Electronic Supplementary Material (ESI) for Lab on a Chip.

Supporting Information:

Food safety monitoring of phenthoate pesticide using smartphone-assisted paper-based sensor with bimetallic Cu@Ag core-shell Nanoparticles

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Procedure for intra-day and inter-day precision and tolerance test

The intra-day precision was determined by calculating the relative standard deviation percentage (% RSD= $\frac{Sd}{mean}x100\%$) of signal intensity of phenthoate (500 μgL^{-1}) deposited on six test regions of paper substrate (S_d=standard deviation) on same day. Similarly, inter-day precision was calculated by depositing phenthoate (500 μgL^{-1}) on paper substrate for six consecutive days on the test zones of paper and (% RSD= $\frac{Sd}{mean}x100\%$) of their signal intensities were estimated.

Procedure for tolerance test for selective detection of phenthoate

Different concentrations (5 -1000 mgL^{-1}) of metal ion (Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, Fe^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}), anions (NO_3^-, SO_4^{2-} and PO_4^{3-} and Cl^-) and biomolecules (arginine, cysteine, thiamine, ascorbic acid, glucose and niacin) were prepared and deposited on fabricated paper containing NPs and recorded the digital image. The signal intensity of different chemical substances was determined before and after deposition on paper substrate using imageJ software. The "tolerance limit" of chemical substances was obtained when there is change in the signal intensity of Cu@Ag NPs for the determination of phenthoate.

