Electronic Supporting Information:

Enhancement of plasmonic resonance through the exchange reaction on the surface of silver nanoparticles: Application for highly selective detection of triazophos pesticide in food and vegetable samples

Kamlesh Shrivas,[a]* Nidhi Nirmalkar,[a] Archana Ghosale, Santosh Singh Thakur[a] and Ravi Shankar[b,c]

[a]Department of Chemistry, Guru Ghasidas Vishwavidyalaya, Koni, Bilaspur, CG

[b]Nanoscience and Nanoengineering Program, South Dakota School of Mines and Technology, Rapid City, South Dakota-57701, USA

[c]Fujifilm Imaging Colorants, Inc. 233 Cherry Lane, New Castle, Delaware-19720, USA

***Corresponding author: Email-kshrivas@gmail.com**

Phone: +91-7752-260488

The structures of different type of pesticides

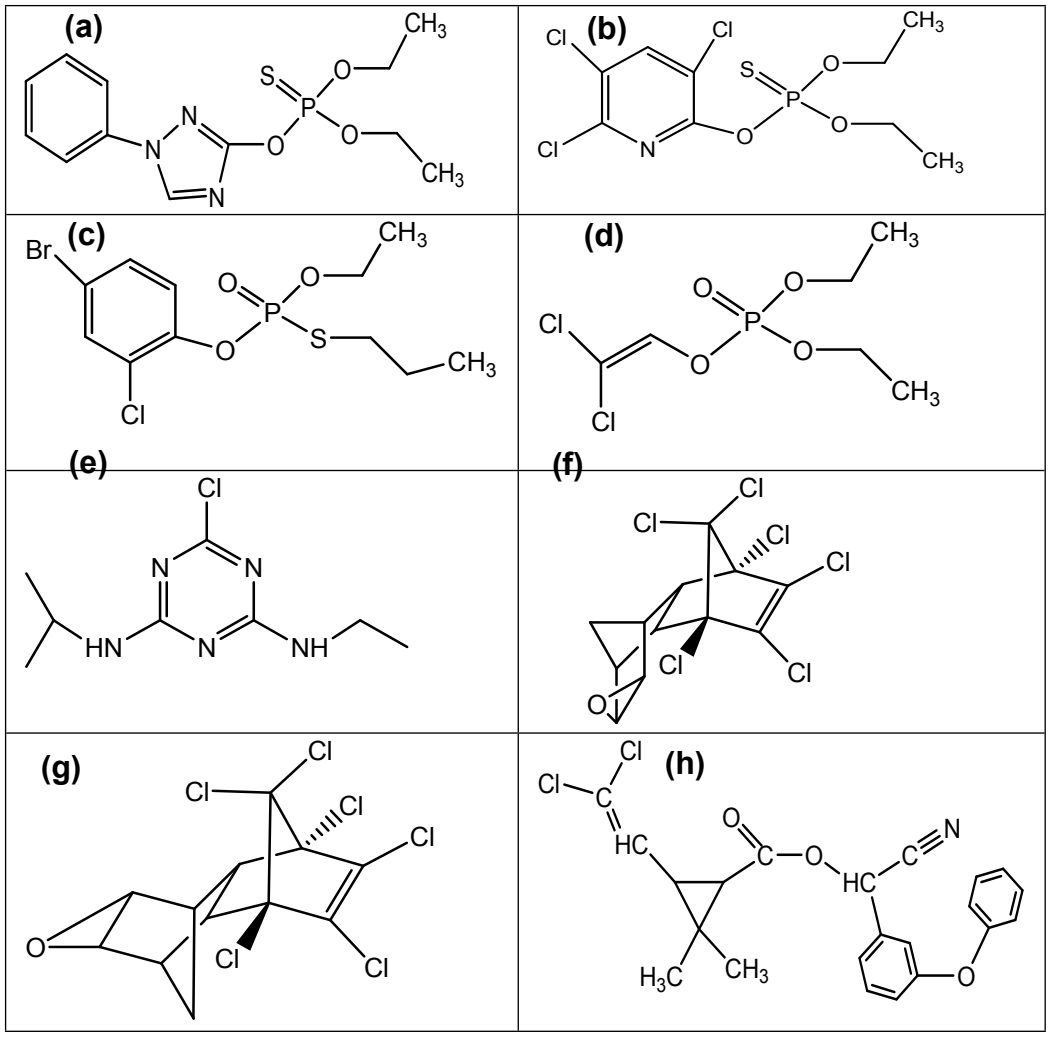

Fig. S1. Structure of pesticides (a) triazophos, (b) chlorpyrifos, (c) profenofos, (d) dichlorvos, (e) atrazine, (f) endrin, (g) dieldrin, (h) cypermethrin

