

Supporting Information

Colorimetric sensor array with unmodified noble metal nanoparticles for naked-eye detection of proteins and bacteria

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Synthesis of AuNPs and AgNPs

AuNPs of different sizes were prepared according to a previously reported protocol. Briefly, 100 mL of 0.01% HAuCl₄ solution in 250 mL flask was put into a water bath. When the solution was heated to its boiling point, a certain volume of 1% sodium citrate was added into it under vigorous stirring. After 30 min of boiling incubation, the solution was cooled down to the room temperature. As we known, different volumes of sodium citrate lead to different size of AuNPs. In this experiment, we added 3 mL, 1.5 mL, 1 mL, 0.85 mL and 0.7 mL of 1% sodium citrate respectively to produce five different gold nanoparticles with diameters of 10-60nm (NP1-NP5). As for silver nanoparticles, it was also prepared based on the literatures described before. In brief, ammonia water was added to 1 mL of 0.1mol/L AgNO₃ dropwise until the precipitate disappeared. The solution was then diluted to 10 mL with ultrapure water and the final solution was 0.01 mol/L Tollens' reagent. Then 2 mL 0.05mol/L glucose and 0.5 g β-cyclodextrin were mixed together. Subsequently, 1.0 mL and 0.9 mL Tollens' reagent were added into the mixture, respectively and diluted to 50 mL with ultrapure water. After the mixture was heated to its boiling point under rapid stirring for 20 min and cooled down to room temperature, two types of AgNPs were obtained. The absorbance spectrum of synthesized nanoparticles are illustrate in Figure S1. The sizes and shapes of synthesized nanoparticles were characterized using transmission electron microscopy (TEM) at 200kV. The diameters of gold and silver nanoparticles are 13nm, 25nm, 35nm, 50nm, 60nm, 25nm, and 31nm, respectively (Figure S2).

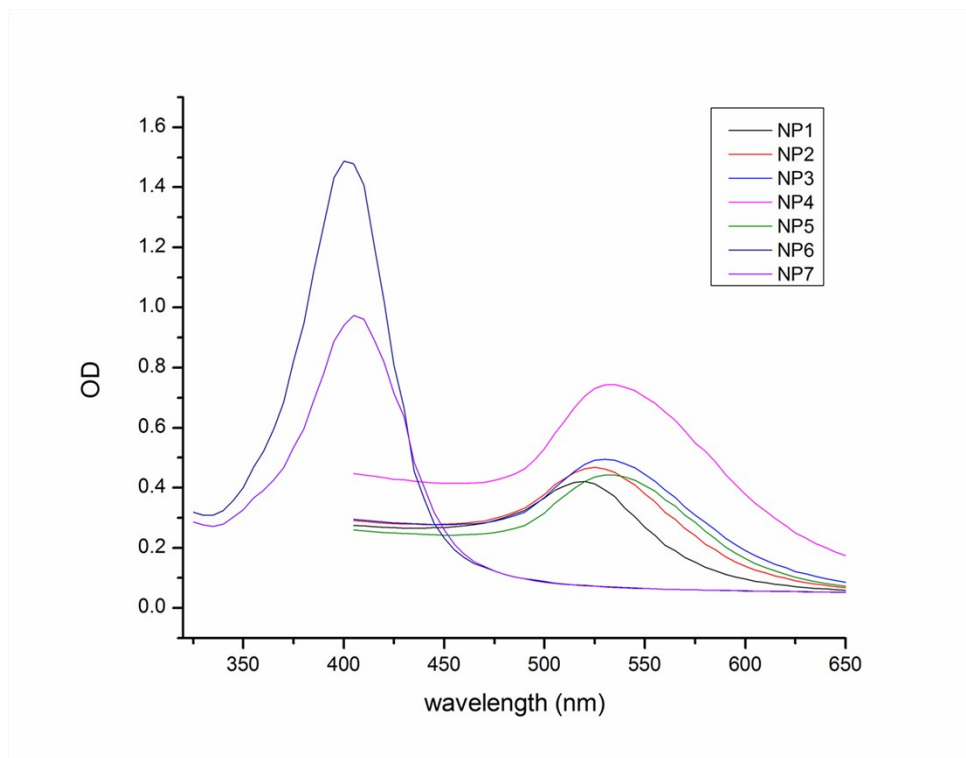


Figure S1 The absorbance spectrum of the synthesized gold and silver nanoparticles.