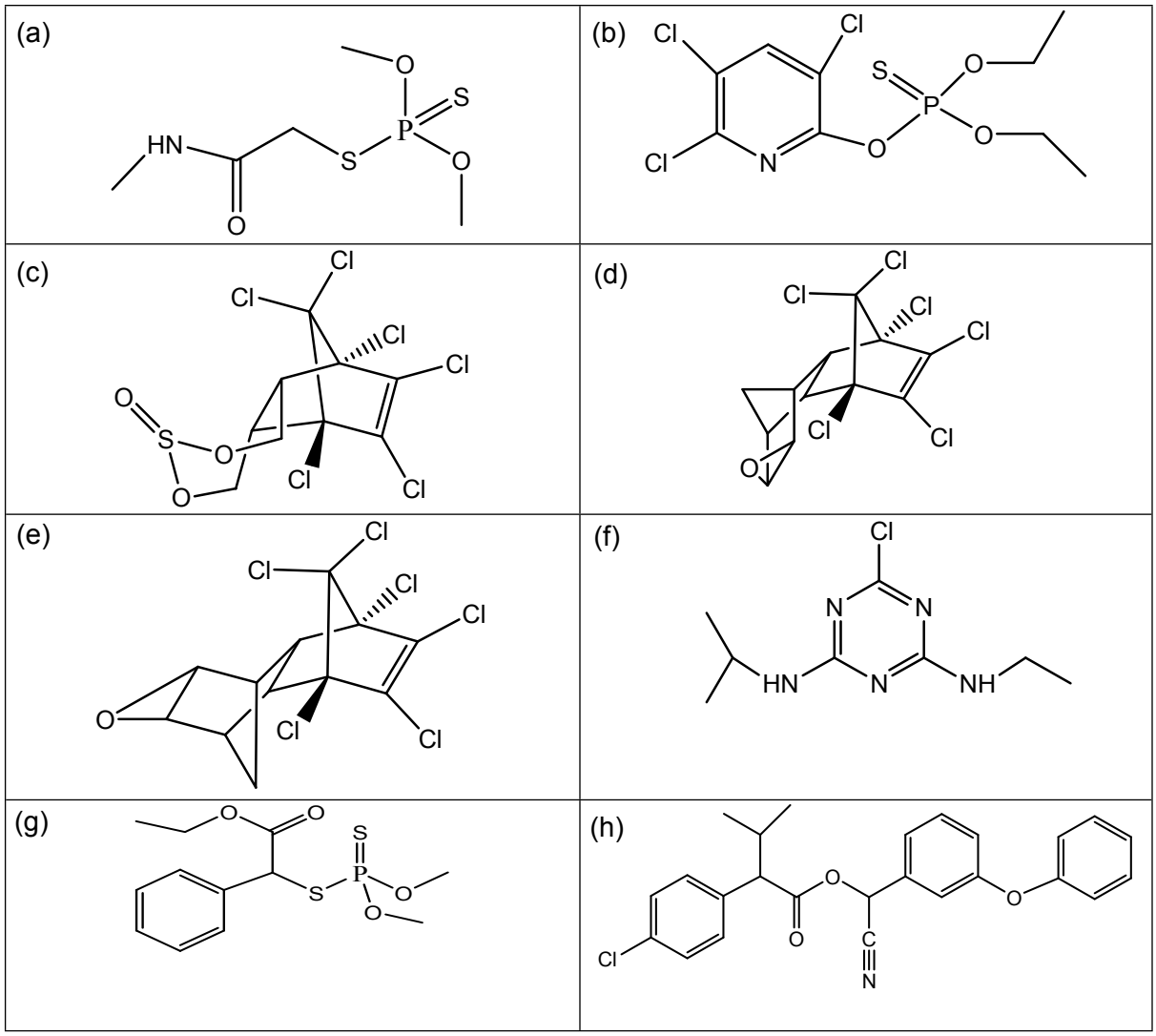

Fig. S1. Structure of pesticides (a) dimethoate, (b) chlorpyrifos, (c) endosulfan, (d) endrin, (e) dieldrin (f) atrazine, (f) endrin, (g) phenthoate (h) fenvalerate

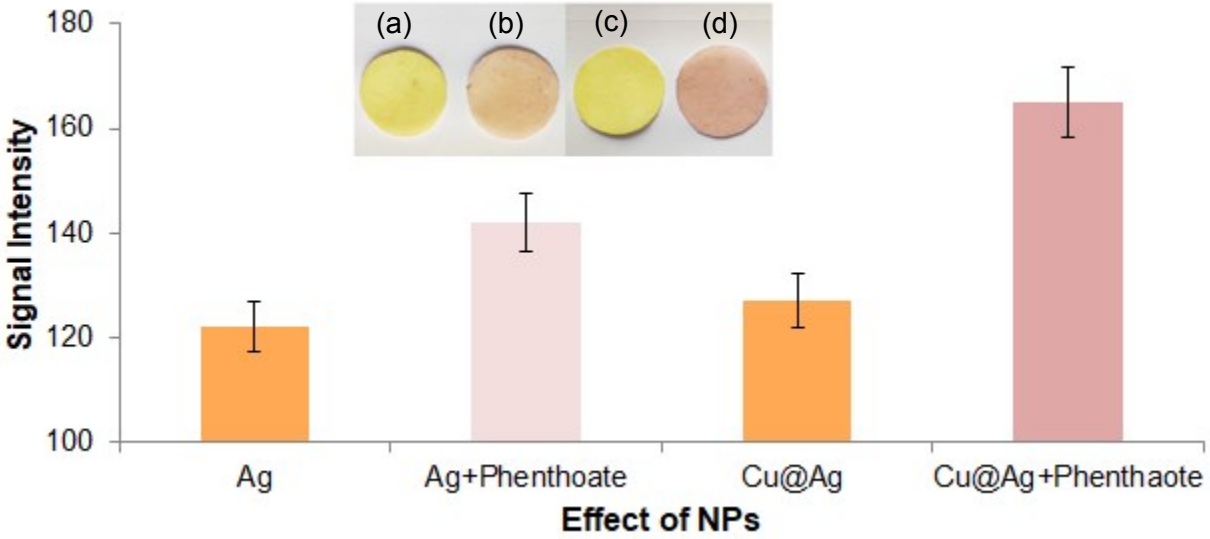

Fig. S2. Photographs of paper substrate containing (a) Ag NPs, (b) Ag NPs+phenthoate (500 μgL^{-1}), (c) Cu@Ag NPs and (d) + Cu@Ag NPs+phenthoate (500 μgL^{-1}) along with their respective mean color intensity of color developed on paper substrate obtained from imageJ software

