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Supplementary information

Plasmonic alloys for quantitative determination and reaction monitoring of biothiols

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Supplementary experimental methods

Study population

Esophageal cancer patients before (n = 3) and after (n = 3) chemotherapy were recruited from Shanghai Chest Hospital, Shanghai Jiao Tong University School of Medicine. All cancerous subjects were verified with pathological results. The exclusion criteria included patients with serious heart, liver and kidney diseases, acute and chronic infectious diseases, and other diseases that can interfere with the diagnosis of esophageal cancer and medication use history. The age and sex of esophageal cancer patients before and after chemotherapy were matched with no significant difference by two-tailed t-test and χ^2 test in SPSS package (version 19.0, SPSS Inc., Chicago), respectively.

Real sample harvesting

Plasma harvesting: All blood samples were drawn into BD Vacutainer tubes (additive: sodium Citrate) by venipuncture and clotted at room temperature within 40 minutes. Plasma was collected at 30,000 g for 10 minutes of centrifugation from the blood and immediately stored at -80℃ for further analysis.

Urine harvesting: The supernatant was collected at 3,000 g for 10 minutes of centrifugation from initial urine sample and immediately stored at -80℃ for further analysis.

All the investigation protocols were approved by the Institutional Ethics Committees of Shanghai Chest Hospital, under the approved protocol #KS22025. All subjects provided informed consent to participate in the study and approved the use of their biological samples for analysis. All experiments were performed following institutional guidelines, in compliance with relevant laws

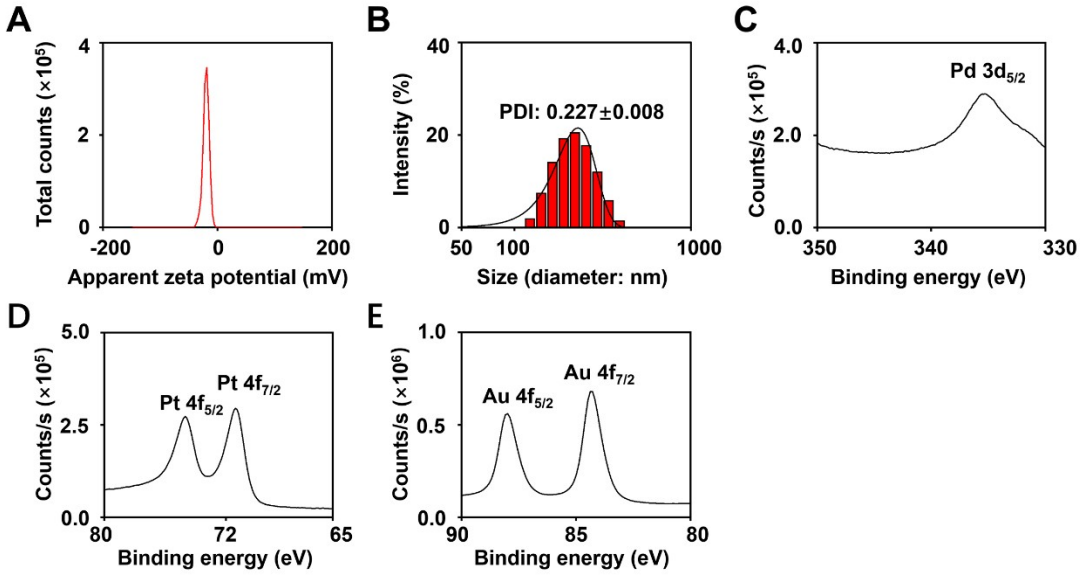

Fig. S1 (A) Zeta potential distributions and (B) hydrodynamic size of PdPtAu alloys in water by dynamic light scattering analysis. X-ray photoelectron spectroscopy analyses of PdPtAu alloys, with high-resolution scan related to (C) Pd 3d, (D) Pt 4f, and (E) Au 4f.