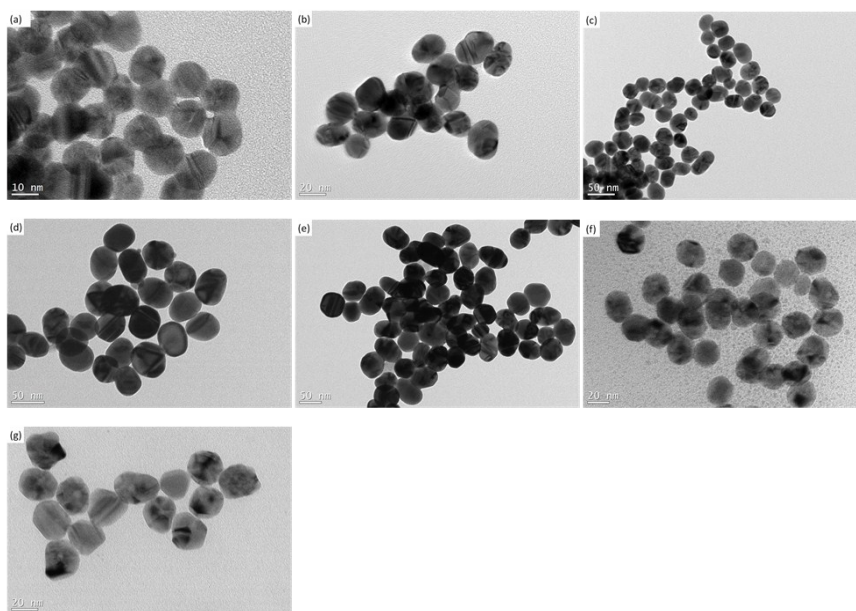


Figure S2 Transmission Electron Microscopy image of gold and silver nanoparticles.

(a)-(e): AuNPs nanoparticles of five different sizes; (f)-(g): AgNPs nanoparticles of two different sizes.

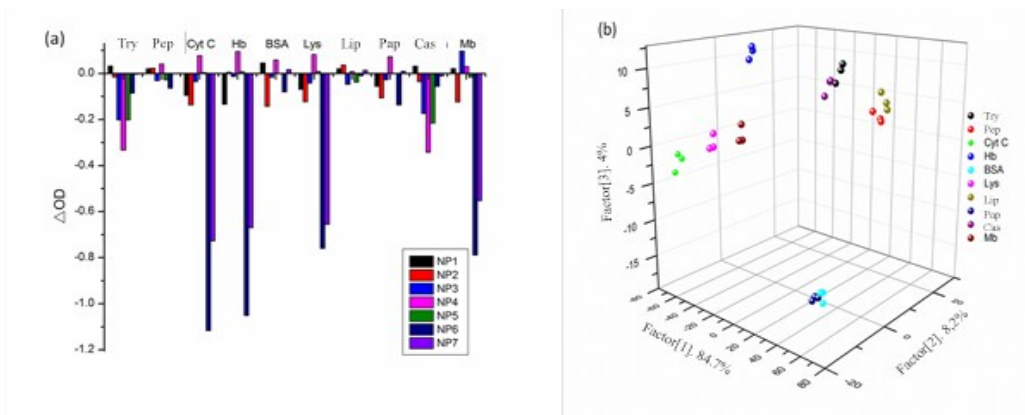


Figure S3. Protein identification with the colorimetric sensor array. (a) Absorbance response patterns of seven noble nanoparticles against ten proteins (all at 0.5 μM): trypsin (Try), pepsin (Pep), cytochrome C(Cyt C), hemoglobin (Hb), bovine serum albumin (BSA), lysozyme (Lys), lipase (Lip), papain (Pap), casein (Cas) and myoglobin (Mb). (b) Canonical score plot for the noble nanoparticles-based sensor array. All the proteins were clearly identified except for a little overlap of Pap and BSA.

