

Supporting Information

in

A ratiometric electrochemical sensor for detection multiplex cancer
biomarkers using bismuth as internal reference and metal sulfide nanoparticles
as signal tags

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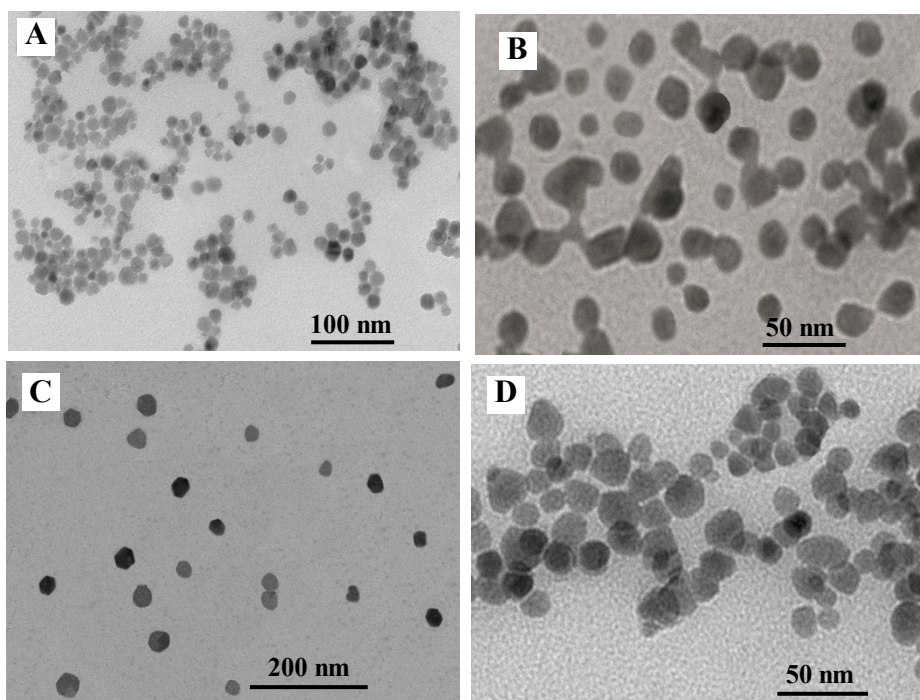


Fig. S1 TEM images of CdS (A), HgS (B), PbS (C), ZnS (D) nanoparticles.

