Supporting information

Chitosan-reduced graphene oxides composites with 3D structures as an effective reverse dispersed solid phase extraction adsorbent for pesticides analysis

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Chemical and materials

Graphite powder, $KMnO_4$, NaCl, $NaNO_3$, H_2SO_4 (98%), H_2O_2 (30%), anhydrous ethanol and ethylene glycol were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). Chitsoan (Mn = 3 kDa) with 90% degree of deacetylation (DD, determined by ^{1}H NMR) was provided by Haidebei Marline Bioengineering Co., Ltd., China. HPLC grade acetronitrile were obtained from Merck (Darmstadt, Germany). Deionized water was obtained by using a Milli-Q system (Millipore, Milford, USA).

70 kinds of pesticides commonly used in tea plant were investigated in our study. Standards of acetamiprid, acetochlor, alachlor, ametryn, atrazine, azoxystrobin, buprofezin, butachlor, carbofuran, chlorantraniliprole, chlorpyrifos, coumaphos, demeton, diafenthiuron methanimidamide, diafenthiuron urea, dichlorvos, diflubenzuron, dimethoate, dimethomorph, dipterex, emanectin benzoate B1b, EPN, epoxiconazole, ethion, ethofenprox, ethoprophos, fenarimol, fenazaquin, fenitrothion, flufenoxuron, hexaconazole, hexythiazox, imidacloprid, indoxacarb, iprobenfos, isazofos, isofenphos-methyl, isoprocarb, malathion, metalaxyl, methidathion, methomyl, omethoate, paclobutrazol, pendimethalin, phorate, phorate-sulfoxide, phosalone, phosfolan, phosfolan-methyl, phosmel, phoxime, prochloraz, profenefos, propamocarb, propargite, pyraclostrobin, pyridaben, quinalphos, tebuconazole, tebufenozide, terbufos, thiacloprid, thiamethoxam, thiophanate-methyl, tolfenpyrad, triadimefon, triazophos, and uniconazole were purchased from Agricultural Environmental Protection Institution of Tianjin, China and Dr. Ehrenstorfer GmbH company, Germany. The purity of the pesticides standards were > 99.0%. A mixture

stock solution containing above pesticides were prepared in acetronitrile at 10 mg L^{-1}. And a standard curve was prepared from the stock solution by serial dilutions. All standard solutions were stored at 4 °C in dark vials.

Adsorption ability of tea catechins and caffeine 3D CS-rGO

The adsorption performance of catechins and caffeine from tea acetonitrile extract were conducted on different adsorbents including 3D CS-rGO, GO, CS, PSA, GCB or C18. 2 mL tea acetonitrile extract were placed in a 5 mL centrifuge tube which containing 100 mg of different adsorbents. The tube vortexed for 2 min and followed by centrifugation at 4000 rpm for 5 min. Then the supernatant was prepared for HPLC analysis. The adsorption quantities of catechins and caffeine on different adsorbents were calculated with the following equation.

Adsorption capacity = $V(C_0 - C)/m$ (eq 1)

In which V is the volume of the solution (mL). C_0 and C are refers to the concentrations of catechins ((-)-epigallo-catechin-gallate(EGCG), epicatechin-gallate(ECG), epicatechin(EC) and epigallo-catechin(EGC)) or caffeine in tea acetonitrile extraction before and after adsorption by different adsorbents (mg mL^{-1}). m is defined as the weight of adsorbents (g).

The working calibration curve for EGCG and caffeine were y = 13685.2x-268214.56 (r^2 = 0.9980) and y = 27238.62x - 66298.46 (r^2 = 0.9990), respectively, where x is EGCG or caffeine concentration (μg mL^{-1}) and y is the peak area of EGCG or caffeine. The concentrations of ECG, EGC, and EC were calculated according to

our previous report[1].

Gravimetric determination of tea co-extract

4.0 g grinded tea powder was added into the mixture of 4 mL water and 20 mL acetonitrile, and then extraction was performed with the help of a homogenizer at 12,000 rpm for 2 min. After that, 5.0 g of NaCl was introduced and vortexed for 1 min, followed by centrifugation at 4000 rpm for 10 min. The supernatant were condensed into 4 mL. Then, 300 mg 3D CS-rGO, PSA, GCB or C18 was added into 3 mL of above tea acetonitrile extracts, vortexed for 2 min, followed by centrifugation at 5000 rpm for 10 min.2 mL of supernatantand 2 mL of tea acetonitrileextracts without purification were transferred to pre-weighed 5 mL glass flasks andevaporated until dryness with nitrogen stream, and the remaining co-extracts were gravimetrically determined by analytical balance. The weight difference was recorded to estimate the adsorption ability of matrix co-extract on different adsorbents

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 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..

