Supporting information

Porous chitosan/partial reduced graphene oxides/diatomite composite as an efficient adsorbent for quantitative colorimetric detecting of pesticides in complex matrix

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Chemical and Materials

Chitsoan(≥95% deacetylated), diatomite, $HAuCl_4 \cdot 3H_2O$ and sodium citrate were purchased from Aladdin company (Shanghai, China). Graphite powder, $NaNO_3$, $KMnO_4$, H_2SO4 (98%), HCl and H_2O_2 (30%) were supplied by Sinopharm Chemical Reagent Co. (Shanghai, China). HPLC grade acetronitrile were obtained from Merck (Darmstadt, Germany). Standards of phosalone and thiram were bought from Dr. Ehrenstorfer GmbH (Germany) The stock solution of pesticides were prepared in acetronitrile. Deionized water was obtained by using a Milli-Q system (Millipore, Milford, USA).

UPLC-MS/MS analysis

The chromatographic separations were performed using an Ultra-Performance LC-30A system (SHIMADZU), equipped with an Acquity UPLC HSS T3 column (100 × 2.1 mm i.d., 1.8 μm particle size, Waters, USA). The column temperature and sample temperature were kept at 40°C and 4°C, respectively. The sample volume injected was maintained at 3.0 μL. The mobile phase A was methanol containing 1 mmol L^{-1} ammonium and mobile phase B was water with 0.1% formic acid. A gradient elution was applied as follows: 90% B at 0-9 min, 0% B at 10-12.0 min, and 90% B at 12.1-14.0 min.

MS/MS analysis in scheduled multiple reaction-monitoring (sMRM) modes was carried out on Triple QUAD 5500 system (SCIEX, USA) equipped with ion-spray interface operated in positive mode. The MS parameters for determination of targeted pesticides were summarized in Table S1. Ion source temperature 500°C, Ionspray voltage 5.5 kV, desolvation gas (N_2) flow rate 50 L h^{-1} and cone

gas (Ar) flow rate 50 L h^{-1}. The dwell time established for each MRM transition was 0.05 s.

Table S1 MS parameters of phosalone and thiram analysis by UPLC-MS/MS.

Pesticide	Quantitative Ion pairs (m/z)	CE	Qualitative Ion pairs(m/z)	CE
Phosalone	368.5>182	18	368.5>322	13
Thiram	241.1>88.1	13	241.1>120	18

Table S2 The RGB values of Au NPs with different concentrations of phosalone in acetonitrile, tea matrix purified by CS/prGO/DM composites and crude tea matrix.

Phosalone												
Con.	Acetonitrile				Purified tea matrix by CS/prGO/DM				Crude tea matrix			
(mg L^{-1})	R	G	B	G/R	R	G	B	G/R	R	G	B	G/R
0	142.91±1.26	80.68±1.14	103.54±1.41	0.56	126.71±1.12	62.93±1.14	86.81±1.08	0.5	128.39±1.35	64.51±1.14	82.19±1.19	0.5
0.05	136.09±1.8	79.03±1.14	104.88±1.77	0.58	125.3±1.13	62.97±1.17	86.78±1.52	0.5	129.63±1.18	65.72±1.09	82.83±1.16	0.51
0.1	132.54±1.07	78.78±1.08	102.65±1.04	0.59	125.03±1.22	62.62±1.14	85.66±1.23	0.5	128±1.16	64.63±1.02	83.82±1.01	0.5
0.2	116.74±1.18	83.56±1.15	102.9±1.39	0.72	119.37±1.28	61.64±1.16	85.35±1.27	0.52	123.03±1.15	61.99±1.12	80.01±1.12	0.5
0.3	106.62±1.12	82.19±1.26	99.45±1.44	0.77	104±1.15	58.01±1.15	84.07±1.19	0.56	120.35±1.79	64.29±1.2	83.3±1.2	0.53
0.4	102.31±1.09	84.31±1.09	100.31±1.1	0.82	96.86±1.21	58.86±1.21	83.84±1.21	0.61	119.22±1.17	62.03±1.24	81.56±1.31	0.52
0.5	105.52±1.49	94.87±1.46	108.37±1.31	0.9	86.4±1.35	58.36±1.32	80.37±1.33	0.68	116.56±1.33	61.88±1.19	82.71±1.18	0.53
0.6	102.14±1.47	99.5±1.25	112.5±1.4	0.97	72.88±1.4	54.89±1.39	76.89±1.39	0.75	115.09±1.37	60.81±1.21	82.03±1.31	0.53
0.7	103.08±1.47	101.1±1.46	112.09±1.46	0.98	69.02±1.35	54.07±1.32	77.06±1.33	0.78	113.55±1.42	61.88±1.22	83.76±1.13	0.54
0.8	98.96±1.36	94.79±1.28	108.31±1.42	0.96	67.52±1.29	53.52±1.29	76.52±1.29	0.79	125.56±1.59	62.7±1.57	81.63±1.52	0.5
0.9	102.74±1.88	102.89±1.29	115.19±1.28	1	64.25±1.46	55.53±1.42	79.07±1.36	0.86	116.57±1.34	62.37±1.15	83.01±1.15	0.54
1	104.03±1.23	104.02±1.24	114.07±1.27	1	64.04±1.36	55.95±1.33	79.84±1.4	0.87	114.85±1.39	61±1.17	81.43±1.19	0.53
1.5					63.26±1.42	58.26±1.42	81.19±1.43	0.92	125.4±1.07	62.37±1.06	81.52±1.16	0.5
2					62.23±1.35	58.23±1.35	81.23±1.35	0.94	120.47±1.69	59.73±1.27	80.26±1.07	0.5