XYZ Coordinates of Triazophos Calculated by DFT-(B3LYP)-3-21

Tag	Symbol	X	Y	Z
1	S	-2.207419	-0.15162	2.133519
2	P	-2.288713	0.080729	0.22762
3	O	-0.898955	0.48222	-0.491637
4	O	-2.756796	-1.127603	-0.651685
5	O	-3.194342	1.252512	-0.305938
6	N	2.295763	-0.390624	-0.118825
7	N	1.360166	0.564805	-0.31562
8	N	0.404097	-1.440248	-0.109116
9	C	3.67476	-0.074849	-0.084919
10	C	0.273757	-0.121531	-0.297403
11	C	-3.787083	-2.04934	-0.265722
12	C	-3.00131	2.618702	0.089654
13	C	1.690246	-1.565797	-0.002797
14	C	4.574291	-0.939764	0.516259
15	C	4.113436	1.106107	-0.658351
16	C	5.921795	-0.629819	0.518774
17	C	5.46223	1.408923	-0.637428
18	C	-3.830589	-3.133582	-1.313201
19	C	-4.083888	3.436724	-0.569161
20	C	6.372883	0.544017	-0.056628
21	H	-3.549951	-2.441239	0.711748
22	H	-4.721975	-1.507325	-0.209506
23	H	-3.05395	2.67489	1.16777
24	H	-2.015698	2.925209	-0.231306
25	H	2.209133	-2.487839	0.138568
26	H	4.237237	-1.837606	0.998048
27	H	3.403984	1.770166	-1.108243
28	H	-4.601525	-3.854084	-1.059235
29	H	-4.055039	-2.721194	-2.289155
30	H	-2.880662	-3.650267	-1.367356
31	H	-3.965872	4.481448	-0.30043
32	H	-4.029372	3.352409	-1.647503
33	H	-5.065037	3.109949	-0.247004
34	H	6.615624	-1.303842	0.986279
35	H	5.800223	2.326446	-1.082562
36	H	7.419658	0.784537	-0.046177

XYZ Coordinates of Triazophos with silver Calculated by DFT-(B3LYP)-3-21

Tag	Symbol	X	Y	Z
1	S	-2.1082776	-0.2530271	1.6854092
2	P	-2.1457853	0.1812547	-0.1862312
3	O	-0.7383767	0.6470369	-0.8282598
4	O	-2.5998374	-0.9233504	-1.1991627
5	O	-3.0336401	1.4095608	-0.6115588
6	N	2.4429925	-0.2832607	-0.4811216
7	N	1.5166082	0.6943257	-0.5953672
8	N	0.5465924	-1.3144502	-0.6243614
9	C	3.8223784	0.0172778	-0.3838079
10	C	0.4267978	0.0177078	-0.6739591
11	C	-3.6428952	-1.8735347	-0.9360298
12	C	-2.8429885	2.7245249	-0.0686486
13	C	1.8294259	-1.459761	-0.5040718
14	C	4.7040886	-0.913055	0.1412799
15	C	4.2794131	1.2493596	-0.8185642
16	C	6.0526638	-0.6147509	0.2060824
17	C	5.628832	1.5386086	-0.7361932
18	C	-3.6681238	-2.8399008	-2.0936952
19	C	-3.9066318	3.6156663	-0.6600055
20	C	6.5221173	0.6103717	-0.2311205
21	H	-3.4295722	-2.3688388	-0.0009192
22	H	-4.5762114	-1.3339199	-0.8427663
23	H	-2.9194751	2.6661193	1.0079199
24	H	-1.8489867	3.0563897	-0.3336407
25	H	2.3406101	-2.3952839	-0.4504345
26	H	4.352052	-1.854614	0.5172904
27	H	3.5833868	1.9625372	-1.2105144
28	H	-4.4479827	-3.5778091	-1.9347114
29	H	-3.8687033	-2.3244766	-3.0248416
30	H	-2.7197017	-3.3546564	-2.1818867
31	H	-3.7896719	4.6250205	-0.2790641
32	H	-3.828399	3.6461151	-1.7397528
33	H	-4.8962945	3.2634891	-0.3958841
34	H	6.7326298	-1.3395973	0.6141406
35	H	5.9810799	2.4958312	-1.0736499
36	H	7.569533	0.8409474	-0.1723598
37	Ag	-0.5130651	-0.3798938	1.2957064