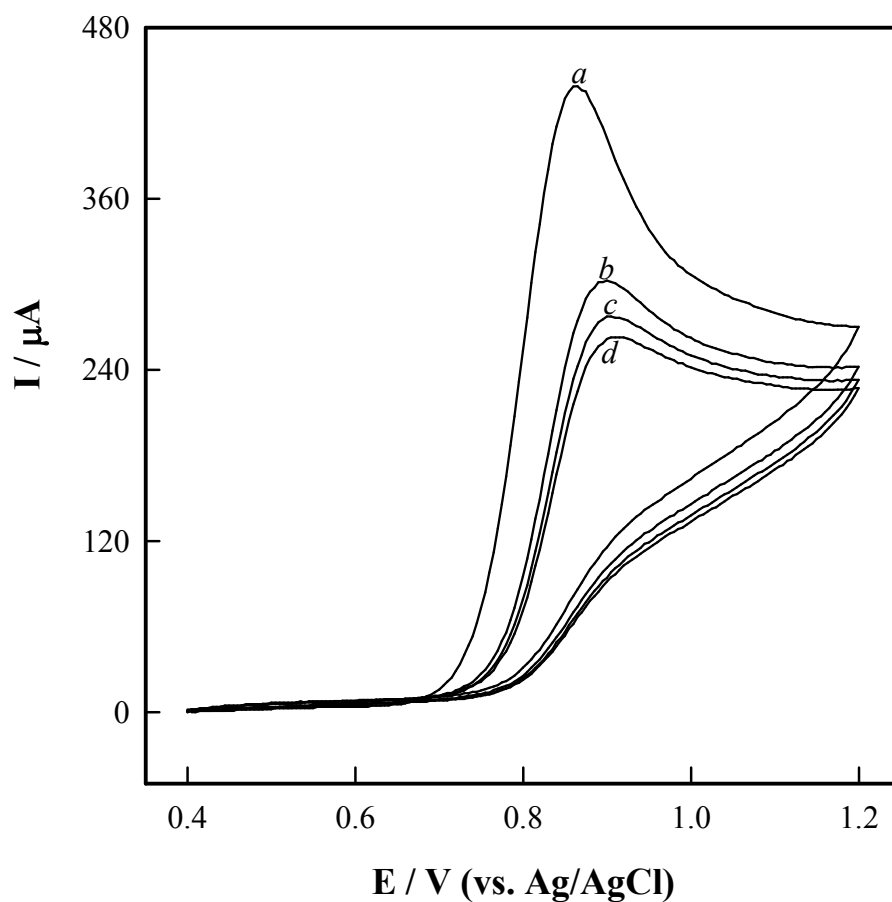


Fig. S2 Repetitive cyclic voltammograms of GCE during the polymerization in 2.0 mM ATA +0.20 mg mL⁻¹ CNTs+ 5.0 mM H₂SO₄ solution. Potential scan rate: 10 mV s⁻¹. Curves *a* to *d* corresponding to scanning cycle number of 1 to 4.

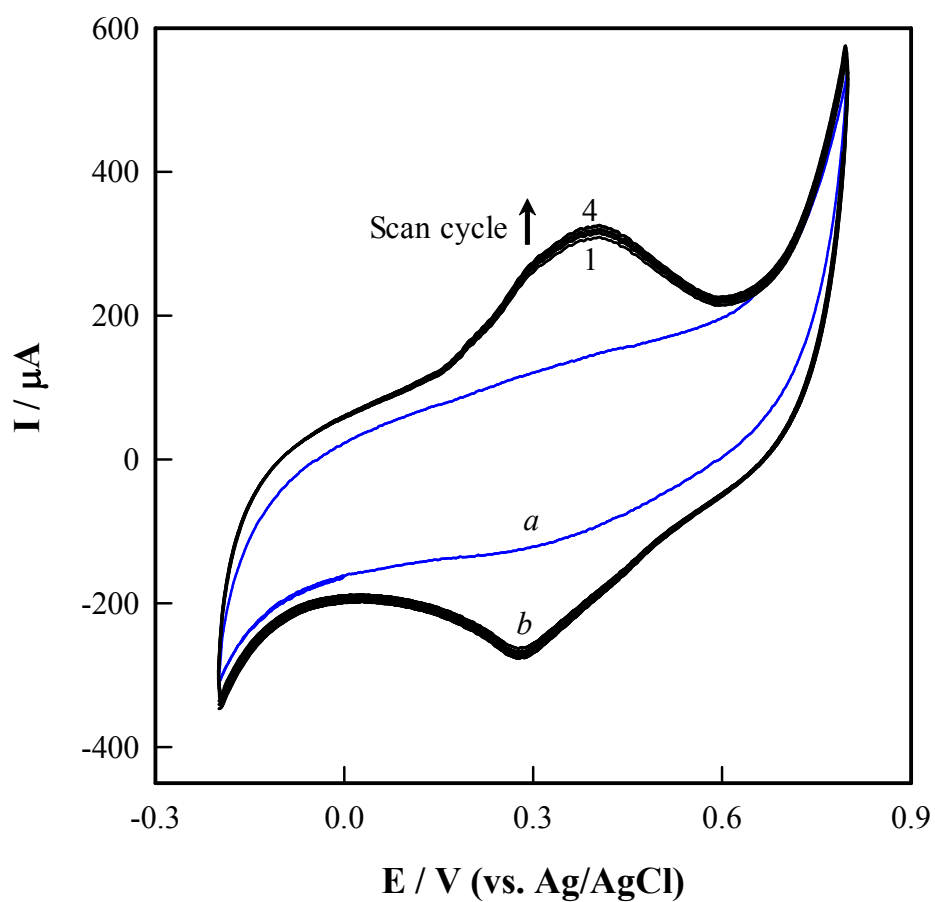


Fig. S3 Repetitive cyclic voltammograms of CNTs-ATA/GCE in 0.1 M H_2SO_4 (a) and 5.0 mM MSA+0.1 M H_2SO_4 (b). Potential scan rate: 50 mV s^{-1} .