Table S3 The RGB values of Au NPs with different concentrations of thiram in acetonitrile, tea matrix purified by CS/prGO/DM composites and crude tea matrix.

Thiram												
Con.	Acetonitrile				Purified tea matrix by CS/prGO/DM				Crude tea matrix			
(mg L^{-1})	R	G	B	G/R	R	G	B	G/R	R	G	B	G/R
0	134.77±2.57	75.12±1.18	95.26±1.24	0.56	139.28±1.35	73.16±1.29	103.71±1.21	0.53	129.68±1.65	65.8±1.16	84.86±1.41	0.51
0.01	136.86±1.48	79.75±1.12	103.47±1.07	0.58	147.35±1.31	74.46±1.1	104.46±1.1	0.51	126.44±1.17	65.44±1.17	82.08±1.38	0.52
0.02	133.07±1.17	80.54±1.16	102.81±1.08	0.61	140.36±1.69	72.34±1.21	103.34±1.21	0.52	123.88±2	64.45±1.06	82.06±1.07	0.52
0.03	132.65±2.13	82.31±1.44	103.71±1.15	0.62	141.62±1.12	78.62±1.12	107.66±1.16	0.56	115.03±1.23	64.21±1.1	81.25±1.17	0.56
0.04	124.87±1.36	81.38±1.33	104.13±1.27	0.65	125.35±1.05	71.86±1.21	102.37±1.57	0.57	117.45±1.28	64.9±1.17	84.71±1.16	0.55
0.05	122.94±1.04	85.94±1.04	102.94±1.04	0.7	121.36±1.25	75.36±1.25	103.36±1.25	0.62	109.02±1.67	63.02±1.1	83.02±1.12	0.58
0.06	117.78±1.16	86.78±1.16	104.78±1.16	0.74	121±1.39	74.73±1.15	102.82±1.16	0.62	105.47±1.31	62.69±1.2	82.02±1.2	0.59
0.07	118.33±1.11	87.26±1.12	104±1.4	0.74	117.85±1.18	72.85±1.18	102.86±1.51	0.62	109.41±1.41	62.21±1.2	82.32±1.18	0.57
0.08	109.6±1.18	91.58±1.15	105.59±1.15	0.84	112.09±1.47	72.75±1.15	100.04±1.37	0.65	104.82±1.24	62.73±1.19	82.73±1.19	0.6
0.09	111.45±1.4	93.45±1.4	105.65±1.44	0.84	109.86±1.22	74.11±1.16	100.05±1.13	0.67	106.86±1.11	61.87±1.12	82.44±1.22	0.58
0.1	110.55±1.3	98.55±1.3	110.55±1.3	0.89	101.21±1.59	75.16±1.26	97.79±1.29	0.74	105.05±1.16	61.96±1.13	82.01±1.12	0.59
0.2	111.94±1.2	104.13±1.14	115.22±1.27	0.93	91.67±1.25	86.69±1.24	108.68±1.24	0.95	107.15±1.44	58.92±1.29	81.03±1.35	0.55
0.3	110.81±1.32	103.4±1.24	114.09±1.17	0.93	100.46±1.35	95.87±1.53	114.62±1.53	0.95	93.2±1.19	58.2±1.18	80.2±1.18	0.62
0.4	112.18±1.17	88.2±1.11	104.21±1.11	0.79	113.91±1.39	117.89±1.35	128.89±1.35	1.03	96.11±1.23	54.09±1.25	78.17±1.25	0.56
0.5	119.5±1.32	81.7±1.14	102.63±1.14	0.68	124.61±1.33	127.61±1.33	134.61±1.33	1.02	89.44±1.37	54.38±1.35	76.4±1.34	0.61

Table S4 The PS and TM concentrations of spiked tea purified matrix determined based on UV-vis and RGB analysis (mg L^{-1}) (n=3)

Pesticides	Added	UV-vis	RSD	RGB	RSD
PS	0.55	0.56±0.07	12.5%	0.60±0.007	1.16%
TM	0.035	0.033±0.004	12.1%	0.037±0.002	5.4%

The relative standard deviations (RSDs) were calculated from the following equation

RSD= (S *100)/x

In this formula, S stands for the standard deviation and x stands for the mean of the concentration calculated with the help of the calibration plot of the developed system. The standard deviation calculation was carried out on the resulting data matrix using EXCEL software.