1. G. Ma, M. Zhang, L. Zhu, H. Chen, X. Liu and C. Lu, Journal of Chromatography A, 2018, 1531, 22-31.

Table S1 Maximum residues limits (MRLs) and parameters for 70 pesticides analysis by UPLC-MS/MS.

Pesticides	MRL			Quantitative		Qualitative	
	EU	Japan	China	Ion pairs(m/z)	CE	Ion pairs(m/z)	CE
Acetamiprid	0.05	30	10	223.1>126.1	27	223.1>56.1	19
Acetochlor	0.05	-	-	270.0>224.0	13	270.0>148.2	26
Alachlor	0.05	-	-	270.2>238.2	16	270.2>162.2	27
Ametryn	-	-	-	228.2>96.1	35	228.2>158.1	29
Atrazine	0.1	0.1	-	216.0>174.2	23	216.0>132.0	30
Azoxystrobin	-	10	-	403.9>372.3	20	403.9>329.1	35
Buprofezin	0.05	30	10	306.2>201.0	16	306.2>116.1	21
Butachlor	-	-	-	312.2>238.1	15	312.2>162.0	30
Carbofuran	0.05	0.2	0.05	222.1>165.2	16	222.1>123.1	29
Chlorantraniliprole	0.02	50	-	484.0>453.0	24	484.0>286.0	18
Chlorpyrifos	0.1	10	-	350.0>198.0	30	350.0>97	44
Coumaphos	-	-	-	363.2>227.2	35	363.2>307.2	24
Demeton	-	-	-	259.3>89.1	15	259.3>61.1	45
Diafenthiuron methanimidamide	-	-	-	353.6>297.4	28	353.6>280.3	35
Diafenthiuron urea	-	-	-	369.3>229.3	35	369.3>271.2	27
Dichlorvos	0.02	0.1	-	221.0>109.1	25	221.0>79.0	35
Diflubenzuron	0.1	20	20	311.1>158.1	19	311.1>141.1	45
Dimethoate	0.05	1	-	230.2>199.3	12	230.2>125.4	25
Dimethomorph	0.05	-	-	387.9>301.1	24	387.9>165.1	32
Dipterex	-	-	-	259.0>109.1	20	259.0>221.0	14
Emanectin benzoate B1b	-	-	-	872.3>158.0	41	872.3>81.5	120
EPN	-	-	-	322.3>145.0	17	322.3>305.1	8
Epoxiconazole	0.05	-	-	330.1>141.1	24	330.1>121.1	24
Ethion	3	0.3	-	385.2>199.3	13	385.2>143.3	34
Ethofenprox	-	-	-	394.0>177.0	18	394.0>359.0	12
Ethoprophos	0.02	-	0.05	243.2>173.0	19	243.2>214.9	14
Fenarimol	0.05	0.05	-	331.0>268.1	30	331.0>259.1	31
Fenazaquin	10	10	15	307.2>57.1	31	307.2>161.2	23
Fenitrothion	0.05	0.2	0.5	278.1>183.8	27	278.1>125.0	25
Flufenoxuron	15	15	-	489.1>158.1	24	489.1>141.1	65
Hexaconazole	0.05	-	-	315.0>70.2	24	315.0>159.9	40
Hexythiazox	4	15	15	353.1>168.1	33	353.1>228.1	43
Imidacloprid	0.05	10	0.5	256.1>209.1	21	256.1>175.1	23
Indoxacarb	5	-	5	528.0>150.0	32	528.0>218	30
Iprobenfos	-	-	-	289.2>205.3	14	289.2>247.3	10
Isazofos	-	-	0.01	314.2>162.4	24	314.2>120.4	37
Isofenphos-methyl	-	-	-	332.2>273.2	8	332.2>231.2	17
Isoprocorb	-	-	-	194.1>95.0	20	194.1>137.0	12