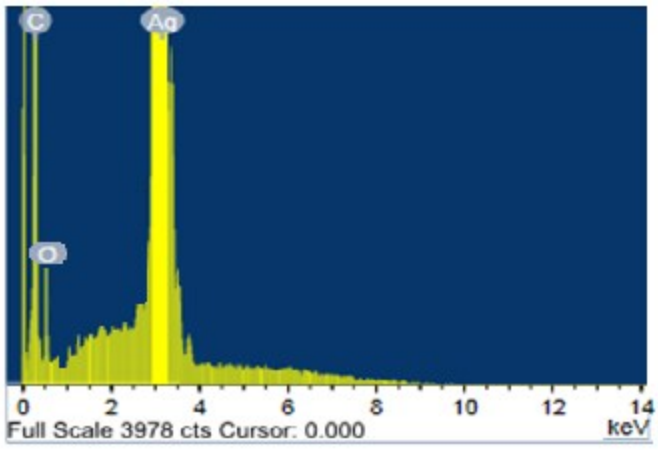

Fig. S2. EDX spectrum of citrate capped AgNPs showing the presence of carbon and oxygen and silver peaks

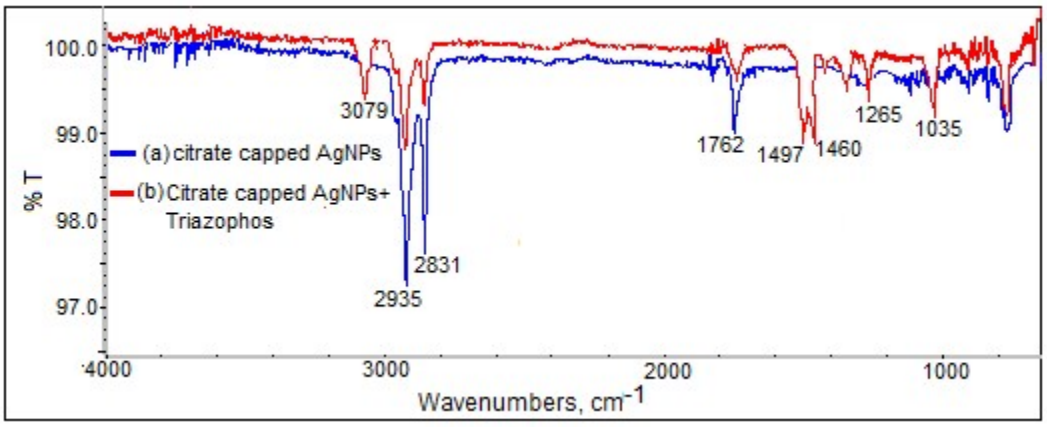

Fig. S3. FTIR spectra of (a) citrate capped AgNPs and (b) citrate capped AgNPs with triazophos

Optimization of the AgNPs-based colorimetric assay for detection of triazophos

NPs concentration is significant variable that influence the LSPR absorption signal intensity in UV-VIS spectra and detection of analyte. Therefore, we tested different concentration of AgNPs for optimum change of absorbance ratio for detection of triazophos by adding NPs solution in the range of 5-60 nM in six glass vial containing aqueous solution and triazophos (100 $ngmL^{-1}$). The solution mixture was kept at 5 min at room temperature. The results obtained are shown in supporting information Fig S4 (a). There was increase in absorbance ratio as the concentration of NPs increased from 5 to 40 nM after no change in the absorbance ratio was obtained. The increase absorption ratio was due to the degree of aggregation increase with the number of NPs concentrations in aqueous solution. Therefore, 40 nM of AgNPs was found sufficient for obtaining a maximum change in absorption ratio for detection of triazophos from sample solution.

Reaction time is also optimized for effective detection of triazophos using AgNPs as a colorimetric probe. Therefore, the NPs solution mixed with triazophos pesticide was kept at different time intervals 1, 2, 3, 4, 5, 6 and 7 min at room temperature. The absorbance ratio of solution mixture was increased with increasing the reaction time from 1 to 5 min after no change was observed, as shown in supporting information Fig. S4 (b).

The pH of the solution mixture is found most important variable that favor the binding or interaction of target analyte molecules with the surface of NPs. The higher value of absorption ratio was obtained when the pH of solution mixture was 7.0 and 8.0 that favored the maximum interaction of triazophos molecule with NPs surface. At highly acidic conditions (pH 2.0 and 4.0), the color of solution was found to be grayish due to the self aggregation NPs caused by the

protonantion of citrate ions on the surface of AgNPs. Hence, al the experiments for detection of triazophos were performed in the pH range of 7.0.