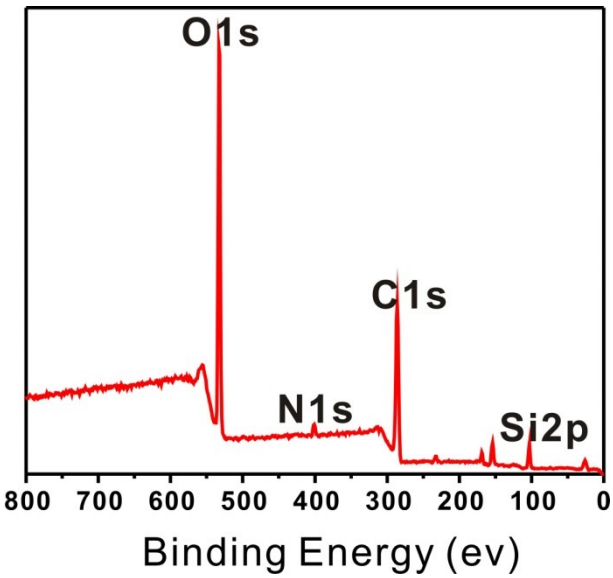

Fig. S1 The survey XPS spectra for porous CS/prGO/DM composites.

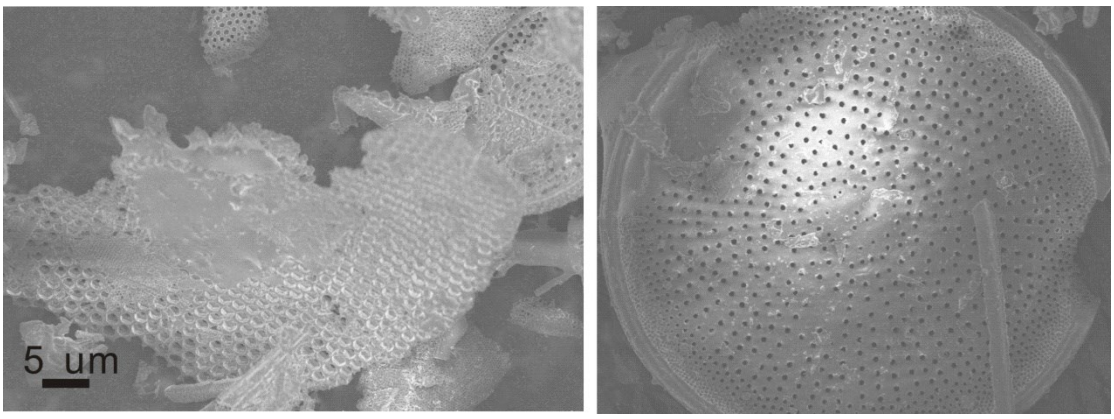

Fig. S2 The SEM images of DM.