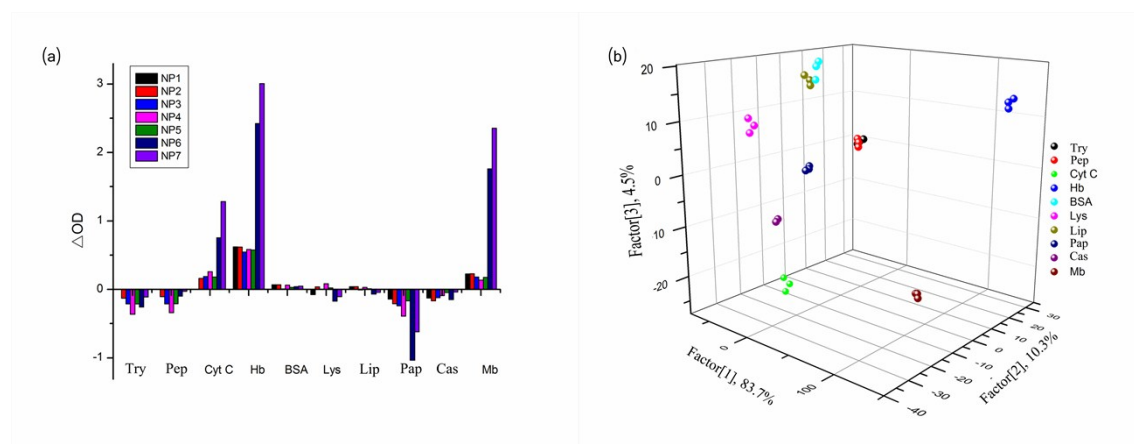


Figure S4. Protein identification with the colorimetric sensor array. (a) Absorbance response patterns of seven noble nanoparticles against ten proteins (all at 50 μM): trypsin (Try), pepsin (Pep), cytochrome C(Cyt C), hemoglobin (Hb), bovine serum albumin (BSA), lysozyme (Lys), lipase (Lip), papain (Pap), casein (Cas) and myoglobin (Mb). (b) Canonical score plot for the noble nanoparticles-based sensor array. All the proteins were clearly identified except for overlap of Pep and Try.

