Electronic Supplementary Material (ESI) for Analyst.

Cationic polymer-based plasmonic sensor array that discriminate proteins

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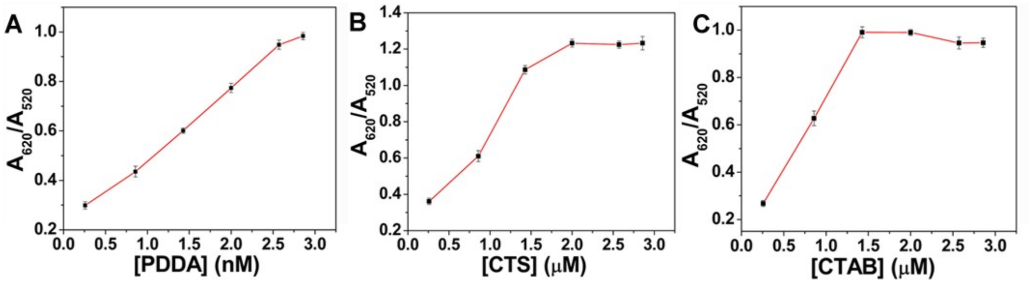

Fig. S1 Absorbance change of the Au NPs with the changes of (A) PDDA, (B) CTS, and (C) CTAB with various concentrations.

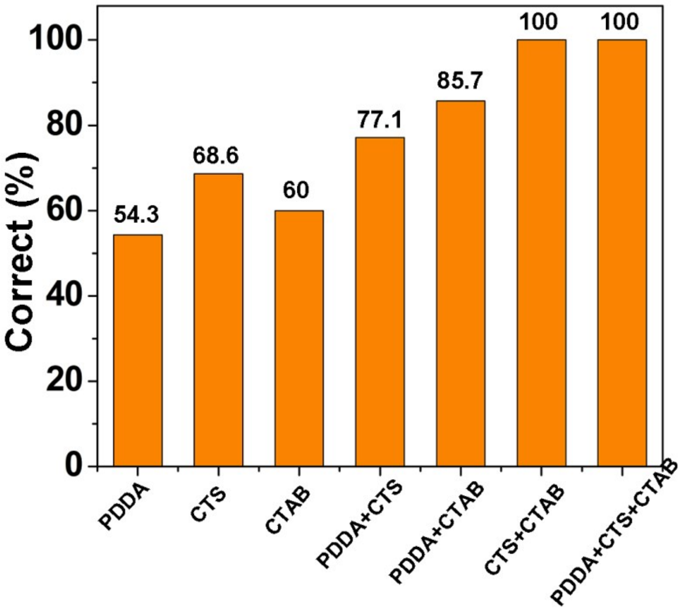

Fig. S2 The classification accuracy of seven proteins for individual sensing elements and the mixtures of the sensing elements.

Table S1. Physical properties of protein analytes.

protein	MW (kDa)	pI
EA	44.3	4.6
BSA	66.3	4.8
Con	102	6.5
TRF	～75	5.6
Hem	64.5	6.8
HRP	～40	～5
Thr	36.7	5.0～5.5

Table S2. The training matrix of the colorimetric response patterns against proteins at 20 nM using this sensor assay.

Proteins	PDDA	CTS	CTAB
Hem	1.036	1.076	0.949
Hem	1.040	1.075	1.019
Hem	0.966	1.022	1.093
Hem	1.001	1.076	0.984
Hem	1.003	1.049	1.021
BSA	0.609	0.574	0.676
BSA	0.738	0.594	0.746
BSA	0.579	0.653	0.810
BSA	0.398	0.637	0.664
BSA	0.504	0.613	0.743
EA	0.872	0.853	0.984
EA	0.821	0.835	1.024
EA	0.639	0.819	0.963
EA	0.926	0.930	1.028
EA	0.835	0.923	0.998
HRP	0.645	0.792	0.768
HRP	0.827	0.807	0.886
HRP	0.801	0.790	0.714
HRP	0.783	0.835	0.791
HRP	1.481	0.829	0.837
TRF	1.114	1.061	1.420
TRF	1.303	1.243	1.167
TRF	1.198	1.199	1.155
TRF	1.208	1.152	1.294
TRF	1.156	1.130	1.288
Thr	0.688	0.885	0.829
Thr	0.921	0.972	0.951
Thr	0.736	0.893	0.890
Thr	0.828	0.937	0.855
Thr	0.804	0.931	0.890
Con	1.094	1.027	1.328
Con	0.813	0.893	1.298
Con	0.804	0.903	1.235
Con	0.813	0.942	1.196
Con	0.815	0.986	1.279

Table S3. Jackknifed classification matrix obtained using LDA based on PDDA, CTS, and CTAB as receptors for discrimination of seven proteins, respectively.

Proteins	PDDA	CTS	CTAB	PDDA+CTS+CTAB
Hem	100%	100%	60%	100%
BSA	80%	100%	80%	100%
EA	40%	20%	60%	100%
HRP	0	100%	60%	100%
TRF	100%	80%	40%	100%
Thr	60%	40%	60%	100%
Con	0	40%	60%	100%

Table S4. The training matrix of the colorimetric response patterns against Con with various concentrations (10-90 nM) using this sensor assay.