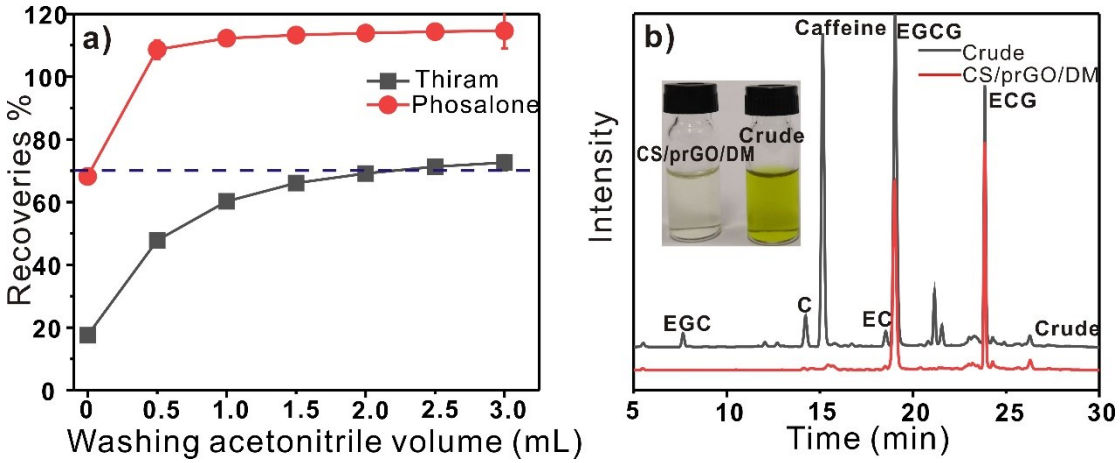

Fig. S3 a) Recoveries of pesticides after purification by CS/prGO/DM composites; and b) The selective removal ability of tea interferants on CS/prGO/DM composites with good recoveries of pesticides.

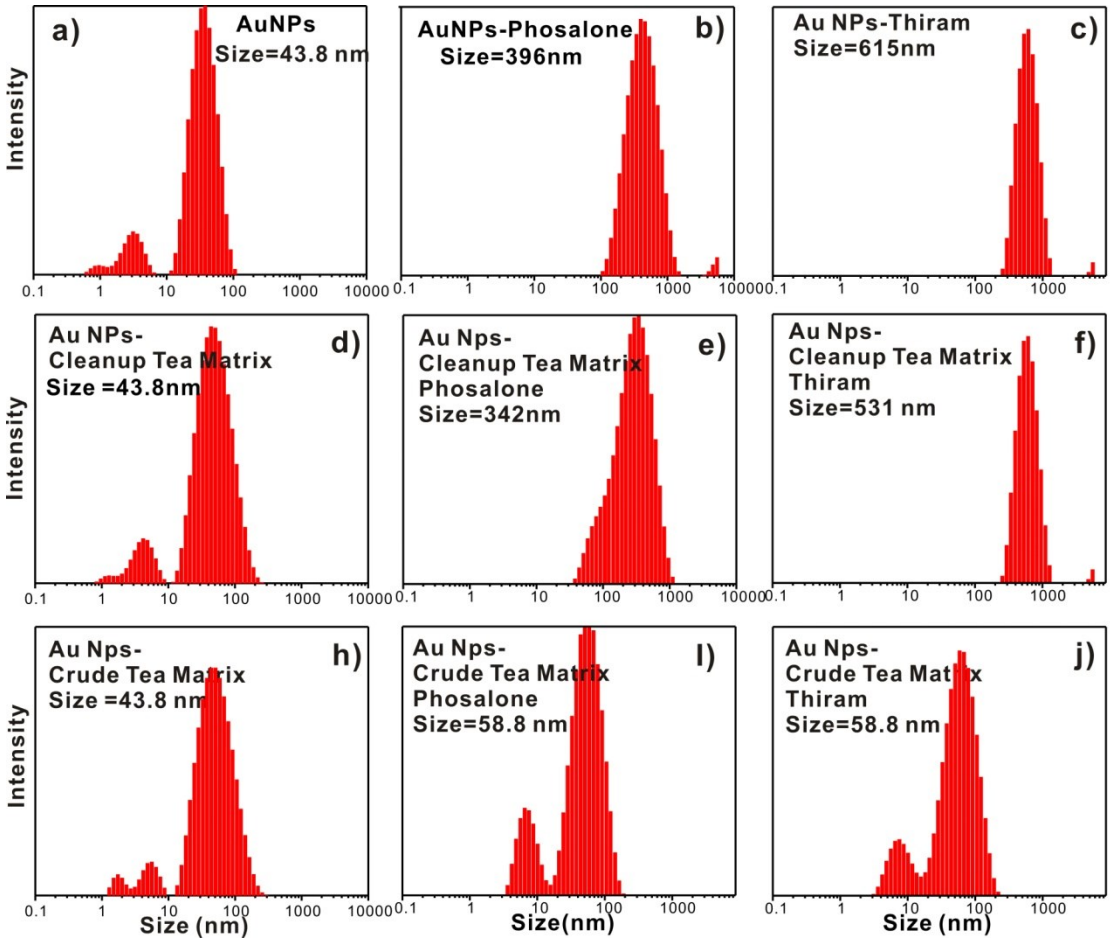

Fig. S4 Size distribution of Au NPs measured by DLS measurement. a), d), h) are size distribution of Au NPs in acetonitrile, tea matrix purified by porous CS/prGO/DM composites and crude tea matrix, respectively; b),e),i) are size distribution of aggregated Au NPs induced by PS at the concentration of 2.0 mg L^{-1} in acetonitrile, purified tea matrix and crude tea matrix, respectively; c),f),j) are size distribution of aggregated Au NPs induced by TM at the concentration of 0.3 mg L^{-1} in acetonitrile, purified tea matrix and crude tea matrix, respectively.