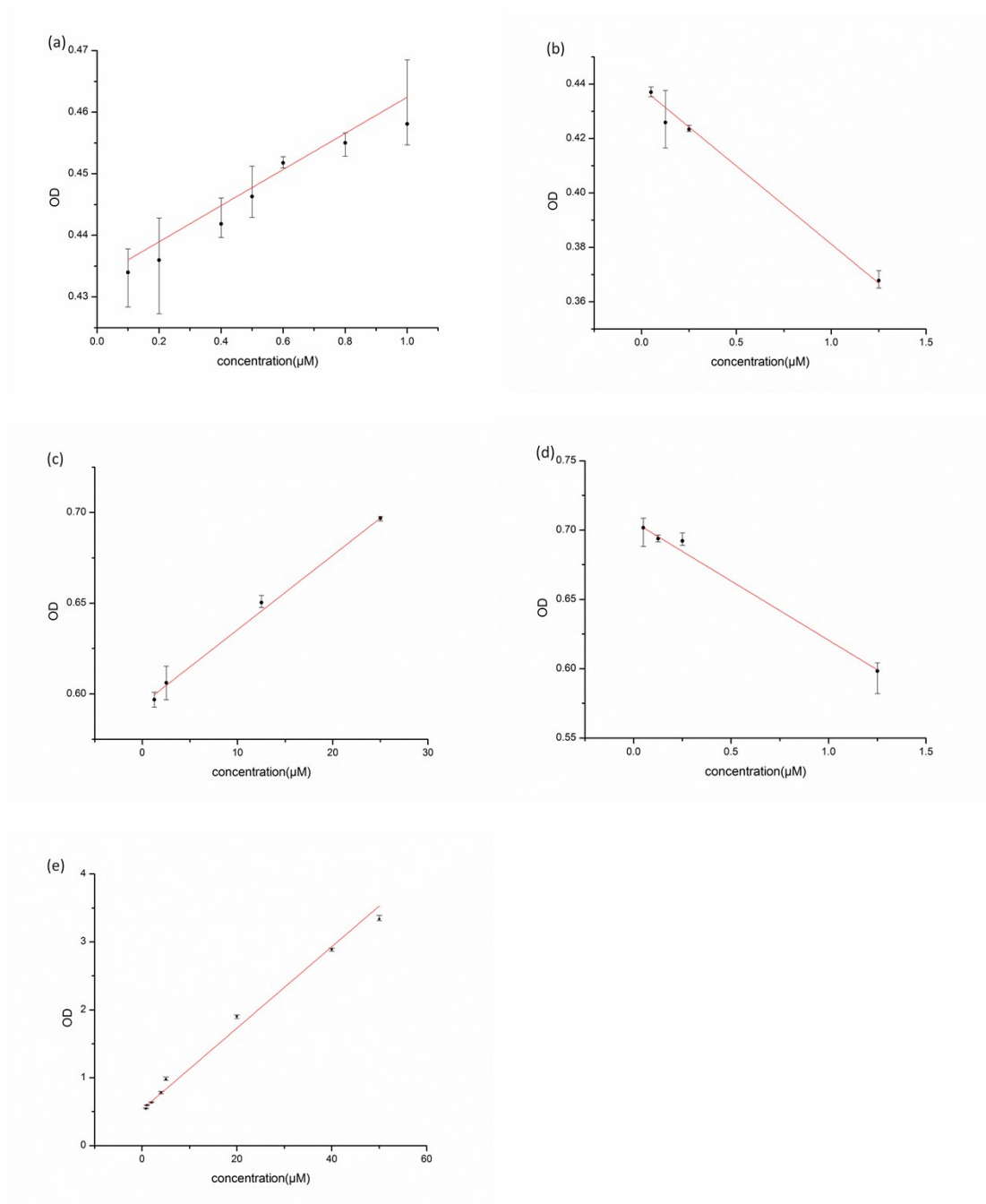


Figure S5. Quantitative analysis of proteins. (a) Linear response of Try on NP1. (b) Linear response of Pap on NP1. (c) Linear response of Cyt C on NP3. (d) Linear response of Pep on NP4. (e) Linear response of Mb on NP7.

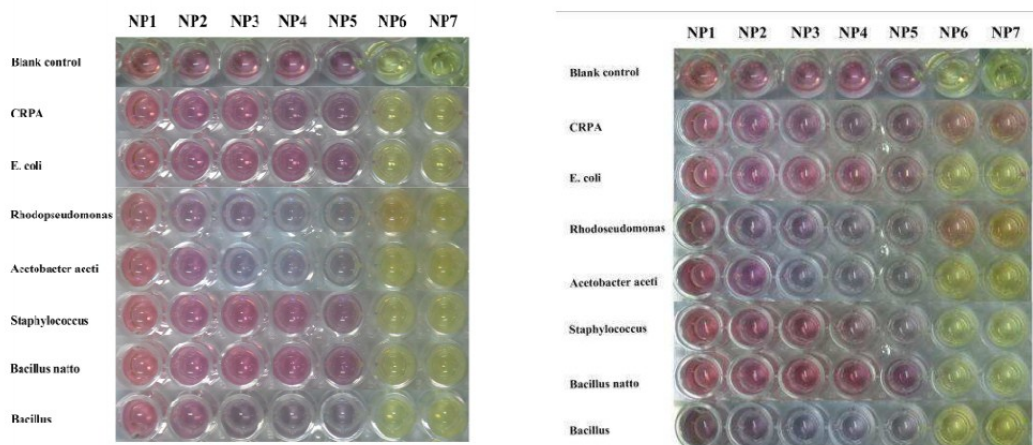


Figure S6. The color change patterns of noble nanoparticles against different bacteria After 20mins (Left); After 6 hours (Right)

NP1: 15 nm AuNPs; NP2: 25 nm AuNPs; NP3: 35 nm AuNPs; NP4: 50 nm AuNPs; NP5: 60 nm AuNPs; NP6: 25nm AgNPs; NP7: 31nm AgNPs

Table S1. Absorbance response patterns of different proteins (all at 0.5 μ M) against noble metal nanoparticle-based sensor array (NP1-NP7).