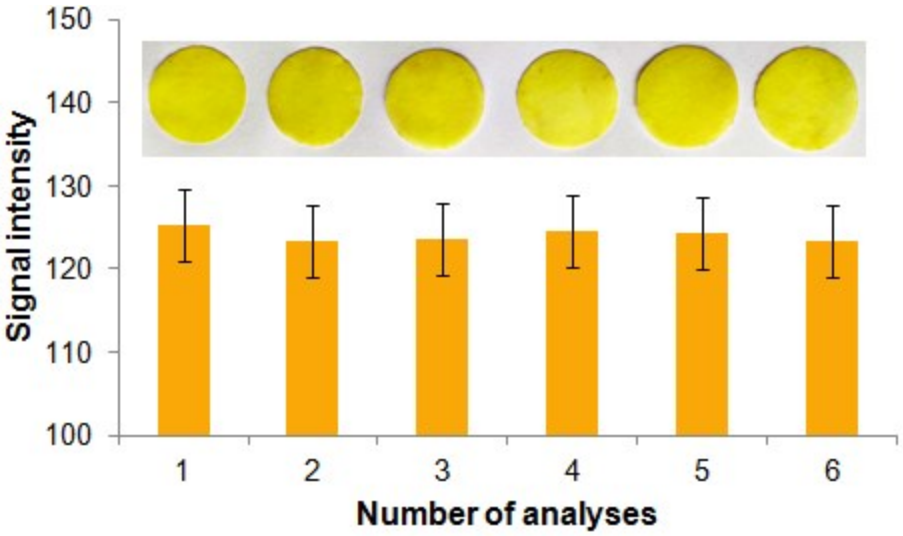

Fig. S3. Paper substrate with six test zones was deposited with Cu@Ag NPs and bar diagram shows their signal intensity