Proteins	PDDA	CTS	CTAB
10 nM	1.235	1.400	1.648
10 nM	1.420	1.335	1.286
10 nM	1.037	1.208	1.870
30 nM	1.075	0.945	1.070
30 nM	1.120	0.862	0.827
30 nM	1.046	0.945	0.875
50 nM	0.907	0.984	0.689
50 nM	0.907	0.730	0.689
50 nM	0.790	0.943	0.694
70 nM	0.494	0.453	0.897
70 nM	0.542	0.524	0.785
70 nM	0.513	0.485	0.976
90 nM	0.419	0.478	0.413
90 nM	0.400	0.688	0.705
90 nM	0.475	0.438	0.565

Table S5. Training matrix of the response patterns against pure BSA and TRF at the same concentrations, as well as the mixtures of the two proteins with various molar ratios (total concentration 20 nM) using this sensor array.

Proteins	PDDA	CTS	CTAB
100%TRF	1.227	1.146	1.188
100%TRF	1.264	1.077	1.208
100%TRF	1.149	1.000	1.141
100%TRF	1.245	1.111	1.198
100%TRF	1.131	1.039	1.175
100% BSA	0.420	0.591	0.349
100% BSA	0.496	0.610	0.359
100% BSA	0.347	0.603	0.382
100% BSA	0.458	0.600	0.354
100% BSA	0.422	0.606	0.370
20%BSA+80%TRF	0.947	0.915	1.085
20%BSA+80%TRF	0.952	1.062	0.946
20%BSA+80%TRF	0.871	0.874	0.984
20%BSA+80%TRF	1.022	0.984	0.938
20%BSA+80%TRF	0.912	0.968	0.897
40%BSA+60%TRF	0.807	0.605	0.527
40%BSA+60%TRF	0.834	0.795	0.604
40%BSA+60%TRF	0.848	0.665	0.654
40%BSA+60%TRF	0.844	0.740	0.625
40%BSA+60%TRF	0.865	0.770	0.672
60%BSA+40%TRF	0.630	0.754	0.745
60%BSA+40%TRF	0.657	0.821	0.830
60%BSA+40%TRF	0.594	0.815	0.794
60%BSA+40%TRF	0.643	0.787	0.787
60%BSA+40%TRF	0.626	0.818	0.812
80%BSA+20%TRF	0.410	0.745	0.566
80%BSA+20%TRF	0.489	0.639	0.618
80%BSA+20%TRF	0.406	0.654	0.509
80%BSA+20%TRF	0.449	0.692	0.592
80%BSA+20%TRF	0.448	0.647	0.563

Table S6. Identification of unknown protein samples at 20 nM using PDDA.

Samples	PDDA	Identification	Verification
1	1.036	Hem	Hem
2	1.040	Hem	Hem
3	0.966	Hem	Hem
4	1.001	Hem	Hem
5	1.003	Hem	Hem
6	0.609	BSA	BSA
7	0.738	Thr	BSA
8	0.579	BSA	BSA
9	0.398	BSA	BSA
10	0.504	BSA	BSA
11	0.872	Con	EA
12	0.821	EA	EA
13	0.639	BSA	EA
14	0.926	HRP	EA
15	0.835	EA	EA
16	0.645	BSA	HRP
17	0.827	EA	HRP
18	0.801	Thr	HRP
19	0.783	Thr	HRP
20	1.481	TRF	HRP
21	1.114	TRF	TRF
22	1.303	TRF	TRF
23	1.198	TRF	TRF
24	1.208	TRF	TRF
25	1.156	TRF	TRF
26	0.688	Thr	Thr
27	0.921	HRP	Thr
28	0.736	Thr	Thr
29	0.828	EA	Thr
30	0.804	Thr	Thr
31	1.094	Hem	Con
32	0.813	EA	Con
33	0.804	Thr	Con
34	0.813	EA	Con
35	0.815	EA	Con

Table S7. Identification of unknown protein samples at 20 nM using CTS.

Samples	CTS	Identification	Verification
1	1.076	Hem	Hem
2	1.075	Hem	Hem
3	1.022	Hem	Hem
4	1.076	Hem	Hem
5	1.049	Hem	Hem
6	0.574	BSA	BSA
7	0.594	BSA	BSA
8	0.653	BSA	BSA
9	0.637	BSA	BSA
10	0.613	BSA	BSA
11	0.853	EA	EA
12	0.835	HRP	EA
13	0.819	HRP	EA
14	0.930	Thr	EA
15	0.923	Thr	EA
16	0.792	HRP	HRP
17	0.807	HRP	HRP
18	0.790	HRP	HRP
19	0.835	HRP	HRP
20	0.829	HRP	HRP
21	1.061	Hem	TRF
22	1.243	TRF	TRF
23	1.199	TRF	TRF
24	1.152	TRF	TRF
25	1.130	TRF	TRF
26	0.885	EA	Thr
27	0.972	Con	Thr
28	0.893	EA	Thr
29	0.937	Thr	Thr
30	0.931	Thr	Thr
31	1.027	Hem	Con
32	0.893	EA	Con
33	0.903	Thr	Con
34	0.942	Con	Con
35	0.986	Con	Con

Table S8. Identification of unknown protein samples at 20 nM using CTAB.

