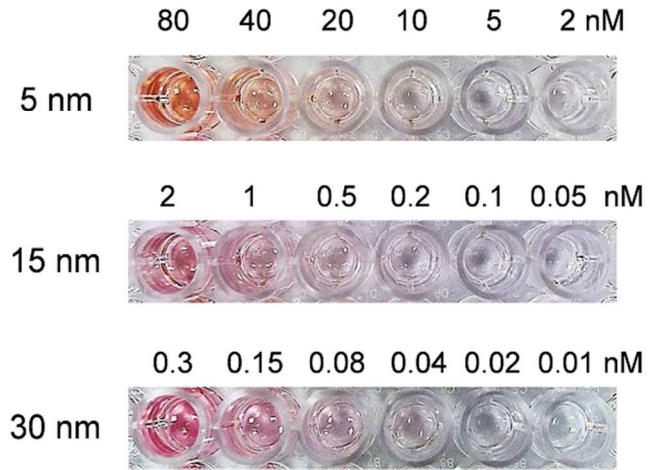
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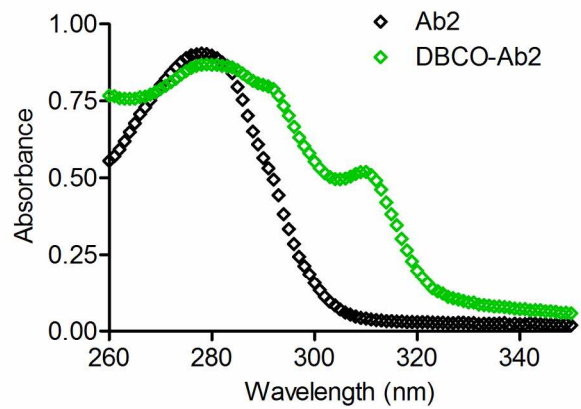
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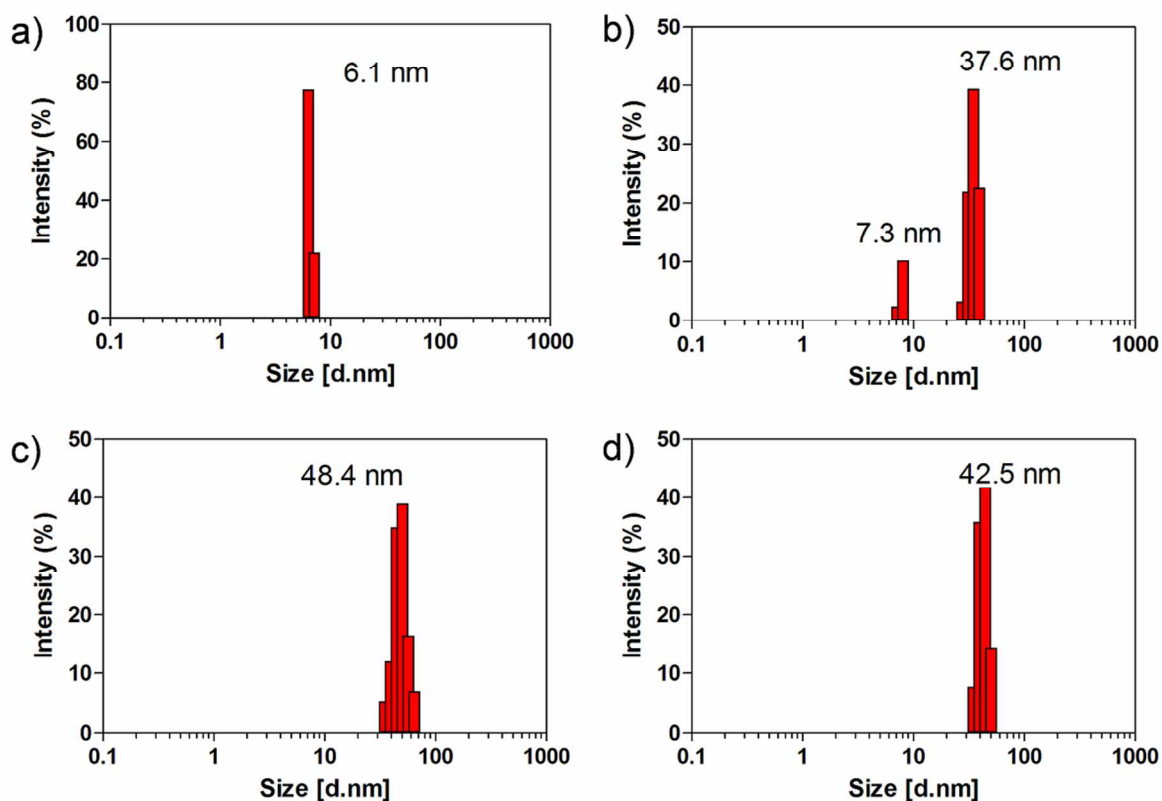
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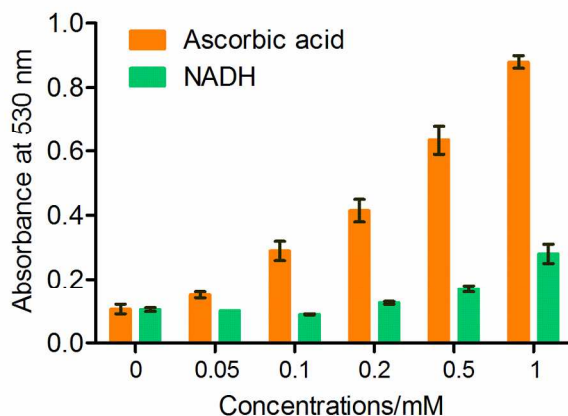
**Figure S1.** Color of various concentrations of AuNP solutions with different sizes of the particles.