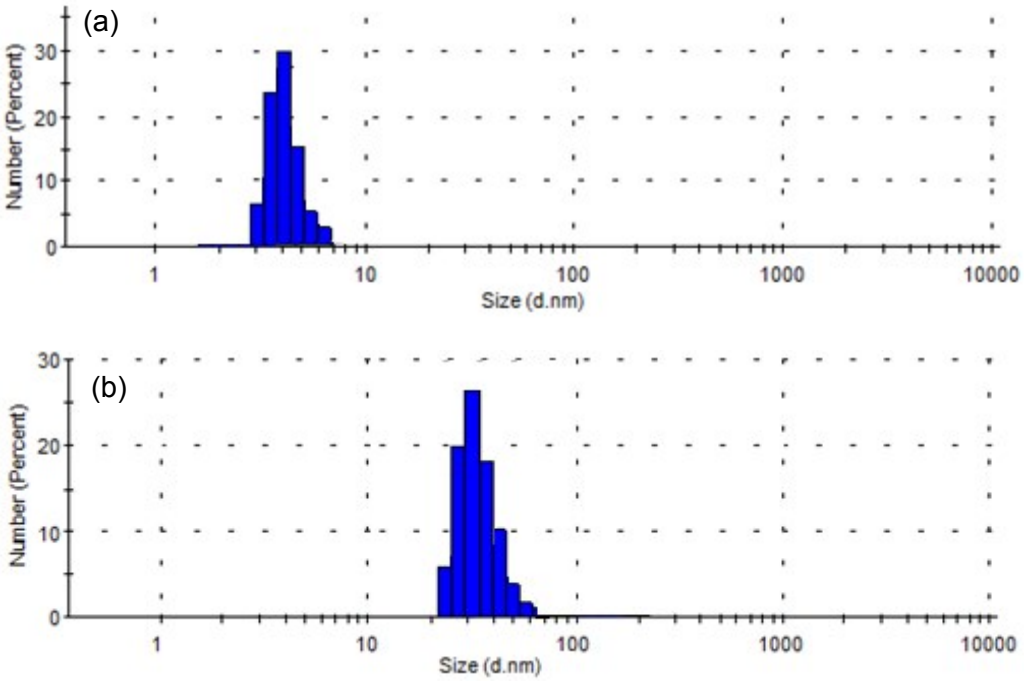

Fig. S4. DLS measurement of (a) Cu@Ag NPs and (b) Cu@Ag NPs+phenthoate

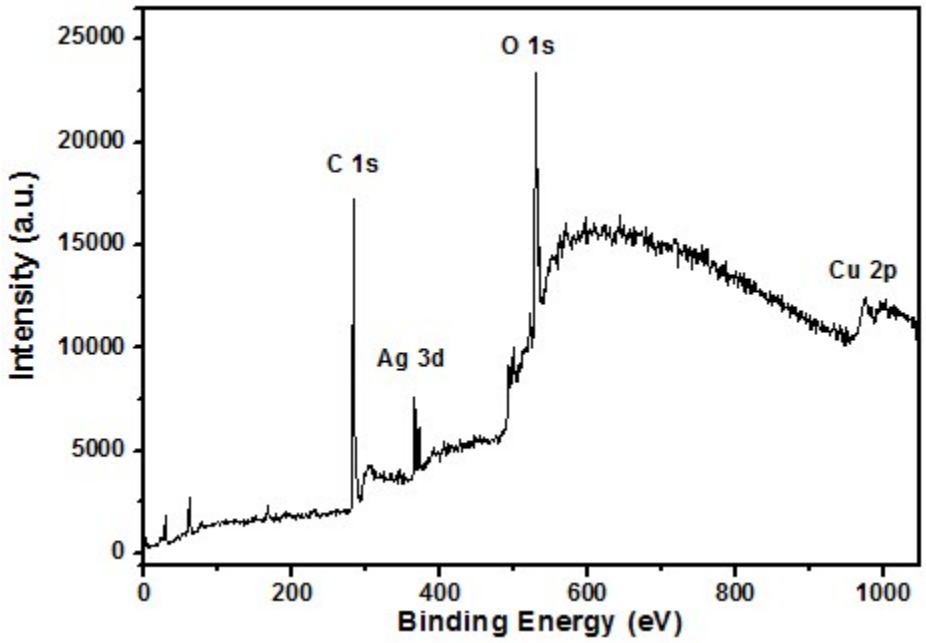