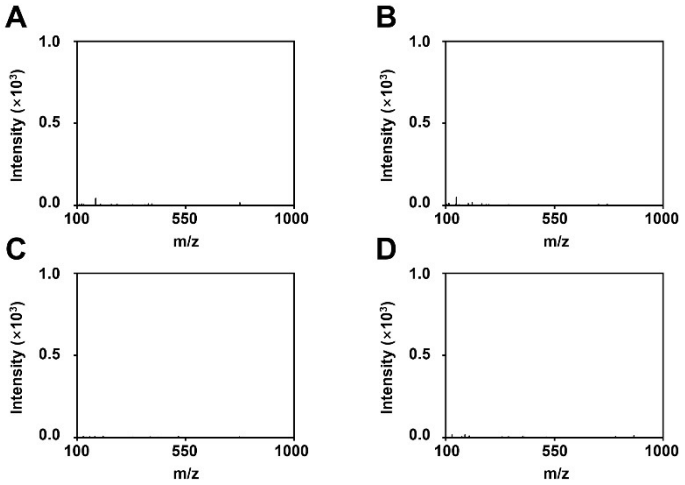

Fig. S2 Typical mass spectra of (A) glutathione, (B) cysteine, (C) methionine, and (D) homocysteine (1 mg/mL) by LDI MS without the assistance of matrix. Mass spectra were collected in positive ion mode.

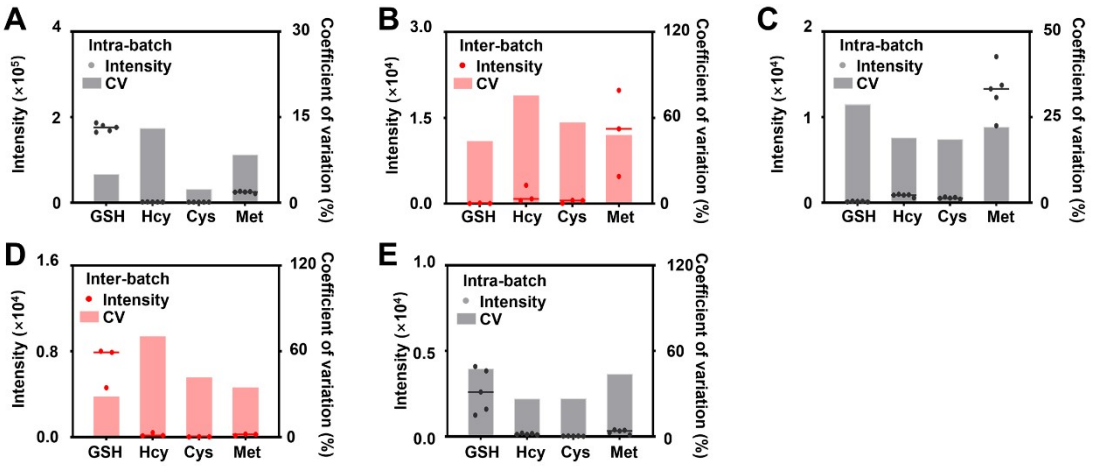

Fig. S3 Intensity reproducibility of sodium adducted MS peaks of four biothiols (including glutathione, homocysteine, cysteine, and methionine; 5 mM) at (A) intra-batch level using PdPtAu alloy as matrix; (B) inter-batch and (C) intra-batch level using Au nanoparticles as matrix; and (D) inter-batch and (E) intra-batch level using DHB as matrix.

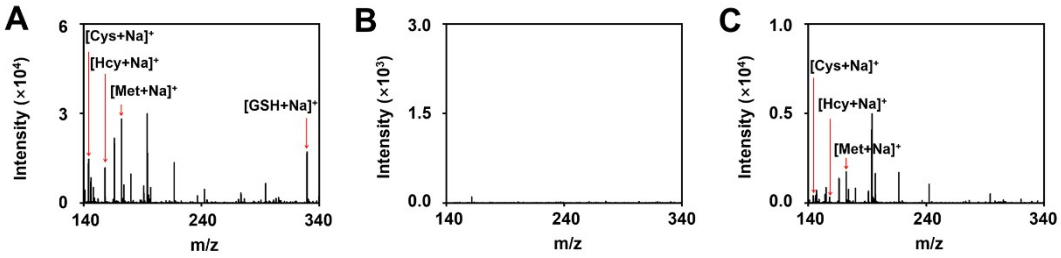

Fig. S4 Typical mass spectra of 5 mM glutathione, homocysteine, cysteine, and methionine in presence of 0.5 M of NaCl and 6.8 mg/mL of bovine serum albumin. Mass spectra were recorded by LDI MS, using (A) PdPtAu alloys, (B) DHB, and (C) Au nanoparticles as matrices, respectively.