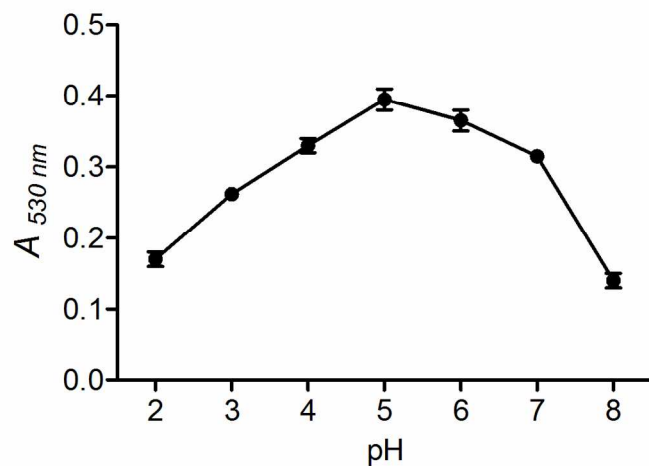
**Figure S2.** UV-vis absorption spectra of purified PSA detection antibody (black) and that labeled with dibenzocyclooctyl (DBCO) moieties (green). The absorption band at 309 nm indicates the DBCO moieties on Ab2.



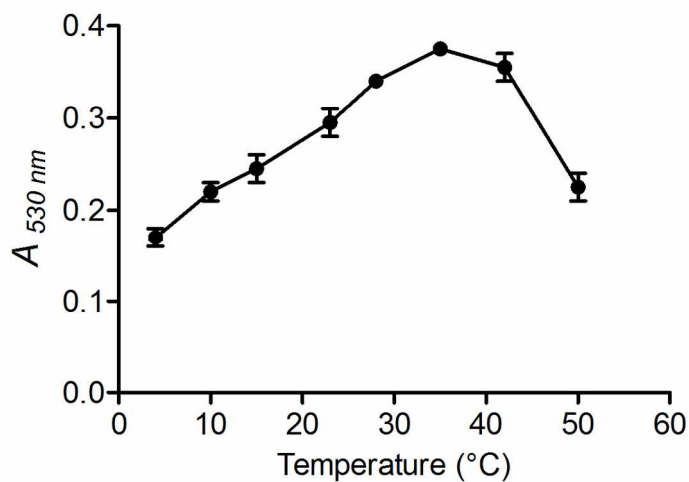
**Figure S3.** Dynamic light scattering (DLS) analysis of 5 nm AuNP seeds (a) and those in the presence of H<sub>2</sub>AuCl<sub>4</sub> (0.6 mM) and 10 (b), 100 (c), and 1000 (d) μM of H<sub>2</sub>O<sub>2</sub> respectively.