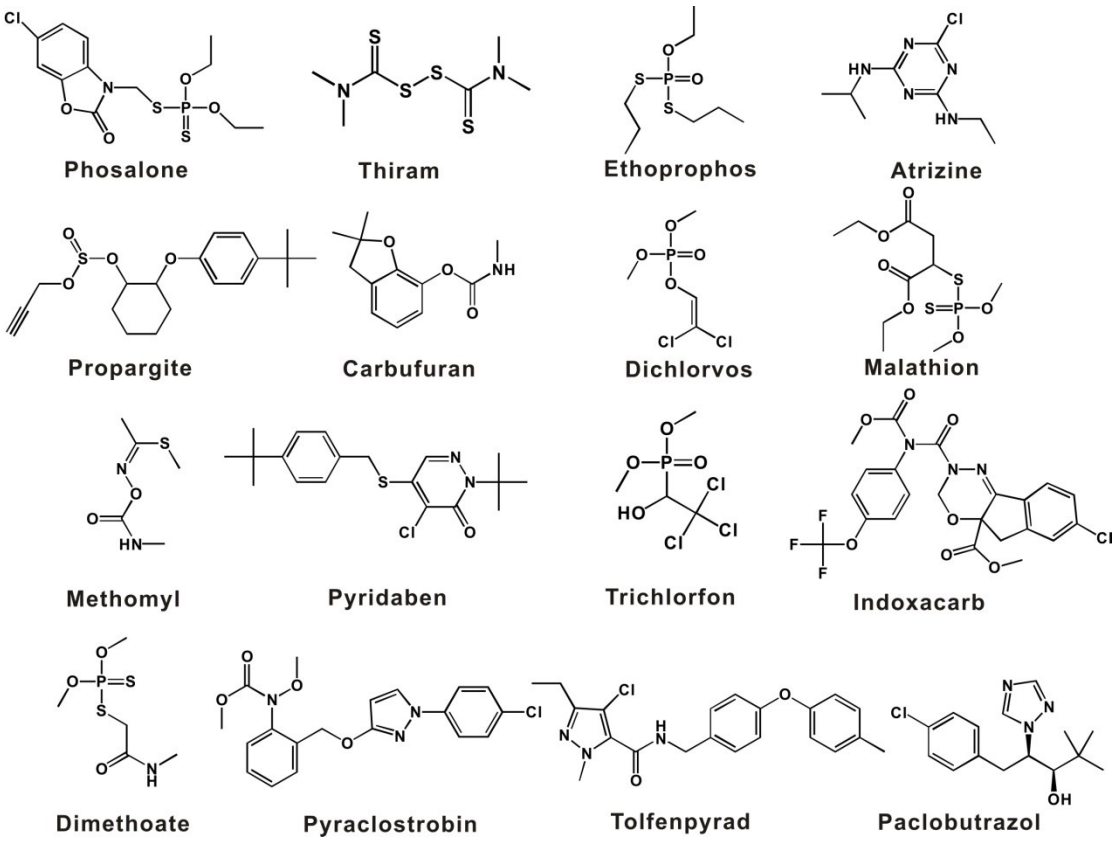

Fig. S5 The chemical structures of pesticides used for selectivity test.

