Graphene/Gold Nanoparticles Composites for Ultrasensitive and Versatile Biomarker Assay Using Single-Particle Inductively-Coupled Plasma/Mass Spectrometry

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Table of Contents

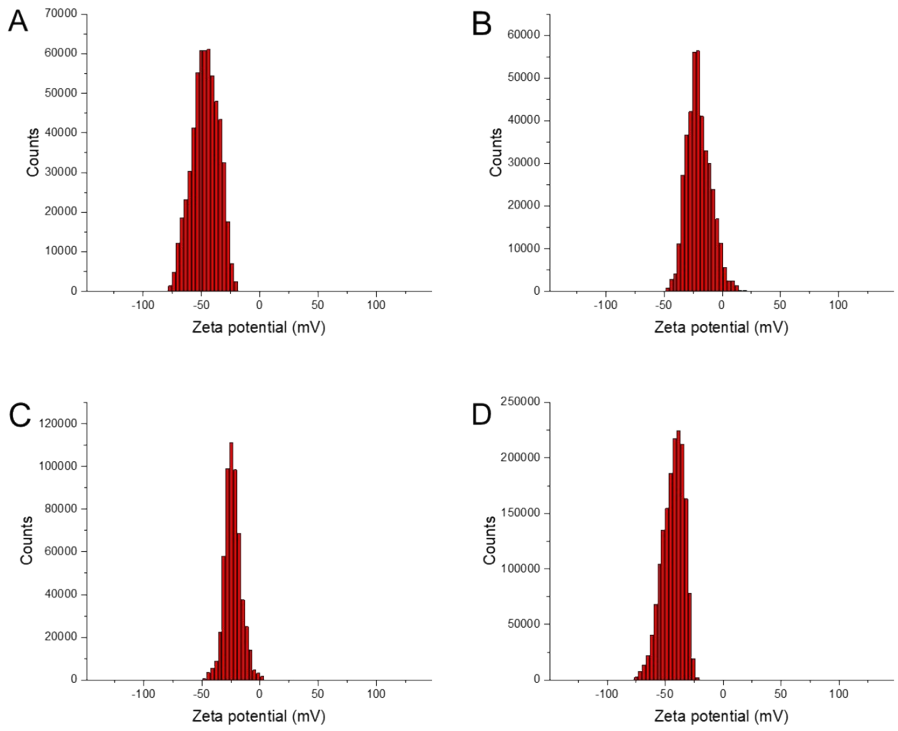

Figure S1. Zeta potential measurements of the nanomaterials. A, bare AuNPs (-43 ± 3 mV); B, AuNPs-TOEG6 (-20 ± 2 mV); C, AuNPs-aptamer (-26 ± 3 mV); D, GO (-43 ± 1 mV).

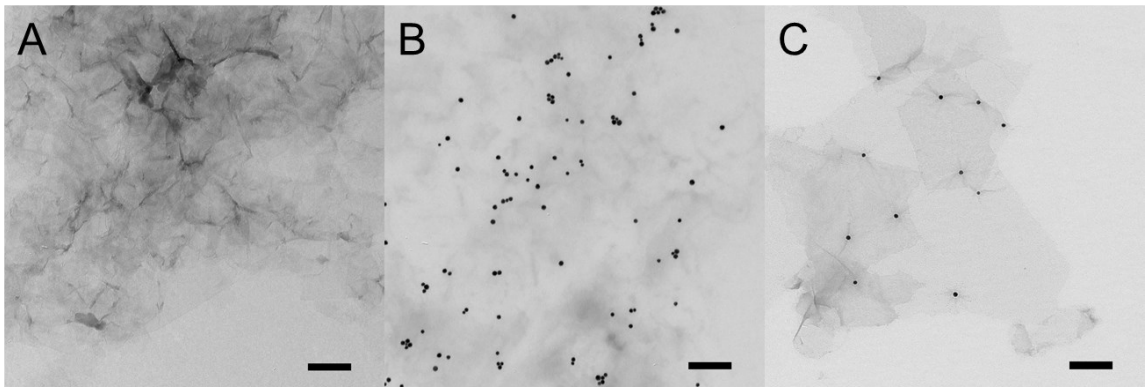

Figure S2. TEM image of GO (A), AuNPs (B), and GO/AuNPs composites (C) re-dispersed in water. The GO/AuNPs composites were obtained by incubating a 50 μL aliquot of 5×10^{11} particle/mL AuNPs-aptamer and 50 μL of 400.0 μg/mL of GO in 1.0 mL of PBS buffer (10 mM with 0.5 mM $MgCl_2$, pH 7.4) at room temperature for 30 min. Scale bar: 200 nm.

Table S1. ICP-MS instrument parameters used for conventional and single-particle measurements.

Parameter	Conventional measurement	Single-particle measurement
Sample introduction		
peristaltic pump	4-channel, 12-roller	4-channel, 12-roller
pump speed (rpm)	20	20
sample tubing (mm ID)	0.508	0.508
internal-standard tubing (mm ID)	0.508	not used
waste tubing (mm ID)	1.295	1.295
nebulizer	Microflow PFA-ST	Microflow PFA-ST
nebulizer gas flow (L/min)	1.09	1.05
spray chamber	quartz cyclonic	quartz cyclonic
spray chamber temperature (℃)	2.70	2.70
Plasma		
torch	ICAP Q quartz	ICAP Q quartz
Rf power (W)	1550	1550
coolant gas flow (L/min)	14	14
plasma gas flow (L/min)	0.8	0.8
sample injector	quartz (2.5 mm ID)	quartz (2.5 mm ID)
Mass spectrometer		
sample cone	nickel	nickel
skimmer cone	nickel	nickel
cone insert	3.5 mm	2.8 mm
mode	KED	STDS
KED gas flow (mL/min)	4.6	0
dwell Time (ms)	50	5
sweeps	10	0
internal standards	^{103}Rh, ^{209}Bi	none

Table S2. AuNPs particle number concentration quantified by spICP-MS and conventional ICP-MS.

Particle number concentration (particle/mL)	Detected number of AuNPs	Predicted number of AuNPs*	Conventional ICP-MS (ppb) LOD: 0.005 ppb	Theoretical Concentration (ppb)#
100	10.5	4.05	[b]	8.1×10^{-6}
500	28.25	20.25	[b]	4.1×10^{-5}
1000	56	40.5	[b]	8.1×10^{-5}
5000	310.5	202.5	[b]	4.1×10^{-4}
10^4	645.25	405	[b]	8.1×10^{-4}
10^5	4957.25	4050	[b]	0.0081
10^6	[a]	40500	0.024	0.081
10^7	[a]	405000	0.274	0.81

*based on the following conditions: flow rate at 0.2 mL/min, collection time for 3 min, Transport efficiency at 6.45%# average mass of 20 nm AuNPs: 8.1×10^{-17} g

[a] particle numbers by spICP-MS were inaccurate because multiple particles were sampled per dwell time

[b] concentration measured conventional ICP-MS was below LOD

Table S3. Effect of TOEG6 concentration on aptamer binding to AuNPs.

AuNPs (nM)	ssDNA (μM)	TOEG6 (μM)	No. of ssDNA/NP
0.5	0.25	3	10
0.5	0.25	5	9
0.5	0.25	7	8
0.5	0.25	10	5
0.5	0.25	15	1