Malathion	0.5	-	-	331.1>127.4	14	331.1>99.4	28
Metalaxyl	0.05	-	-	280.1>220.2	19	280.1>192.2	24
Methidathion	0.1	1	-	303.1>145.4	13	303.1>85.5	25
Methomyl	0.05	20	0.2	163.1>88.1	13	163.1>106	13
Omethoate	0.05	1	0.05	214.0>125.0	29	214.0>155.0	23
Paclobutrazol	0.02	-	-	294.2>70.0	24	294.2>125.0	50
Pendimethalin	0.05	-	-	282.1>212.0	20	282.1>91	28
Phorate	0.05	0.1	0.01	261.0>75.0	16	261.0>199.0	10
Phorat sulfone	-	-	-	293.1>114.8	32	293.1>96.6	32
Phorat-sulfoxide	-	-	-	277.1>96.6	44	277.1>143.0	25
Phosalone	0.05	15	-	368.5>182.0	18	368.5>322.0	13
Phosfolan	-	-	0.03	256.2>140.0	31	256.2>228.0	16
Phosfolan-methyl	-	-	0.03	228.0>168.0	12	228.0>109.0	30
Phosmet	0.1	0.5	-	318.2>160.4	14	318.2>160.4	50
Phoxime	0.1	0.1	0.2	299.1>129.1	16	299.1>97.1	28
Prochloraz	0.1	0.1	-	376.0>266.0	20	376.0>70	48
Profenefos	0.05	0.2	-	373.0>302.9	25	373.0>345.0	17
Propamocarb	0.05	-	-	189.2>102.1	16	189.2>144.2	17
Propargite	10	5	-	368.1>231.0	13	368.1>175.1	20
Pyraclostrobin	0.1	25	-	388.1>194.0	18	388.1>164.0	24
Pyridaben	0.05	10	5	365.2>147.2	30	365.2>390.2	18
Quinalphos	0.05	0.1	-	299.1>147.1	30	299.1>163.1	30
Tebuconazole	0.05	50	-	308.2>70.0	25	308.2>125.0	50
Tebufenozide	0.1	25	-	353.3>133.1	20	353.3>297.2	11
Terbufos	0.01	0.005	0.01	289.0>103.0	10	289.0>57.0	28
Thiacloprid	10	30	-	253.1>126	28	253.1>186.1	18
Thiamethoxam	20	20	10	292.1>211.2	17	292.1>181.2	30
Thiophanate-methyl	0.1	-	-	343.1>151.1	27	343.1>192.2	21
Tolfenpyrad	-	20	-	384.2>170.9	31	384.2>197.2	34
Triadimefon	0.05	1	-	294.2>197.1	20	294.2>69.0	26
Triazophos	0.02	-	-	314.2>162.4	23	314.2>119.4	45
Uniconazole	-	-	-	292.1>70.1	28	292.1>125.1	38

Table S2 The elemental analysis and atomic ratios of GO and 3D CS-rGO.

	Elemental Composition (%)				Atomic Ratios	
	C	H	O	N	H/C	O/C
GO	42.5	3.6	53.9	0	0.09	1.27
3D CS-rGO	62.1	4.2	33.7	0.16	0.06	0.54

Table S3 Comparison of Matrix effect* of 70 pesticides before and after purification by 3D CS-rGO.

Pesticides	Matrix Effect		Pesticides	Matrix Effect	
	Crude	3D CS-rGO		Crude	3D CS-rGO
Acetamiprid	-77	-62	Isazofos	-33	-25
Acetochlor	-46	-11	Isofenphos-methyl	-41	-23
Alachlor	-41	-28	Isoprocorb	-64	-9
Ametryn	-66	-64	Malathion	-30	-25
Atrazine	-52	-45	Metalaxyl	-26	-25
Azoxystrobin	-34	-5	Methidathion	-45	-41
Buprofezin	-59	-26	Methomyl	-71	-36
Butachlor	-33	-31	Omethoate	-80	-73
Carbofuran	-51	8	Paclobutrazol	-25	-23
Chlorbenzuron	-44	-35	Pendimethalin	-52	-48
Chlorpyrifos	-44	-36	Phorate	-21	-17
Coumaphos	-31	-16	Phorat sulfone	-58	-55
Demeton	-22	-20	Phorat-sulfoxide	-43	-40
Diafenthiuron methanimidamide	-4	-1	Phosalone	-26	-10
Diafenthiuron urea	-24	-22	Phosfolan	-63	-60
Dichlorvos	-46	-39	Phosfolan-methyl	-67	-63
Diflubenzuron	-26	-19	Phosmet	-33	-15
Dimethoate	-60	-58	Phoxime	-43	-24
Dimethomorph	-14	-10	Prochloraz	-15	-14
Dipterex	-55	-52	Profenefos	-35	-21
Emanectin benzoate B1b	-11	-8	Propamocarb	-37	-28
EPN	-47	-27	Propargite	-39	-36
Epoxiconazole	-29	-23	Pyralostrobin	-26	-15
Ethion	-39	-33	Pyridaben	-64	-10
Ethofenprox	-36	-20	Quinalphos	-40	-26
Ethoprophos	-35	-25	Tebuconazole	-26	-21
Fenarimol	-25	-20	Tebufenozide	-26	-14
Fenazaquin	-45	-35	Terbufos	-39	-32
Fenitrothion	-57	-48	Thiacloprid	-41	-13
Flufenoxuron	-39	-29	Thiamethoxam	-75	-57
Hexaconazole	-34	-30	Thiophanate-methyl	-64	-62
Hexythiazox	-57	-44	Tolfenpyrad	-6	1
Imidacloprid	-82	-40	Triadimefon	-14	-6
Indoxacarb	-59	10	Triazophos	-36	-28
Iprobenfos	-38	-22	Uniconazole	-28	-23