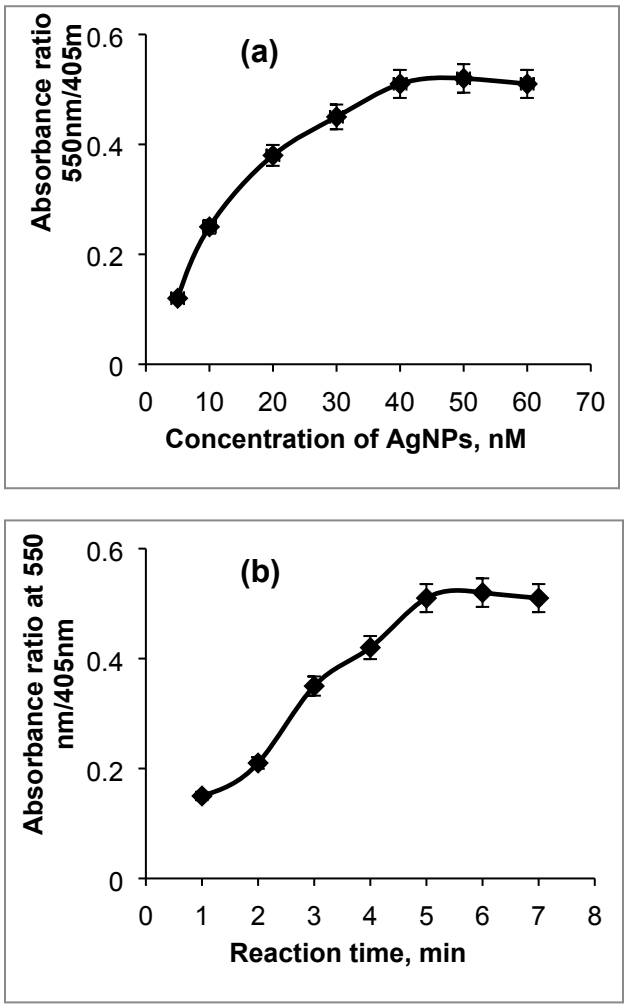

Fig. S4. (a) Effect of concentration of AgNPs and (b) Effect of reaction time for detection of triazophos (100 ngmL^{-1}) for 5 min reaction time at room temperature

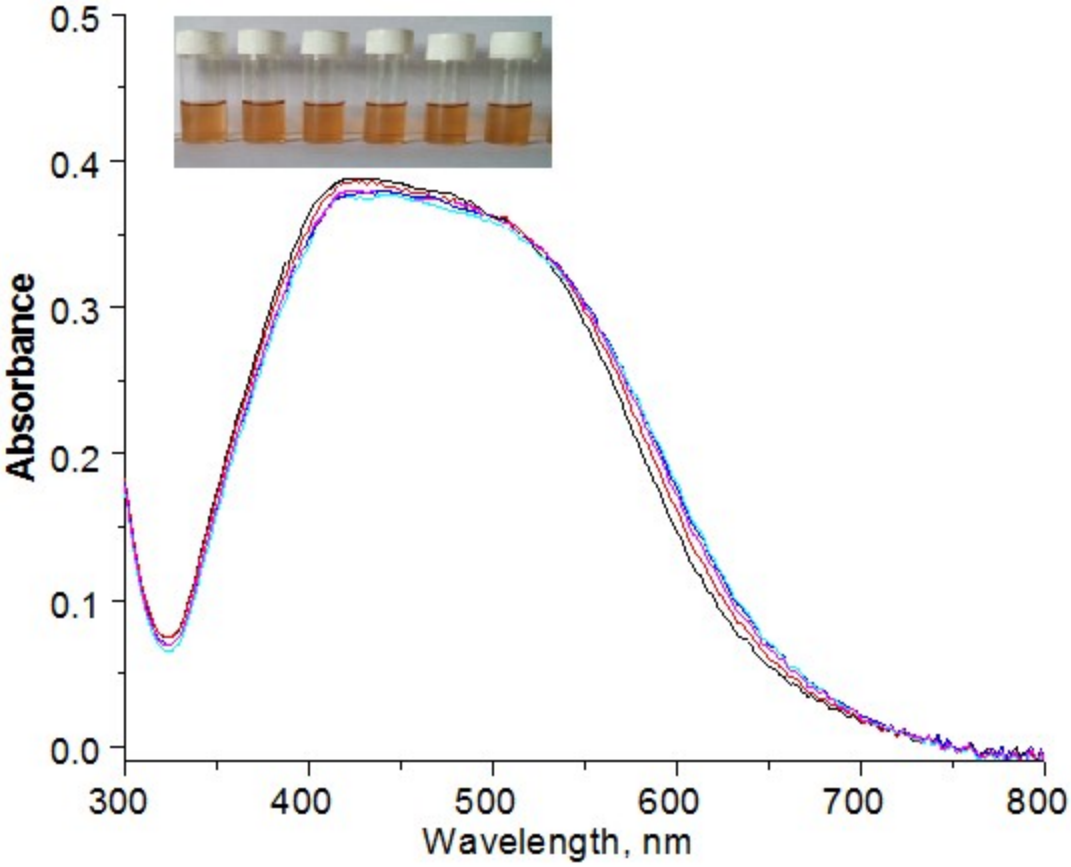

Fig. S5. Reproducibility curve for determination of 100 ngmL^{-1} of triazophos using AgNPs as a colorimetric probe for 5 min reaction time at room temperature