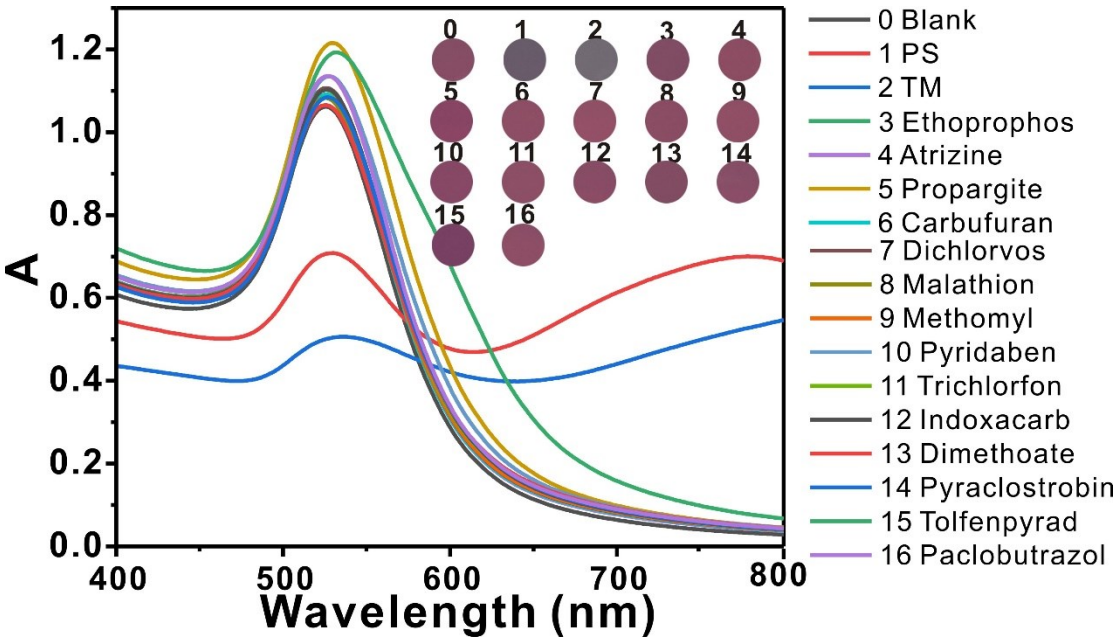

Fig. S6 The UV-vis spectra of Au NP dispersions with different pesticides.

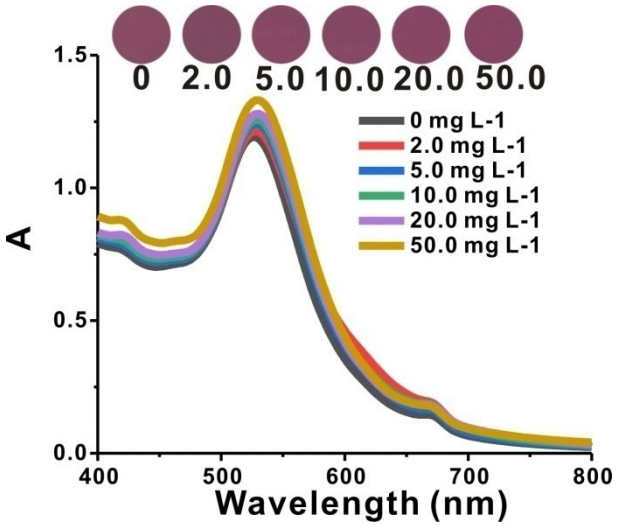

Fig. S7 UV-vis spectra of Au NPs in crude tea matrix with the concentration of phosalone in the range of 2.0 mg L^{-1} to 50 mg L^{-1} and their corresponding photographic images.

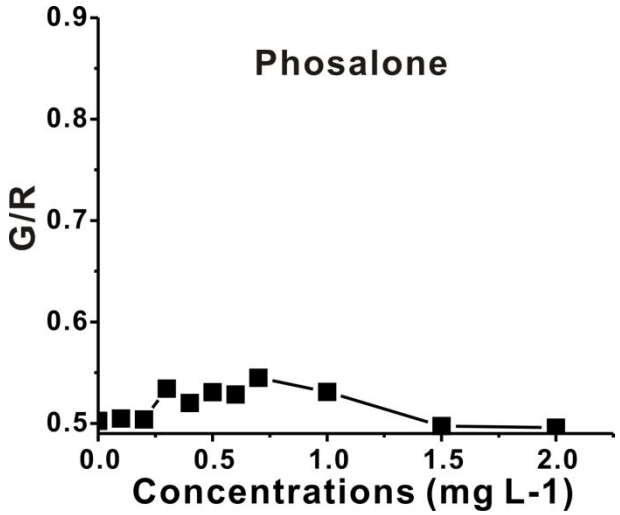

Fig. S8 The plot of G/R values vs different concentration of phosalone in crude tea matrix.