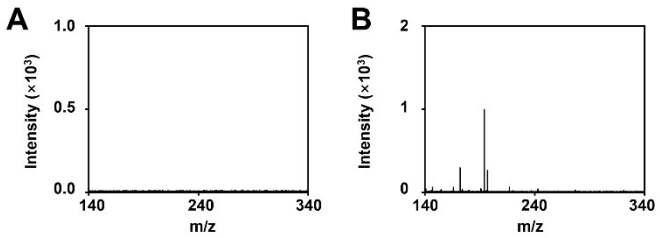

Fig. S5 Typical mass spectra of biothiol-spiked human serum (including glutathione, homocysteine, cysteine, and methionine; 5 mM), using (A) DHB, and (B) Au nanoparticles as matrices, respectively.

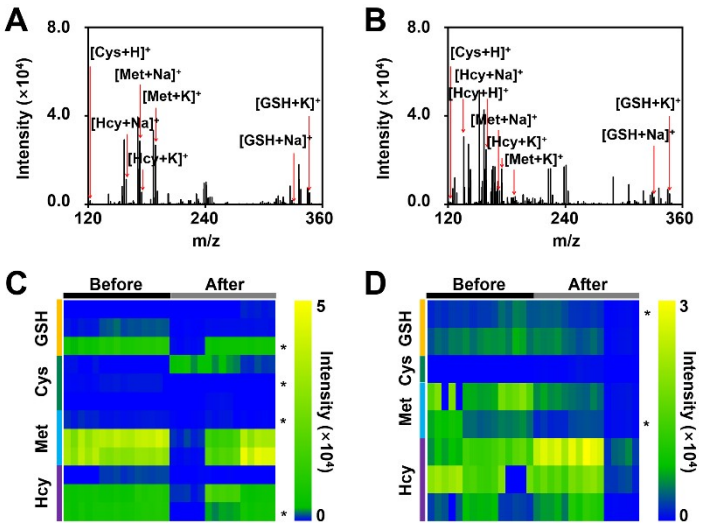

Fig. S6 Typical mass spectra of (A) plasma and (B) urine from esophageal cancer patients using PdPtAu alloys as matrices. Metabolic fingerprints of (C) plasma and (D) urine extracted from raw mass spectra of esophageal cancer patients before (n = 3) and after (n = 3) chemotherapy containing biothiol-related m/z features (*: $p < 0.05$).

Table. S1 Absorption rates of PdPtAu alloys for broad kinds of molecules.

Category	Metabolites	Average adsorption rate (%) (RSD (%), n=3)
Biothiols	Cysteine	13.15 (0.87)
	Homocysteine	8.86 (0.74)
	Methionine	2.08 (0.25)
Amino acids	Lysine	2.73 (0.10)
	Histidine	2.57 (0.04)
	Arginine	14.05 (0.69)
	Tyrosine	0.00 (0.00)
	Asparagine	0.09 (0.01)
	Aspartic acid	0.09 (0.02)
	Glutamate	0.27 (0.01)
	Phenylalanine	29.01 (0.84)
Sugars	Fructose	17.82 (0.61)
	Lactose	7.45 (0.86)
DNA bases	Guanine	11.42 (0.31)
	Uracil	0.57 (0.02)
Fatty acid	Oleic acid	0.00 (0.00)

Table. S2 Clinical characteristics of esophageal cancer patients before and after chemotherapy.

Characteristics	Before chemotherapy	After chemotherapy
Patient number	3	3
Age (median(range))[(a)]	63.0 (55-69)	64.3 (56-75)
Sex[(a)]	Male	Male

(a) The age and sex of esophageal cancer patients before and after chemotherapy was matched with no significant difference ($p > 0.05$).

Table. S3 Methionine levels in spiked human serum samples obtained by PdPtAu alloy-assisted LDI MS.

Sample	Added (μM)	Measured (μM)	Recovery (%)	Average recovery (%) (RSD (%), n=3)	Average recovery (%) (RSD (%), n=18)
Serum sample	90	91.84	1.02	101.52 (2.15)	103.19 (6.52)
	90	93.03	1.03		
	90	89.24	0.99		
	70	70.04	1.00	100.86 (2.94)	
	70	68.88	0.98		
	70	72.88	1.04		
	50	52.29	1.05	101.52 (4.50)	
	50	51.82	1.04		
	50	48.18	0.96		
	30	28.96	0.97	101.79 (5.04)	
	30	31.98	1.07		
	30	30.67	1.02		
	10	11.89	1.19	111.09 (10.63)	
	10	11.53	1.15		
	10	9.90	0.99		
	5	4.62	0.92	102.34 (8.65)	
	5	5.43	1.09		
	5	5.30	1.06		