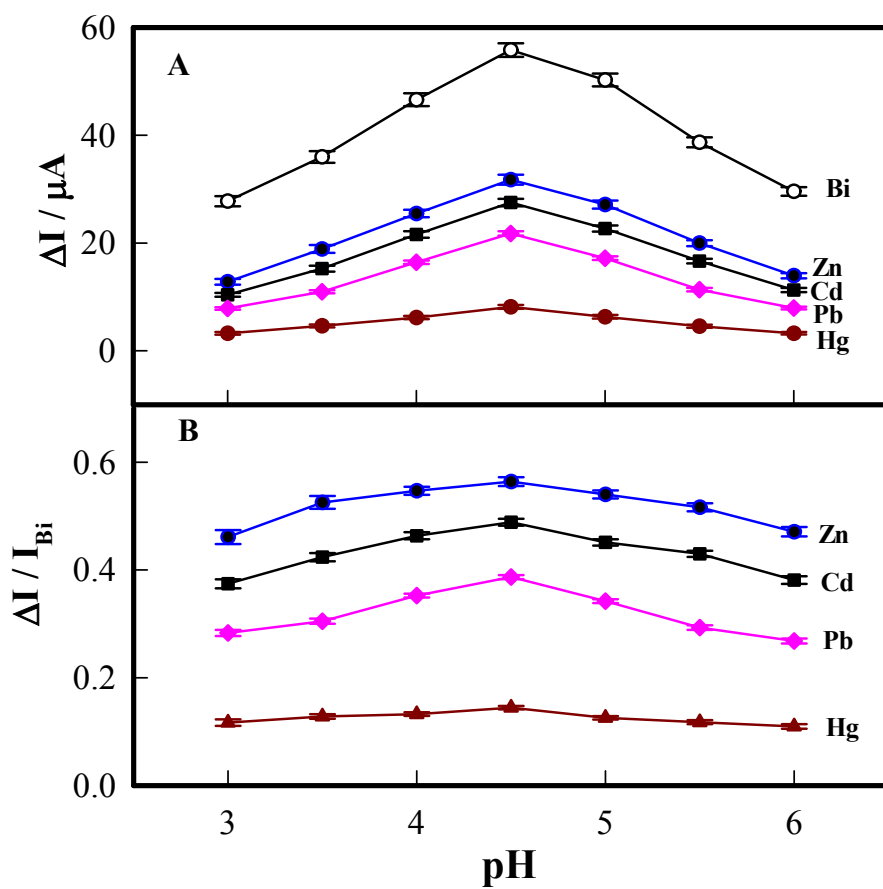


Fig. S4 Influence of pH on the DPASV peak currents (A) and current ratio of target analytes to Bi (B) using the MSA-CNTs-ATA/GCE. The concentrations of Hg(II), Pb(II), Cd(II) and Zn(II) were $30 \mu\text{g L}^{-1}$. All the solutions were contained $400 \mu\text{g L}^{-1}$ Bi(III)..