Fig. S5. Full scan XPS spectra of Cu@Ag NPs

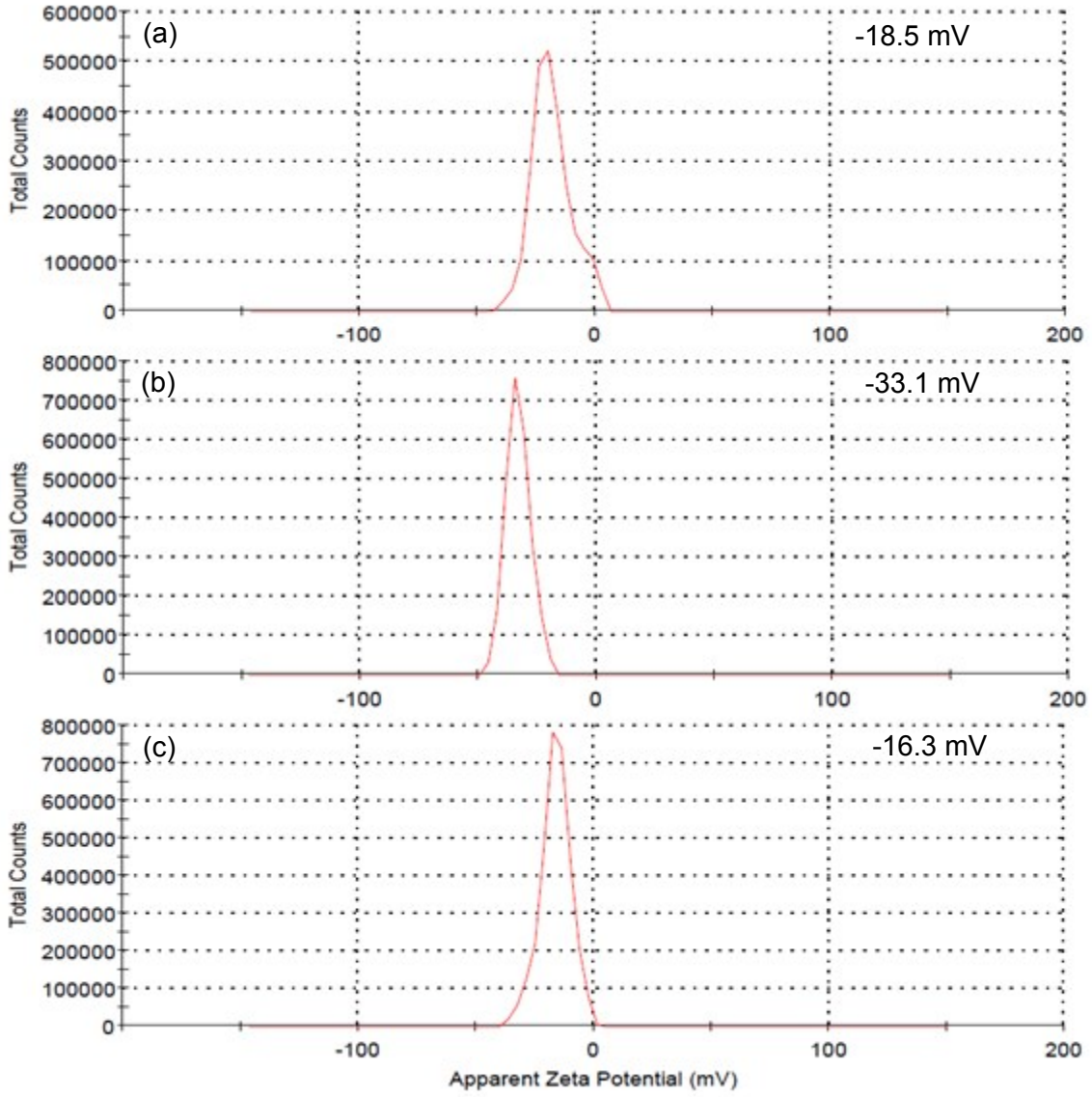

Fig. 6. Zeta potential measurements of (a) Cu@Ag, (b) Cu@Ag+phenthoate and (c) Cu@Ag+atrazine