The matrix effects were calculated with the following equation.

$$ME\ (\%) = \left(\frac{\text{slope of calibration curve in matrix}}{\text{slope of calibration curve in solvent}} - 1\right) \times 100$$

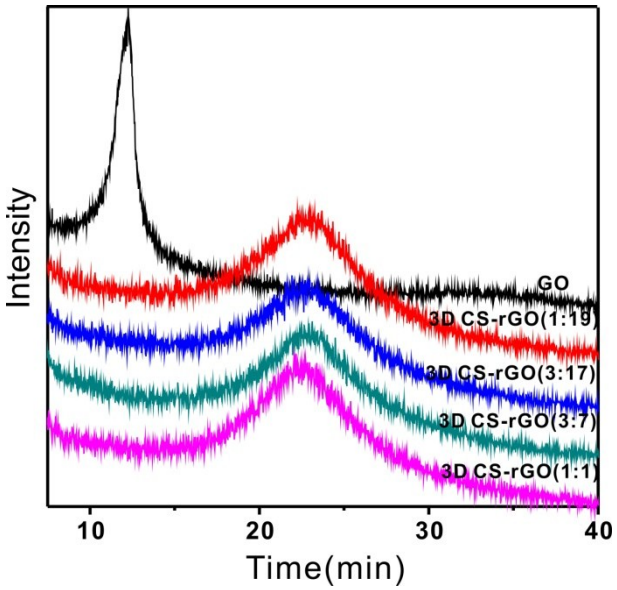

Fig.S1. XRD spectra of GO and 3D CS-rGO with different CS adding amounts.

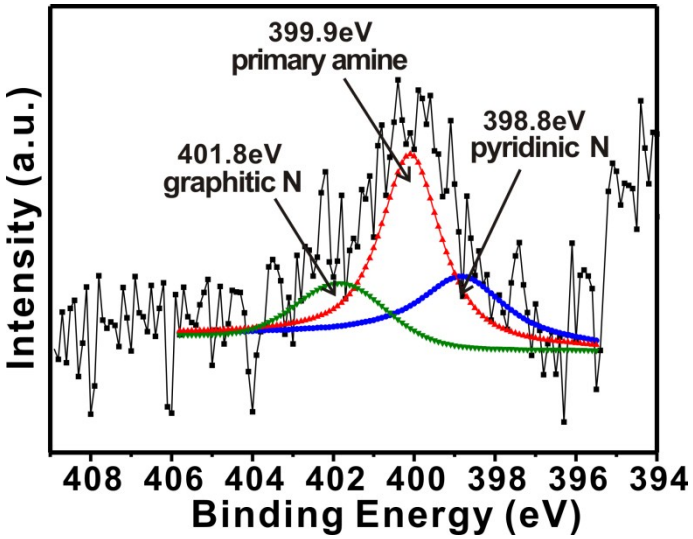

Fig.S2. XPS spectra of 3D CS-rGO for N 1s.