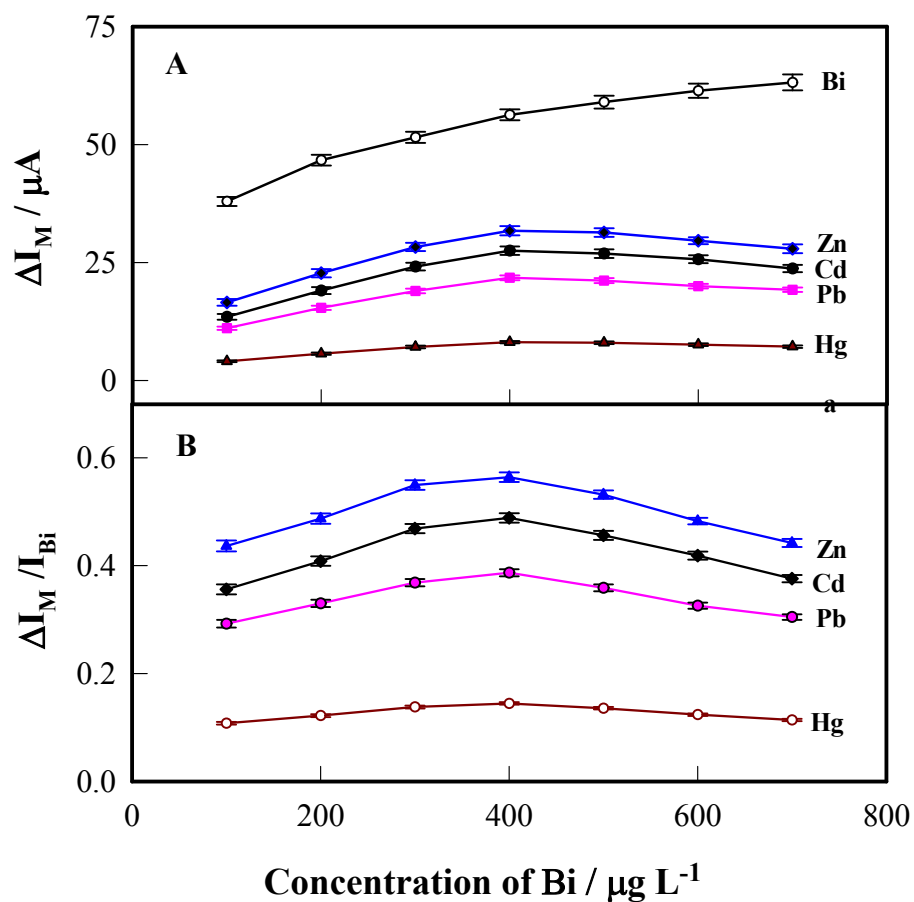


Fig. S5 Influence of concentration of Bi(III) on the DPASV peak currents (A) and current ratio of target analytes to Bi (B) using the using the MSA-CNTs-ATA/GCE (pH4.5). The concentrations of Hg(II), Pb(II), Cd(II) and Zn(II) were $30 \mu\text{g L}^{-1}$.

Table S1 Comparison of analytical performance of some electrochemical immunosensors for the four biomarkers.

Signal tags	Biomarker	Linear range *	LOD *	Refs.
Fc-AuNPs-Ab ₂	CEA	0.05–20	0.01	S1
Cu-CP-Ab ₂	CEA	0.1-100	0.02	S2
Envision/PbS- Ab ₂	CEA	0.001-50	0.0002	S3
Thi-SA/DNA-Ab ₂	CEA	0.0002-0.6	4.8×10 ⁻⁵	S4
ZnS NPs -Ab ₂	CEA	0.003-10	0.00023	This work
Aq-SA/DNA-Ab ₂	AFP	0.0002-0.8	6.2×10 ⁻⁵	S4
Envision/CdS-Ab ₂	AFP	0.001-50	0.0005	S3
Pd/APTES-M-CeO ₂ -GS-Ab ₂	AFP	0.0001-50	3.3×10 ⁻⁵	S5
AuNPs-polymer brush-Ab ₂	AFP	0.01-100	0.0018	S6
PbS NPs -Ab ₂	AFP	0.003-10	0.00011	This work
Cd-CP-Ab ₂	CA125	1-150	0.3	S2
AuNPs-aptamer-HCR	CA125	0.0001-10	5×10 ⁻⁵	S7
AuNP-Lox-Ab ₂	CA125	0.01–100	0.002	S8
Cd NPs -Ab ₂	CA125	0.03-100	0.00068	This work
Pb-CP-Ab ₂	CA19-9	1-150	0.4	S2
V ²⁺ -Ab ₂	CA19-9	0.01-200	0.0039	S9
HgS NPs-Ab ₂	CA19-9	0.03-100	0.0014	This work

* AFP and CEA: ng mL⁻¹, CA125 and CA19-9 : U mL⁻¹

Aq-SA: anthraquinone 2-carboxylic acid-streptavidin, Fc: ferrocene, AuNPs-aptamer-HCR: gold nanoparticles-aptamer-hybridization chain reaction, AuNP-Lox: gold nanoparticle-lactate oxidase, CP: chitosan–poly(acrylic acid) nanospheres, Pd/APTES-M-CeO₂-GS: graphene Oxide and CeO₂ mesoporous nanocomposite functionalized by the 3-aminopropyl-triethoxysilane supported Pd octahedral nanoparticles, Thi-SA : thionine- streptavidin, V²⁺: bipyridinium.

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