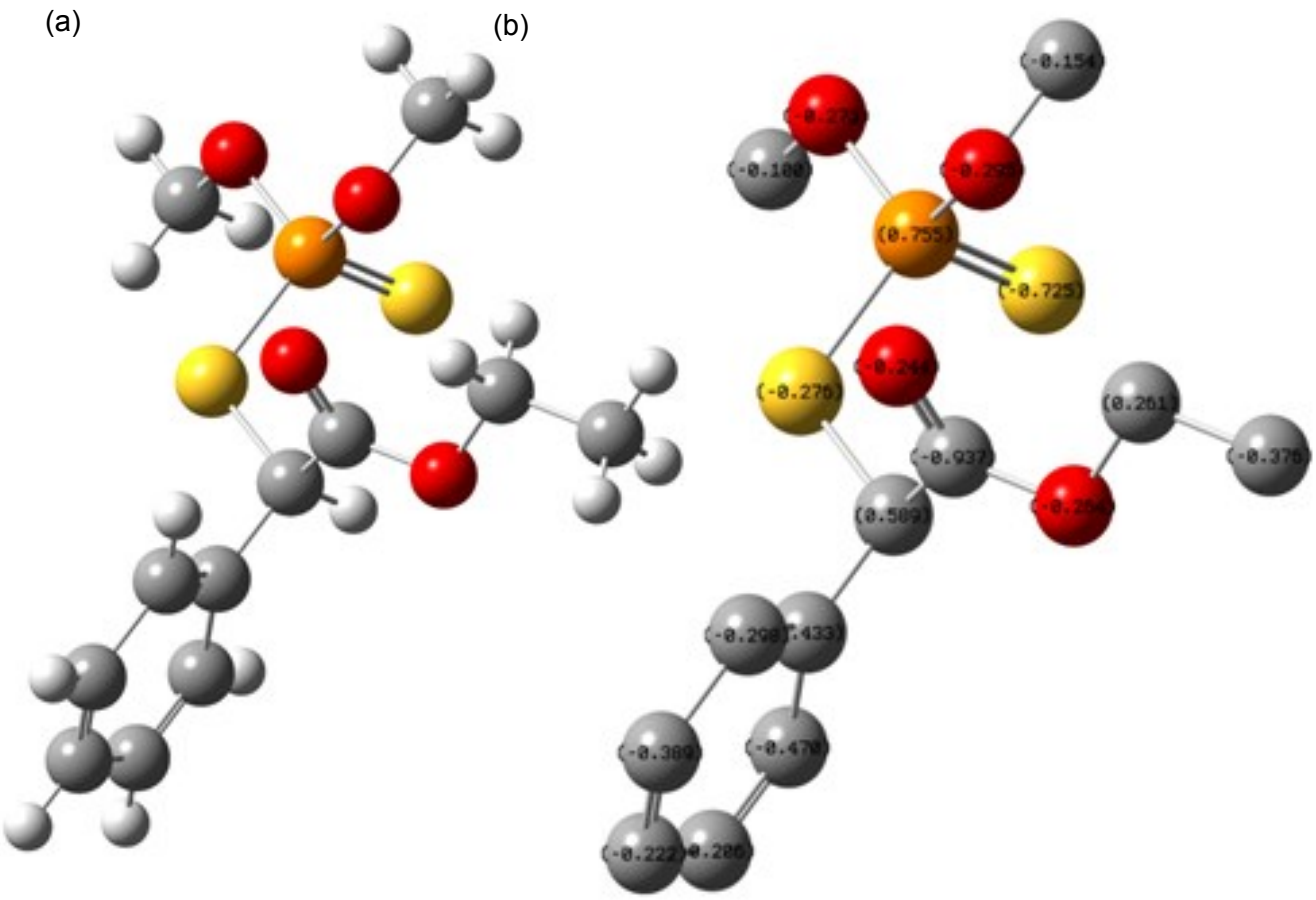

Fig. S7. (a) Optimized structure of phenthoate calculated by DFT-B3LYP and basis set 6-311++G(2d,2p) (Energy=-1906.44196318 a.u) and (b) Charge distribution (Mulliken type) on various atom of phenthoate ranging from -1.433 to + 1.433 (hydrogen atoms are omitted for clarity).