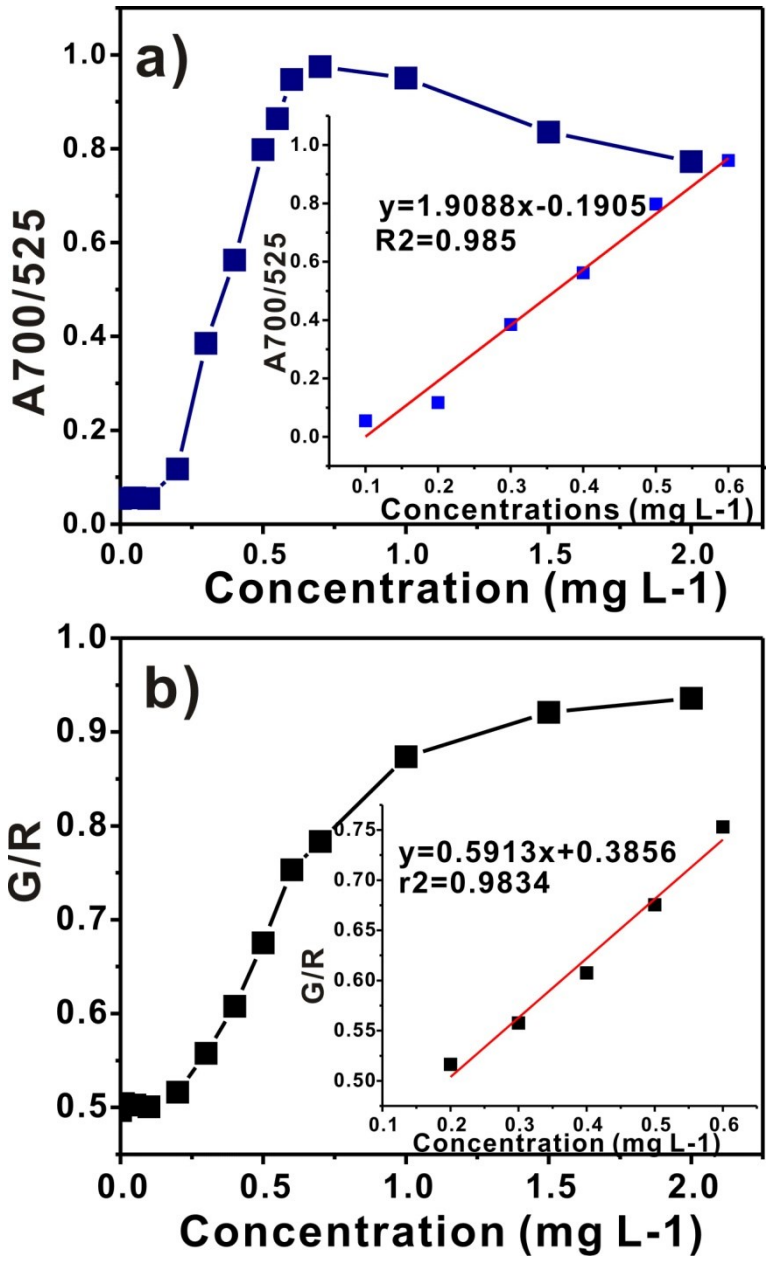

Fig. S9 The plots of A700/525 values and G/R values vs different concentrations of phosalone in tea matrix purified by porous CS/prGO/DM composites.

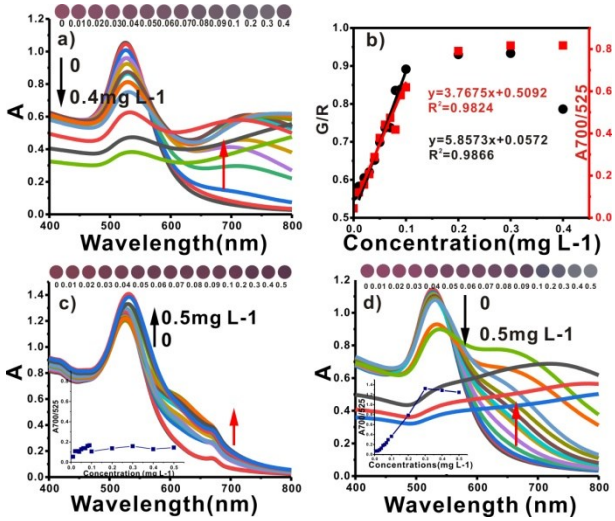

Fig. S10 UV-vis spectra of colloid Au NPs with the addition of different concentrations of TM in different matrix and their corresponding images. a) TM in acetonitrile; c)TM in crude tea matrix and d) TM in tea matrix purified by porous CS/prGO/DM SPE column. b) the plots of G/R values and A700/525 values versus different concentrations of TM in acetonitrile; Inserts in c) and d) are the plots of A700/525 values versus the concentrations of TM in crude tea matrix and tea matrix purified by porous CS/prGO/DM SPE column, respectively.

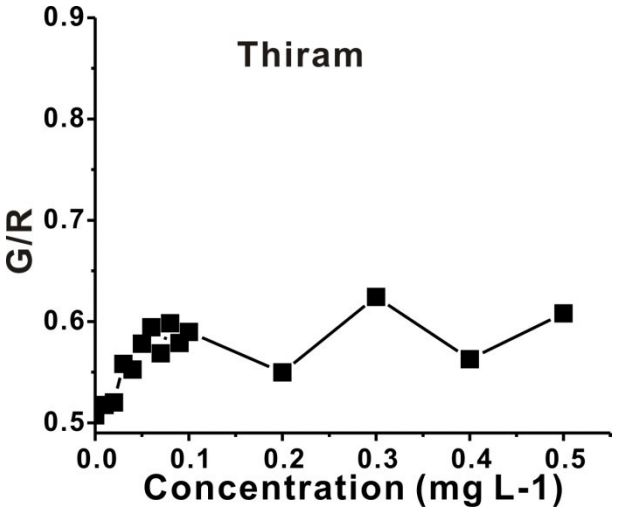

Fig. S11 The plot of G/R values vs different concentration of TM in crude tea matrix.