Protein	NP1	NP2	NP3	NP4	NP5	NP6	NP7
Try	0.0343	-0.0239	-0.1999	-0.3306	-0.1985	-0.0919	-0.0051
Try	0.0307	-0.0077	-0.2028	-0.3343	-0.2065	-0.0938	0.0022
Tryn	0.0335	-0.0143	-0.2012	-0.334	-0.2006	-0.0726	-0.0035
Pep	0.0207	0.0205	-0.0373	0.038	-0.0328	-0.1073	-0.0257
Pep	0.0171	0.0281	-0.023	0.0478	-0.0276	-0.0932	0.0141
Pep	0.0235	0.0197	-0.0329	0.0377	-0.0227	0.0081	0.014
Cyt C	-0.0948	-0.1342	-0.0341	0.0878	-0.0062	-1.1183	-0.7298
Cyt C	-0.0959	-0.1322	-0.0226	0.0738	0.008	-1.1185	-0.7278
Cyt C	-0.0968	-0.1437	-0.0491	0.069	0.0111	-1.1136	-0.7255
Hb	-0.1308	0.0061	-0.0139	0.0971	0.0109	-1.0529	-0.6717
Hb	-0.1379	0.0001	-0.0066	0.092	0.0127	-1.0494	-0.6711
Hb	-0.1322	0.0079	-0.0206	0.0954	-0.0009	-1.0504	-0.6645
BSA	0.0468	-0.1419	-0.0134	0.0397	0.0004	-0.0955	0.0043
BSA	0.0453	-0.1373	-0.011	0.0372	-0.0022	-0.1097	0.0175
BSA	0.0448	-0.1472	-0.0246	0.101	0.0021	-0.0337	0.0289
Lys	-0.0694	-0.1186	-0.0459	0.0853	-0.0016	-0.7282	-0.6551
Lys	-0.0679	-0.1244	-0.041	0.0809	0.0148	-0.7573	-0.6531
Lys	-0.0708	-0.1257	-0.0402	0.0792	0.0117	-0.7912	-0.6591
Lip	0.0215	0.0348	-0.0323	0.0049	-0.0301	0.0036	0.0295
Lip	0.0198	0.0382	-0.056	0.0373	-0.037	-0.0002	0.023
Lip	0.0203	0.0376	-0.055	-0.0153	-0.0439	-0.0351	-0.0104
Pap	-0.056	-0.1114	-0.034	0.0764	-0.0027	-0.1199	0.0045

Pap	-0.0553	-0.101	-0.0211	0.0764	0.0001	-0.1711	0.0227
Pap	-0.0574	-0.1065	-0.0262	0.0675	0.0043	-0.1186	0.0016
Cas	0.032	-0.0294	-0.2141	-0.345	-0.2147	-0.0558	-0.0041
Cas	0.0291	-0.0322	-0.1574	-0.3411	-0.2153	-0.0417	-0.0167
Cas	0.0319	-0.0427	-0.1508	-0.342	-0.2168	-0.0692	-0.0122
Mb	0.0369	-0.1309	0.104	0.0295	-0.0091	-0.7824	-0.5501
Mb	0.0192	-0.1161	0.0935	-0.0077	-0.0179	-0.7894	-0.5627
Mb	0.0091	-0.1231	0.0939	0.0679	-0.0202	-0.795	-0.5462

Table S2. Absorbance response patterns of different proteins (all at 5 μ M) against noble metal nanoparticle-based sensor array (NP1-NP7).