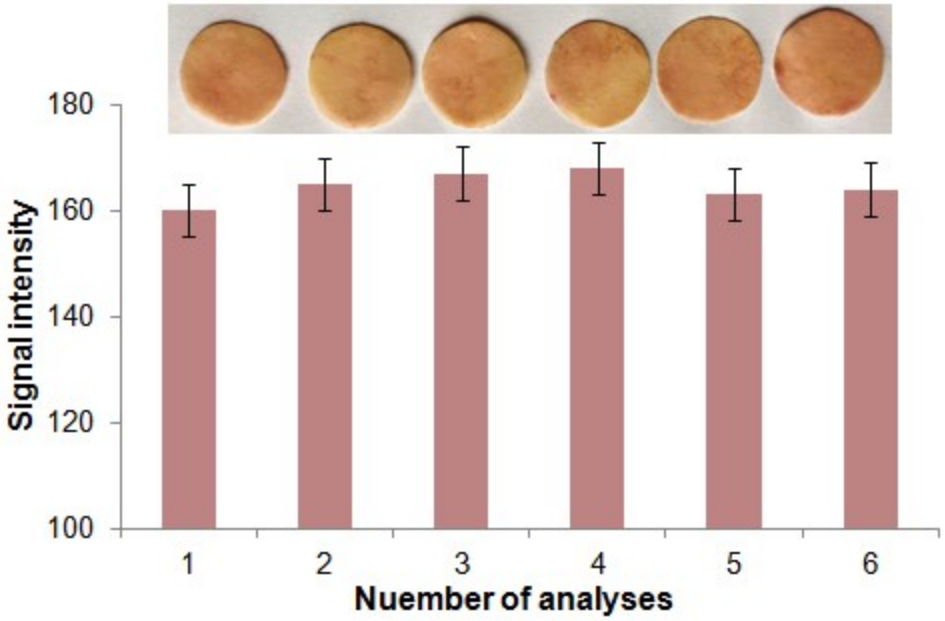

Fig. S8. Paper substrate with six test zones was deposited with Cu@Ag NPs and phentoate (500 µgL^{-1}) and bar diagram shows the signal intensity

Table 1. Cartesian coordinates of phenthoate calculated using DFT-(B3LYP)- 6-311++G(2d,2p) (E= -1906.44196318 a.u.)

Tag	Symbol	X	Y	Z
1	S	0.1480059	-1.305284	-0.379949
2	S	2.470677	-0.637896	1.6643642
3	P	2.111053	-0.742424	-0.1093289
4	O	-0.8867852	2.4701893	0.4789961
5	O	2.371512	0.7840591	-0.834665
6	O	3.1408821	-1.9002781	-0.832465
7	O	-0.3240562	1.3460092	-1.482518
8	C	-0.9239812	-0.1000319	0.3727891
9	C	-2.3915013	-0.520811	0.1704811
10	C	-0.6894152	1.2746952	-0.2804369
11	C	-3.0703184	-0.1058229	-0.926588
12	C	-3.0876404	-1.413168	1.2148422
13	C	-4.5378385	-0.526603	-1.128896
14	C	-4.3790585	-1.7834541	1.0368112
15	C	-5.1504405	-1.311876	-0.2098579
16	C	-0.0091331	3.4912584	-0.0027129
17	C	-0.2216852	4.7787135	0.8151381
18	C	3.7342101	1.1747822	-0.646808
19	C	2.9230721	-3.1768102	-0.2258979
20	H	-0.7117142	-0.0383349	1.4197062
21	H	-2.5866373	0.5141921	-1.6522151
22	H	-2.5516803	-1.7408221	2.0810352
23	H	-5.0737995	-0.1989469	-1.9950871
24	H	-4.8627385	-2.4034681	1.7624392
25	H	-6.1700816	-1.604234	-0.3504209
26	H	1.0054089	3.1670523	0.0997241
27	H	-0.2192892	3.6849514	-1.033838
28	H	-1.2362282	5.1029205	0.7127021
29	H	-0.0115301	4.5850204	1.8462632
30	H	0.4350189	5.5427305	0.4546981
31	H	4.3786062	0.4502771	-1.099296
32	H	3.9464772	1.2364792	0.4001101
33	H	3.8971872	2.1299502	-1.100672
34	H	3.5674681	-3.9013152	-0.678386
35	H	1.903431	-3.4691692	-0.366462
36	H	3.1353391	-3.1151132	0.8210201

Table 2. The Z-matrix and Cartesian coordinates of Cu@Ag nanoparticles calculated using DFT-(UB3LYP)-LANL2DZ (E= -1945.67164970 a.u.)