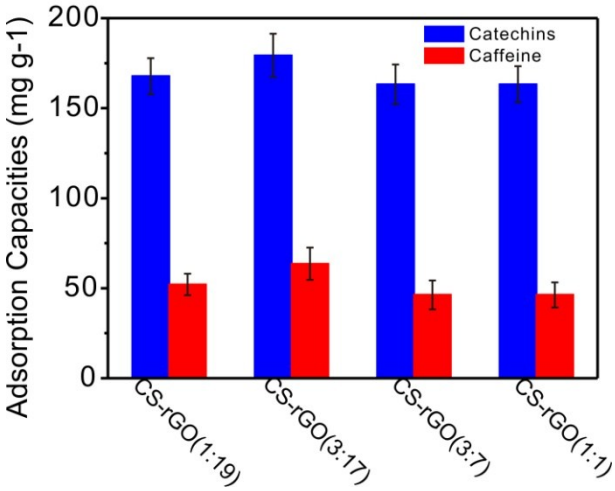

Fig.S3. Adsorption capacities of catechins and caffeine on different CS adding amounts of 3D CS-rGOs.

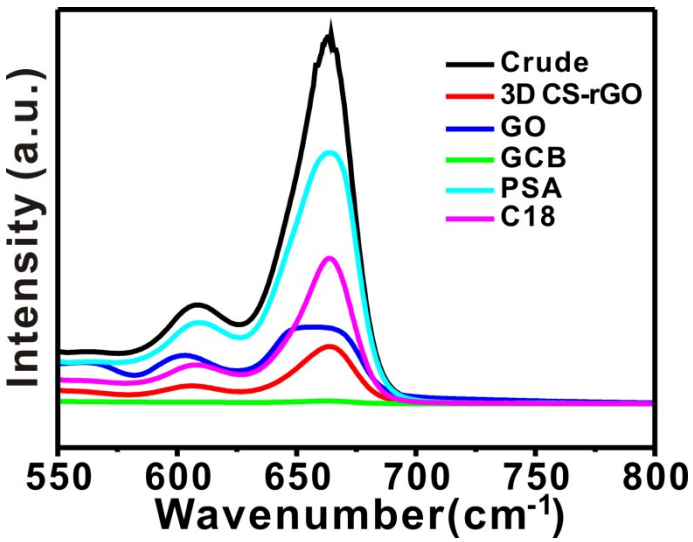

Fig.S4 Adsorption capacity of different adsorbents to chlorophyll b in tea acetonitrile extracts.

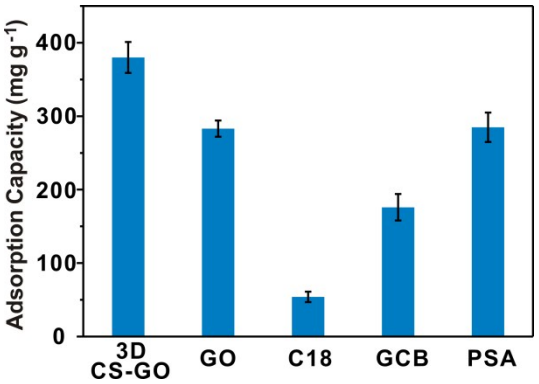

Fig. S5. The Adsorption capacities determined gravimetrically after purification by various adsorbents.

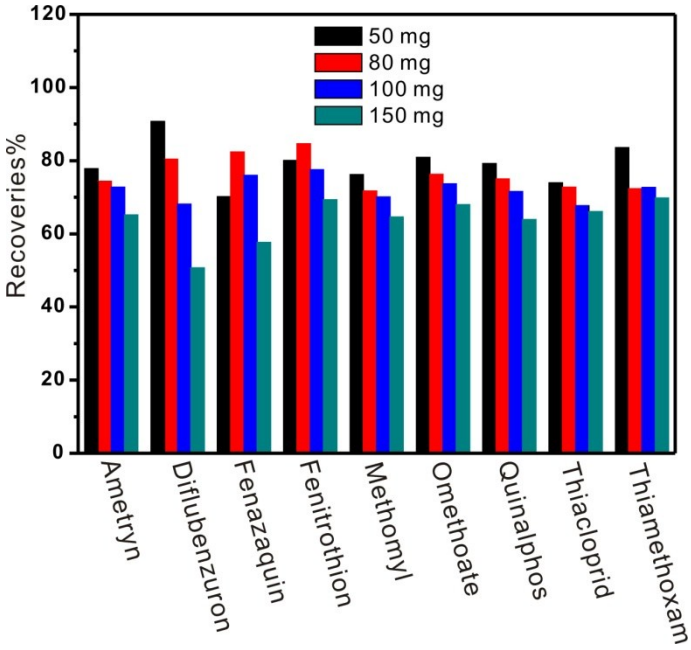

Fig. S6 Recoveries of 9 pesticides analyzed by UPLC-MS/MS when cleanup with different amounts of 3D CS-rGO (50 mg, 80 mg, 100 mg and 150 mg).