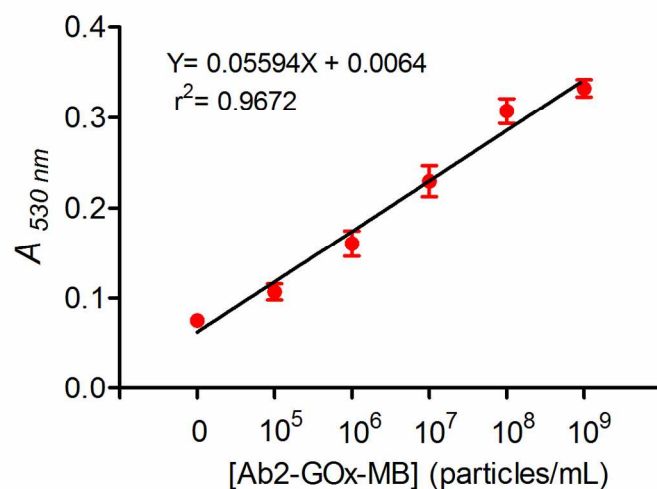
**Figure S4.** Various concentrations of ascorbic acid and nicotinamide adenine dinucleotide (NADH) cause the growth of 5 nm AuNPs respectively, which was indicated by the absorbance at 530 nm. Error bars show the standard deviations of three independent measurements.



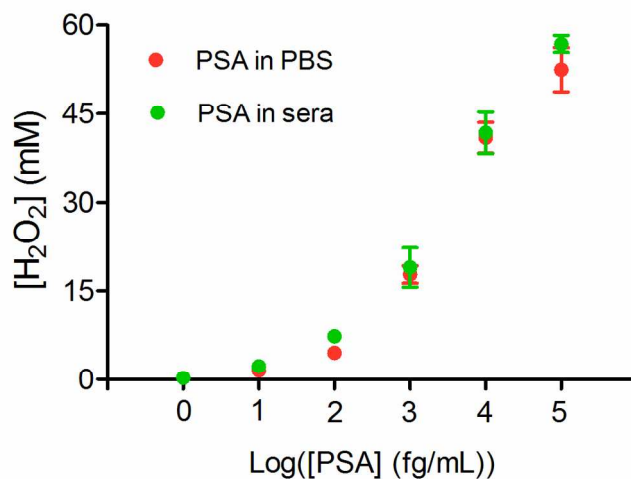
**Figure S5.** The effect of pH values on the biocatalytic reaction of glucose oxidase with glucose, which was monitored by the colorless-to-red assay. Error bars show the standard deviations of three independent measurements.



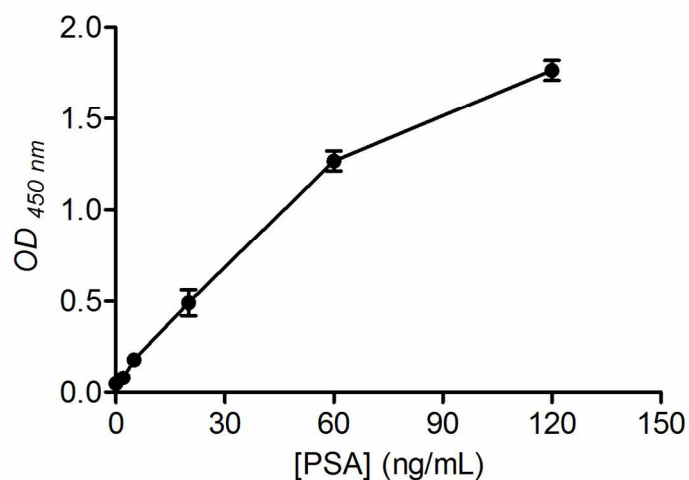
**Figure S6.** The effect of temperatures on the biocatalytic reaction of glucose oxidase with glucose, which was monitored by the colorless-to-red assay. Error bars show the standard deviations of three independent measurements.



**Figure S7.** Detection of the colorless-to-red assay for various concentrations of Ab2-GOx-MB ranging from  $10^5$  to  $10^9$  particles/mL. Error bars show the standard deviations of three independent measurements.