Tag	Symbol	Bond	Angle	Dihedral	X	Y	Z
1	Ag				-0.974	2.34573	-0.2579
2	Ag	2.67408			-0.4052	0.81168	-2.3731
3	Ag	2.67376	60.1016		-2.4297	0.15696	-0.747
4	Ag	2.67417	60.1104	-137.82	-1.6846	0.73981	1.75883
5	Ag	2.67065	108.229	37.1053	-1.5844	-1.7843	0.89198
6	Ag	2.67063	108.446	37.1668	-0.8045	-1.7495	-1.6723
7	Ag	2.66982	108.175	0.19936	1.67449	-0.7618	-1.7567
8	Ag	2.66998	61.0655	-138.07	1.60174	1.77528	-0.8991
9	Ag	2.66814	108.249	-62.831	0.79709	1.76211	1.65036
10	Ag	2.66946	108.091	-36.698	0.41782	-0.7799	2.38855
11	Ag	2.66782	108.038	63.9424	0.94982	-2.3464	0.27649
12	Ag	2.67347	108.587	-1.0909	2.43437	-0.1689	0.74305
13	Cu	2.53223	58.6275	31.5451	0.0114	-0.0014	-0.0051

Table 3. Cartesian coordinates of phenthoate interacted with Cu@Ag calculated using DFT-(UB3LYP)-LANL2DZ (E= -1428.33912332 a.u.)

Tag	Symbol	X	Y	Z
1	S	3.823989	-0.5632606	-0.4433086
2	S	1.4617027	-2.6527451	-0.7136388
3	P	2.9213428	-2.2641413	0.2886988
4	O	0.9500024	1.5542504	1.3785372
5	O	2.4462496	-2.0043028	1.9106947
6	O	4.0240198	-3.5693091	0.2198378
7	O	3.0411996	0.75864	2.0280618
8	C	2.6761741	0.7953349	-0.3716292
9	C	3.3509699	2.0668656	-0.9188585
10	C	2.2483119	1.0293421	1.0891156
11	C	4.0268886	2.8896159	-0.0805366
12	C	3.2576714	2.4034564	-2.4187265
13	C	4.7016799	4.1611489	-0.6277656
14	C	3.8514876	3.5224058	-2.9002883
15	C	4.6195775	4.4573487	-1.9476492
16	C	0.5076034	1.0600712	2.645411
17	C	-0.8905758	1.6253566	2.9570963
18	C	1.8196556	-3.1850112	2.4188364
19	C	4.42132	-3.7866011	-1.1365685
20	H	1.814625	0.5659626	-0.9632564
21	H	4.0917092	2.6557531	0.9615796
22	H	2.7239953	1.7538556	-3.080624
23	H	5.2353535	4.8107525	0.0341328
24	H	3.7866645	3.7562709	-3.9424037
25	H	5.0884301	5.3408156	-2.3278673
26	H	0.4616677	-0.0085132	2.6151318
27	H	1.1939754	1.3661224	3.4070721
28	H	-0.8446399	2.6939417	2.9873763
29	H	-1.5769474	1.3193068	2.1954346
30	H	-1.2216026	1.255586	3.9050361
31	H	2.509635	-4.0016948	2.3757477
32	H	0.9581068	-3.4143841	1.8272098
33	H	1.5223749	-3.0224223	3.4337698
34	H	5.1112991	-4.6032851	-1.179657
35	H	4.8901703	-2.903134	-1.5167863
36	H	3.5597714	-4.0159739	-1.7281952

37	Ag	-3.7487588	2.2221645	0.4555722
38	Ag	-4.0780083	-1.7380246	-1.3076074
39	Ag	-0.2720355	-0.3832161	0.2984346
40	Cu	-2.6996009	0.0336413	-0.1845335

Table S4. Effect of different metal, anions and biomolecules on determination of phenthoate using smartphone-assisted paper based sensor

Name of diverse ions	Tolerance limit, mgL^{-1}
Na^{+}, K^{+}, Ca^{2+} NO_3^{-}, SO_4^{2-} arginine and thiamine	600
Mg^{2+}, Cu^{2+} , Zn^{2+}, Fe^{3+}, PO_4^{3-} , ascorbic acid and niacine	500
Fe^{2+} , Ni^{2+} , Cl^{-} cysteine and glucose	450