Samples	CTS	Identification	Verification
1	0.949	EA	Hem
2	1.019	Hem	Hem
3	1.093	Hem	Hem
4	0.984	EA	Hem
5	1.021	Hem	Hem
6	0.676	BSA	BSA
7	0.746	BSA	BSA
8	0.810	HRP	BSA
9	0.664	BSA	BSA
10	0.743	BSA	BSA
11	0.984	EA	EA
12	1.024	Hem	EA
13	0.963	EA	EA
14	1.028	Hem	EA
15	0.998	EA	EA
16	0.768	HRP	HRP
17	0.886	Thr	HRP
18	0.714	BSA	HRP
19	0.791	HRP	HRP
20	0.837	HRP	HRP
21	1.420	Con	TRF
22	1.167	TRF	TRF
23	1.155	TRF	TRF
24	1.294	Con	TRF
25	1.288	Con	TRF
26	0.829	HRP	Thr
27	0.951	EA	Thr
28	0.890	Thr	Thr
29	0.855	Thr	Thr
30	0.890	Thr	Thr
31	1.328	Con	Con
32	1.298	Con	Con
33	1.235	TRF	Con
34	1.196	TRF	Con
35	1.279	Con	Con

Table S9. Identification of unknown protein samples at 20 nM using PDDA+CTS+CTAB.

Samples	PDDA	CTS	CTAB	Identification	Verification
1	1.036	1.076	0.949	Hem	Hem
2	1.040	1.075	1.019	Hem	Hem
3	0.966	1.022	1.093	Hem	Hem
4	1.001	1.076	0.984	Hem	Hem
5	1.003	1.049	1.021	Hem	Hem
6	0.609	0.574	0.676	BSA	BSA
7	0.738	0.594	0.746	BSA	BSA
8	0.579	0.653	0.810	BSA	BSA
9	0.398	0.637	0.664	BSA	BSA
10	0.504	0.613	0.743	BSA	BSA
11	0.872	0.853	0.984	EA	EA
12	0.821	0.835	1.024	EA	EA
13	0.639	0.819	0.963	EA	EA
14	0.926	0.930	1.028	EA	EA
15	0.835	0.923	0.998	EA	EA
16	0.645	0.792	0.768	HRP	HRP
17	0.827	0.807	0.886	HRP	HRP
18	0.801	0.790	0.714	HRP	HRP
19	0.783	0.835	0.791	HRP	HRP
20	1.481	0.829	0.837	HRP	HRP
21	1.114	1.061	1.420	TRF	TRF
22	1.303	1.243	1.167	TRF	TRF
23	1.198	1.199	1.155	TRF	TRF
24	1.208	1.152	1.294	TRF	TRF
25	1.156	1.130	1.288	TRF	TRF
26	0.688	0.885	0.829	Thr	Thr
27	0.921	0.972	0.951	Thr	Thr
28	0.736	0.893	0.890	Thr	Thr
29	0.828	0.937	0.855	Thr	Thr
30	0.804	0.931	0.890	Thr	Thr
31	1.094	1.027	1.328	Con	Con
32	0.813	0.893	1.298	Con	Con
33	0.804	0.903	1.235	Con	Con
34	0.813	0.942	1.196	Con	Con
35	0.815	0.986	1.279	Con	Con

Table S10. Training matrix of the response patterns against proteins (each at 20 nM) in the presence of human serum using the sensor array

Proteins	PDDA	CTS	CTAB
Hem	1.011	0.854	0.850
Hem	0.913	0.865	0.894
Hem	0.974	0.834	0.845
Hem	0.962	0.860	0.872
Hem	0.943	0.850	0.870
BSA	0.595	0.688	0.711
BSA	0.439	0.761	0.915
BSA	0.432	0.770	0.919
BSA	0.517	0.724	0.813
BSA	0.435	0.765	0.917
EA	0.879	0.874	0.974
EA	0.781	0.742	0.997
EA	0.757	0.992	1.070
EA	0.830	0.808	0.986
EA	0.769	0.867	1.034
HRP	0.940	0.882	1.212
HRP	0.931	0.792	1.095
HRP	0.985	0.814	1.124
HRP	0.936	0.837	1.153
HRP	0.958	0.803	1.110
TRF	1.254	1.024	0.835
TRF	1.146	0.975	0.842
TRF	1.015	1.035	0.844
TRF	1.200	1.000	0.838
TRF	1.080	1.005	0.843
Thr	0.927	1.065	0.954
Thr	1.038	1.025	0.954
Thr	1.124	0.999	0.975
Thr	0.983	1.045	0.954
Thr	1.081	1.012	0.965
Con	1.121	1.057	0.721
Con	1.033	1.312	0.815
Con	1.018	1.124	0.791
Con	1.077	1.184	0.768
Con	1.025	1.218	0.803