Protein	NP1	NP2	NP3	NP4	NP5	NP6	NP7
Try	-0.0333	-0.142	-0.2098	-0.3567	-0.2113	-1.1042	-0.2999
Try	-0.0335	-0.1426	-0.2128	-0.3565	-0.2082	-1.1021	-0.3613
Try	-0.02	-0.1441	-0.2113	-0.3543	-0.2146	-1.1032	-0.3445
Pep	0.0335	-0.1281	-0.2138	-0.3392	-0.2136	-0.0161	-0.0277
Pep	0.0376	-0.1286	-0.2163	-0.3618	-0.2133	-0.003	-0.0108
Pep	0.0347	-0.1275	-0.2064	-0.2893	-0.2183	0.0068	-0.0224
Cyt C	-0.1034	-0.1126	0.0004	0.1105	0.029	-0.8916	-0.5765
Cyt C	-0.0997	-0.1089	0.0088	0.1049	0.0266	-0.8587	-0.5483
Cyt C	-0.1024	-0.0992	0.0064	0.1036	0.0292	-0.9237	-0.5391
Hb	0.043	0.1069	0.0318	0.1089	0.0593	-0.448	0.0244
Hb	0.0532	0.1067	0.0286	0.1366	0.0552	-0.395	0.0617
Hb	0.0416	0.1112	0.0329	0.1233	0.0518	-0.4086	0.0672
BSA	0.0581	0.0475	-0.0321	0.0726	0.0088	-0.0758	-0.0155
BSA	0.0594	0.0477	-0.0214	0.0738	0.0006	-0.0343	0.0023
BSA	0.0581	0.0544	-0.0538	0.0814	0.0043	-0.0423	-0.0232
Lys	-0.0739	-0.0876	-0.0098	0.0938	0.0131	-0.1282	-0.0435
Lys	-0.0715	-0.0838	-0.0077	0.0955	0.0162	-0.1741	-0.0452
Lys	-0.0722	-0.0785	-0.0048	0.0906	0.0156	-0.1369	-0.0625
Lip	0.0282	0.0442	-0.0783	-0.1465	-0.0446	-0.025	-0.0108
Lip	0.0361	0.0345	-0.07	-0.1359	-0.0512	-0.0308	-0.0163
Lip	0.0278	0.0412	-0.0766	-0.135	-0.0706	-0.0323	-0.0516
Pap	-0.0663	-0.0972	-0.044	0.0823	0.0009	-0.9369	-0.5682
Pap	-0.074	-0.0997	-0.036	0.0818	0.0095	-0.8809	-0.5663
Pap	-0.0752	-0.0997	-0.0255	0.0879	0.0111	-0.9327	-0.568
Cas	0.0169	-0.0647	-0.0857	-0.1267	-0.0782	-0.1125	-0.0848
Cas	0.0223	-0.062	-0.0877	-0.1319	-0.072	-0.089	-0.0577
Cas	0.0198	-0.0612	-0.0836	-0.1274	-0.131	-0.1604	-0.0772
Mb	0.0343	-0.0743	-0.0027	0.1031	0.0228	-0.2226	-0.2116
Mb	0.0338	-0.0704	-0.0199	0.0866	0.0164	-0.2818	-0.1861
Mb	0.0343	-0.0749	-0.015	0.0822	0.0221	-0.2275	-0.184

Table S3. Absorbance response patterns of different proteins (all at 50 μ M) against noble metal nanoparticle-based sensor array (NP1-NP7).

Protein	NP1	NP2	NP3	NP4	NP5	NP6	NP7
Try	-0.0013	-0.1274	-0.2205	-0.3715	-0.2109	-0.2468	-0.1136
Try	0.0023	-0.1337	-0.2072	-0.3496	-0.217	-0.24	-0.1029
Try	0.0123	-0.1292	-0.2111	-0.3677	-0.2039	-0.2858	-0.1102
Pep	0.0019	-0.1082	-0.2085	-0.3431	-0.2072	-0.0914	-0.0073
Pep	0.0035	-0.1056	-0.2123	-0.3383	-0.2054	-0.0964	-0.0215
Pep	0.0045	-0.1071	-0.2112	-0.3363	-0.2115	-0.108	-0.048
Cyt C	0.0025	0.1556	0.1878	0.2506	0.1842	0.6808	1.2014
Cyt C	0.0092	0.1593	0.1829	0.2598	0.1667	0.7857	1.3022
Cyt C	0.0001	0.1752	0.1885	0.2663	0.1925	0.7948	1.3398
Hb	0.6028	0.6033	0.5036	0.5777	0.5708	2.5411	3.0077
Hb	0.6393	0.6225	0.5631	0.5845	0.5884	2.5224	3.0077
Hb	0.6254	0.6257	0.5706	0.5966	0.5766	2.3208	2.9769
BSA	0.0672	0.0556	0.0204	0.0684	0.0324	0.0039	0.0656
BSA	0.0729	0.0788	0.0033	0.068	0.0281	0.0515	0.0524
BSA	0.0653	0.066	-0.0026	0.0543	0.0306	0.0722	0.0288
Lys	-0.0714	0.0426	0.0035	0.0854	0.022	-0.1693	-0.1413
Lys	-0.0701	0.0371	-0.005	0.0821	0.0195	-0.175	-0.0926
Lys	-0.0808	0.0371	-0.0048	0.0767	0.0196	-0.1617	-0.0865
Lip	0.0359	0.0432	-0.0087	0.0396	0.0119	-0.0591	-0.0723
Lip	0.0412	0.0419	-0.0052	0.0236	0.0122	-0.0595	-0.0154
Lip	0.0423	0.0436	-0.0063	0.0312	0.0083	-0.0817	-0.0346
Pap	-0.1398	-0.208	-0.2372	-0.3908	-0.1692	-1.0413	-0.6096
Pap	-0.1373	-0.2107	-0.239	-0.3857	-0.1678	-1.0333	-0.6207
Pap	-0.1468	-0.2104	-0.2371	-0.3928	-0.1651	-1.0262	-0.6289
Cas	-0.1237	-0.1646	-0.1182	-0.0881	-0.0426	-0.146	-0.0359
Cas	-0.1282	-0.1646	-0.1263	-0.0913	-0.044	-0.16	-0.0384
Cas	-0.1258	-0.1705	-0.1144	-0.0904	-0.0485	-0.1343	-0.0429
Mb	0.223	0.221	0.1713	0.1445	0.1742	1.7407	2.3463
Mb	0.225	0.233	0.187	0.1506	0.1861	1.7374	2.3471
Mb	0.2273	0.2329	0.189	0.106	0.165	1.8096	2.3664