**Figure S8.** Measurements of the generated  $H_2O_2$  by a  $H_2O_2$  Assay Kit (ab102500) for various concentrations of PSA spiked in PBS and sera respectively. Error bars show the standard deviations of three independent measurements.



**Figure S9.** HRP-based ELISA for the detection of various concentrations of PSA spiked in fetal bovine sera. The OD values at 450 nm were recorded by a Synergy 2 Multi-Mode Microplate Reader. Error bars show the standard deviations of three independent measurements.

**Table S1** A comparison of detection performance for biosensors based on nanotechnology.

Readout	Target	Nanomaterial	Linear range	Detection limit	Real sample	Ref.
Fluorescence	PSA	MPs	N/A	1.5 fg/mL	Serum	[1]
Fluorescence	CEA	Au film	0.2 pg/mL–20 ng/mL	1 pg/mL	Serum	[2]
Fluorescence	Troponin I	Chimeric NPs	0.1 pg/mL–10 ng/mL	0.1 fg/mL	Serum	[3]
Fluorescence	CEA	QDs	5 pg/mL–50 ng/mL	0.5 ng/mL	Serum	[4]
Electrochemistry	IL-6	SWNTs	N/A	0.5 pg/mL	Serum	[5]
Electrochemistry	IL-8	MPs	1–500 fg/mL	1 fg/mL		[6]
Electrochemistry	Thrombin	MPs	0.001–100 ng/mL	0.2 pg/mL	N/A	[7]
Electrochemistry	CEA	AuNPs	0.01–160 ng/mL	0.005 ng/mL	Serum	[8]
Scanometric	PSA	AuNPs	0.1 fg–10 pg/mL	1 fg/mL	N/A	[9]
Scanometric	HIV	AuNPs	N/A	N/A	blood	[10]

SPR	PSA	MPs	N/A	10 fg/mL	Serum	[11]
DLS	PSA	AuNPs	0.1–10 ng/mL	0.1 ng/mL	N/A	[12]
Raman	aPR3	SWNTs	N/A	0.15 pg/ml	Serum	[13]
Raman	VEGF	AuNPs	0.1–10 ng/mL	7 fg/mL	Blood	[14]
Plasmonics	PSA	AuNSs	$10^{-18}$ – $10^{-14}$ g/mL	$10^{-18}$ g/mL	Serum	[15]
Plasmonics	HIV	AuNPs	N/A	98 ± 39 copies/mL	Blood	[16]
Colorimetric	PSA and P24	AuNPs	N/A	$1 \times 10^{-18}$ g/mL	Serum	[17]
Colorimetric	PSA	AuNPs	0.05–20 ng/mL	0.03 ng/mL	Serum	[18]
Colorimetric	EV71	AuNPs	N/A	$1 \times 10^4$ copies/mL	HTS	[19]
Colorimetric	PSA	AuNPs	$10$ – $10^5$ fg/mL	4.6 fg/mL	Serum	This study

*Abbreviation:* PSA, prostate-specific antigen; MPs, magnetic particles; N/A, not available; CEA, carcinoembryonic antigen; NPs, nanoparticles; QDs, quantum dots; IL-6, interleukin 6; SWNTs, single-walled carbon nanotubes; IL-8, interleukin 8; AuNPs, gold nanoparticles; aPR3, anti-proteinase 3; VEGF, vascular endothelial growth factor; EV71, enterovirus 71; HTS, human throat swab.

**Table S2** Extinction coefficients for gold nanoparticles with various sizes (the data was obtained from TED PELLA, INC. [http://www.tedpella.com/gold\\_html/gold-tec.htm](http://www.tedpella.com/gold_html/gold-tec.htm)).

Size (nm)	5	10	15	20	30	40	50	60	80	100
Extinction coefficient ( $M^{-1}cm^{-1}$ )	$9.696 \times 10^6$	$9.550 \times 10^7$	$3.640 \times 10^8$	$9.406 \times 10^8$	$3.585 \times 10^9$	$9.264 \times 10^9$	$1.935 \times 10^{10}$	$3.531 \times 10^{10}$	$9.124 \times 10^{10}$	$1.905 \times 10^{11}$

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