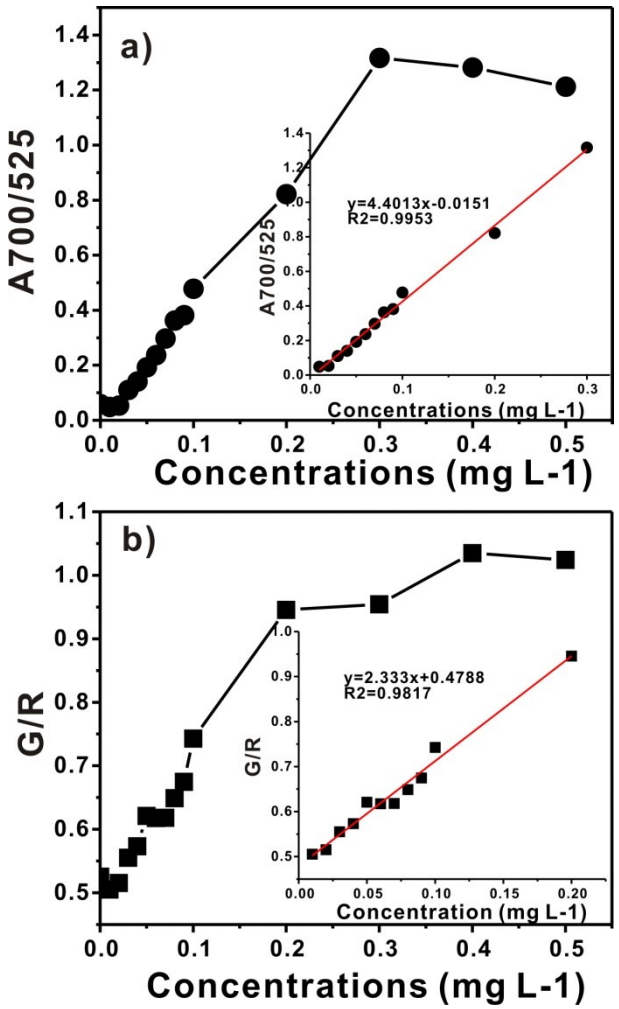

Fig. S12 The plots of A700/525 values and G/R values vs different concentration of TM in tea matrix purified by porous CS/prGO/DM composites.

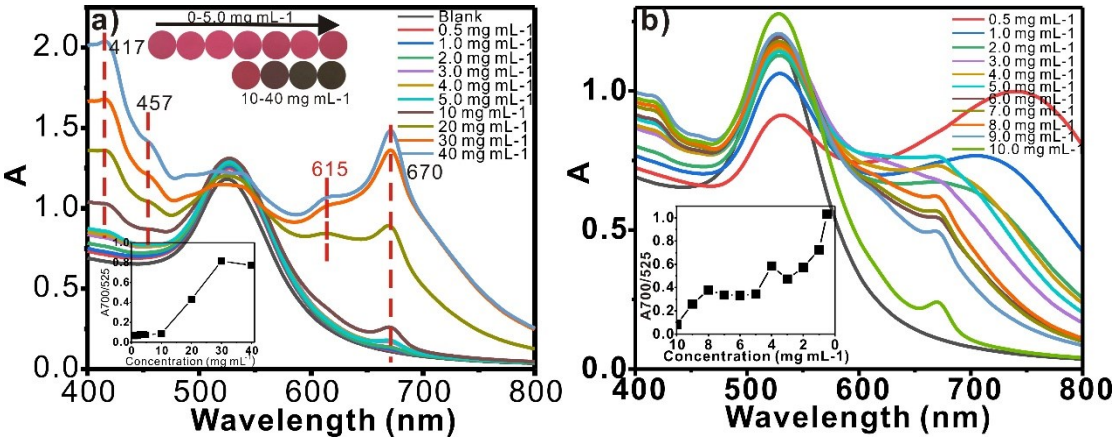

Fig.S13 a) UV-vis spectra of Au NPs containing different concentrations of tea matrix and the color changes of Au NPs sensing system. Insert is the A700/525 vs different concentrations of tea matrix; b) UV-vis spectra of Au NPs containing different concentrations of tea matrix in the presence of phosalone at 2.0 mg L-1. Insert is the A700/525 vs different concentrations of tea matrix.