Table S4. Absorbance responses of different bacteria against noble metal nanoparticle-based sensor array (NP1-NP7).

Bacteria	NP1	NP2	NP3	NP4	NP5	NP6	NP7
E. coli	0.03425	0.03395	0.03015	0.03475	0.02555	0.0564	0.0661
E. coli	0.05055	0.03765	0.03845	0.03265	0.02245	0.0744	0.0592
E. coli	0.05275	0.04075	0.03675	0.03675	0.02195	0.0571	0.0582
E. coli	0.04915	0.04095	0.04055	0.03725	0.03745	0.0528	0.067

E. coli	0.05045	0.04275	0.04105	0.03365	0.03335	0.052	0.0576
E. coli	0.04895	0.03665	0.04185	0.03465	0.03225	0.0406	0.055
CRPA	0.06175	0.06095	0.06765	0.06035	0.05835	0.0612	0.0565
CRPA	0.06485	0.06105	0.06475	0.05385	0.05485	0.0659	0.0595
CRPA	0.06745	0.06125	0.06725	0.05525	0.04495	0.0556	0.054
CRPA	0.06235	0.05975	0.06625	0.05955	0.05155	0.0614	0.0717
CRPA	0.06655	0.06105	0.06545	0.05305	0.04435	0.0616	0.0515
CRPA	0.06275	0.06245	0.06765	0.05045	0.04515	0.0579	0.0566
Acetobacter aceti	0.11845	0.11455	0.03305	-0.04585	-0.04595	0.0411	0.0647
Acetobacter aceti	0.12045	0.12055	0.02145	-0.04965	-0.06935	0.0448	0.0765
Acetobacter aceti	0.13035	0.12445	0.02245	-0.04575	-0.06945	0.0579	0.0599
Acetobacter aceti	0.12805	0.12335	0.02775	-0.04465	-0.07135	0.0512	0.048
Acetobacter aceti	0.12305	0.11945	0.03315	-0.04215	-0.05885	0.0634	0.0402
Acetobacter aceti	0.12595	0.11255	0.03365	-0.03555	-0.06655	0.0517	0.0566
Rhodopseudomonas	0.05955	0.04715	0.03635	-0.09775	-0.12865	-0.0265	0.0833
Rhodopseudomonas	0.03765	0.04815	0.02945	-0.09515	-0.13305	-0.003	0.077
Rhodopseudomonas	0.05595	0.04345	0.03035	-0.09615	-0.13275	-0.014	0.0722
Rhodopseudomonas	0.04575	0.04105	0.03855	-0.09725	-0.13445	-0.0446	0.0723
Rhodopseudomonas	0.04415	0.03565	0.04475	-0.08715	-0.13125	-0.05	0.059
Rhodopseudomonas	0.04585	0.03125	0.01965	-0.13655	-0.17515	-0.0023	0.0604
Bacillus natto	0.08165	0.06675	0.11835	0.06575	0.06645	0.0623	0.0783
Bacillus natto	0.07655	0.06705	0.13205	0.06845	0.07555	0.0537	0.0863
Bacillus natto	0.07705	0.06745	0.13555	0.06665	0.07535	0.0512	0.0909
Bacillus natto	0.08175	0.07005	0.13105	0.07045	0.07555	0.054	0.0746
Bacillus natto	0.04415	0.06855	0.12635	0.06775	0.07215	0.0501	0.0919
Bacillus natto	0.07785	0.06745	0.13005	0.06635	0.06995	0.0495	0.0812
Staphylococcus	0.06825	0.05815	0.10885	0.02835	0.00355	0.0419	0.0657
Staphylococcus	0.06515	0.05665	0.10815	0.02735	-0.00205	0.0468	0.0651
Staphylococcus	0.06535	0.05525	0.10835	0.01155	-0.04865	0.0348	0.059
Staphylococcus	0.06185	0.05585	0.10585	0.02195	-0.07035	0.0434	0.0535
Staphylococcus	0.06305	0.05675	0.09135	0.01965	-0.01065	0.0448	0.055
Staphylococcus	0.06055	0.05515	0.09875	0.01645	-0.05395	0.0298	0.0466
Bacillus	0.09105	0.07675	0.04755	-0.05115	-0.07015	0.0948	0.1101
Bacillus	0.09785	0.07465	0.04355	-0.05055	-0.05765	0.0923	0.1062
Bacillus	0.08915	0.07345	0.04185	-0.06195	-0.07585	0.0905	0.1071
Bacillus	0.09035	0.07095	0.04575	-0.05755	-0.08405	0.0932	0.1061
Bacillus	0.08325	0.07415	0.04475	-0.04235	-0.06785	0.0844	0.1015
Bacillus	0.08105	0.06875	0.06075	-0.03365	-0.06015	0.0823	0.1141

Table S5. Absorbance response patterns of different cancer cells against noble metal nanoparticle-based sensor array (NP1-NP7).

Cancer cells	NP1	NP2	NP3	NP4	NP5	NP6	NP7
Oral squamous carcinoma cells	0.2597	0.2610	0.2520	-0.0180	0.0014	0.7110	0.4842

Oral squamous carcinoma cells	0.2637	0.2664	0.2509	-0.0104	0.0013	0.7143	0.4808
Oral squamous carcinoma cells	0.2612	0.2655	0.2575	-0.0185	0.0018	0.6732	0.4824
Oral squamous carcinoma cells	0.2587	0.2577	0.2552	-0.0106	0.0000	0.6614	0.4990
Oral squamous carcinoma cells	0.2636	0.2591	0.2411	-0.0061	0.0017	0.6694	0.4872
Oral squamous carcinoma cells	0.2768	0.2471	0.2679	-0.0076	0.0017	0.7287	0.4825
HeLa cells	0.2736	0.2545	0.1604	-0.0066	0.0095	0.6644	0.4403
HeLa cells	0.2835	0.2473	0.1809	-0.0017	0.0084	0.6744	0.4699
HeLa cells	0.2563	0.2501	0.1518	0.0018	-0.0002	0.6785	0.4473
HeLa cells	0.2611	0.2475	0.1421	-0.0012	-0.0007	0.6389	0.4310
HeLa cells	0.2610	0.2485	0.1574	0.0006	0.0074	0.6595	0.4268
HeLa cells	0.2531	0.2621	0.1369	-0.0050	0.0020	0.6585	0.4060
PC3 cells	0.2298	0.1973	0.1330	-0.0063	0.0052	0.6963	0.5245
PC3 cells	0.2468	0.1960	0.1462	0.0195	0.0036	0.6939	0.5451
PC3 cells	0.2334	0.2041	0.1681	0.0109	0.0118	0.7195	0.5207
PC3 cells	0.2376	0.2150	0.1831	0.0238	0.0075	0.7233	0.5544
PC3 cells	0.2505	0.2126	0.2008	0.0103	0.0057	0.7242	0.5408
PC3 cells	0.2342	0.2011	0.1940	0.0162	0.0024	0.7040	0.5183
A549	0.2435	0.2266	0.2781	0.0159	0.0164	0.6641	0.5361
A549	0.2405	0.2145	0.2677	0.0144	0.0089	0.6773	0.5067
A549	0.2418	0.2064	0.2620	0.0279	0.0051	0.7117	0.5186
A549	0.2403	0.2141	0.2723	0.0162	0.0059	0.7262	0.5081
A549	0.2430	0.1971	0.2521	0.0269	0.0063	0.7092	0.5170
A549	0.2340	0.2095	0.2428	0.0049	0.0054	0.7010	0.4619