Supporting Information

Green synthesis of water-compatible molecularly imprinted resin on graphene oxide for highly selective extraction of chlorogenic acid in aqueous systems

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reciprocal 3D response interaction on the recovery of CGA. (a: effect of adsorbent dosage and elution volume, b: effect of adsorbent dosage and centrifugal speed, c: effect of elution volume and centrifugal speed).

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Materials and reagents

Graphene oxide (GO) was acquired from Jining Leader Nano Technology Co., Ltd. (Shandong, China). Dopamine hydrochloride (DA), chlorogenic acid (CGA), caffeic acid (CFA), rutin (RU), kaempferol-3-rutinoside (K-3-RU) were procured from Beijing Innochem Science & Technology Co., Ltd. (Beijing, China). Hexamethylenetetramine (HMTA) was obtained from Huadong Chemical Co., Ltd. (Tianjin, China). Methanol and acetonitrile were obtained from Shanghai Xingke Co., Ltd. (Shanghai, China). Ultrapure water was filtered using a 0.22 μm membrane before use. A standard stock solution of CGA (1.00 mg mL^{-1}) was prepared in methanol.

HPLC analysis

A Thermo UltiMate 3000 DGLC HPLC system (Thermo Fisher Scientific, USA) equipped with a Chromeleon 7.2 workstation, UV detector, and a chromatographic column (Accucore C_{18}, 100 × 4.6 mm, 2.6 μm) was employed for the determination of CGA. The mobile phase was water-acetonitrile (9:1, v/v, containing 0.1% TFA). The wavelength of the UV was set at 290 nm. The injection volume was 20 μL.

Method validation

The methodology parameters included detection limit (LOD), quantitation limit (LOQ), working range, trueness, and precision. The LOD and LOQ were calculated using the equation LOD = 3Sa/b and LOQ = 10Sa/b, where Sa is the standard deviation of the blank sample response and b is the slope of the calibration curve.[1] The working range was constructed by concentrations (0.02–25.00 μg mL^{-1}) of CGA. And response values of each concentration are plotted on the y-axis against the concentrations of each

point. The trueness of the proposed method was assessed through recovery experiments using spiked samples at three spiking levels (0.5, 5.0, and 25 μg mL^{-1}). The method precision was represented as repeatability and reproducibility, which were calculated by extracting and quantifying each analyte from real matrix using the whole methods in one day (intra-day, n = 6) and three consecutive days (inter-day, n = 3), respectively.

Fig. S1 Sample preparation and CPTE procedure.

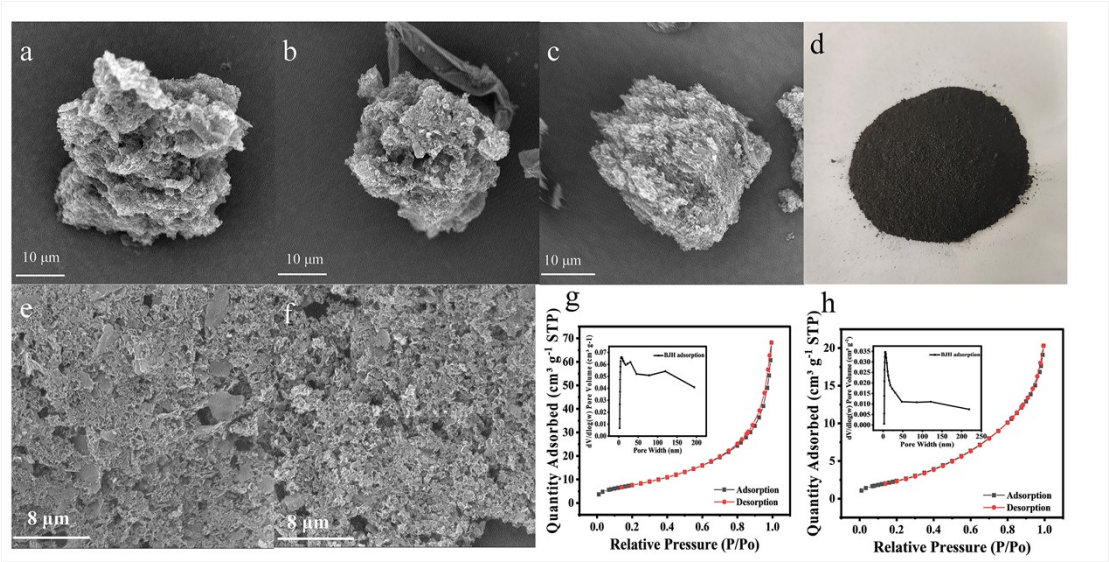

Fig. S2 The low-resolution (5000×) SEM images (a–c) and optical photograph (d) of SMIR/PGO; The SEM images of (e) SMIR/PGO (10000×) and (f) SNIR/PGO (10000×); N_2 adsorption–desorption isotherms and BJH size distribution isotherms of SMIR/PGO (g) and SNIR/PGO (h).

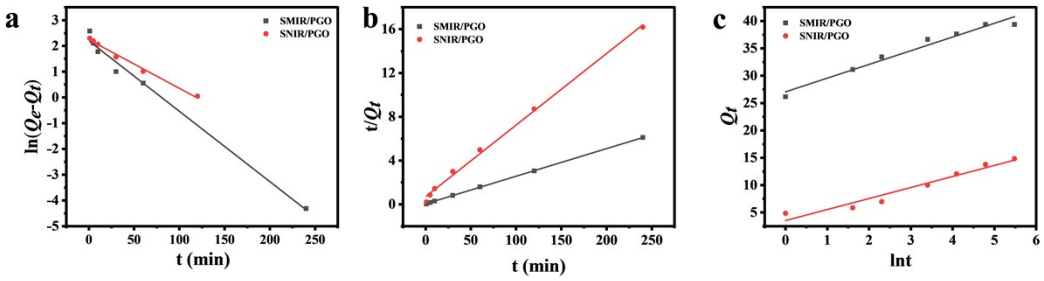

Fig. S3 The fitting curves of a: pseudo-first-order model; b: pseudo-second-order model, and c: Elovich model for SMIR/PGO and SNIR/PGO.

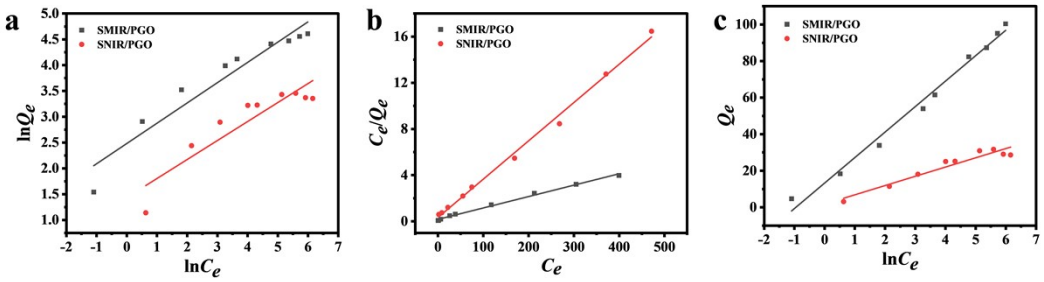

Fig. S4 Adsorption isotherm models of SMIR/PGO and SNIR/PGO. (a: Freundlich linear fits for CGA; b: Langmuir linear fits for CGA; c: Temkin linear fits for CGA).

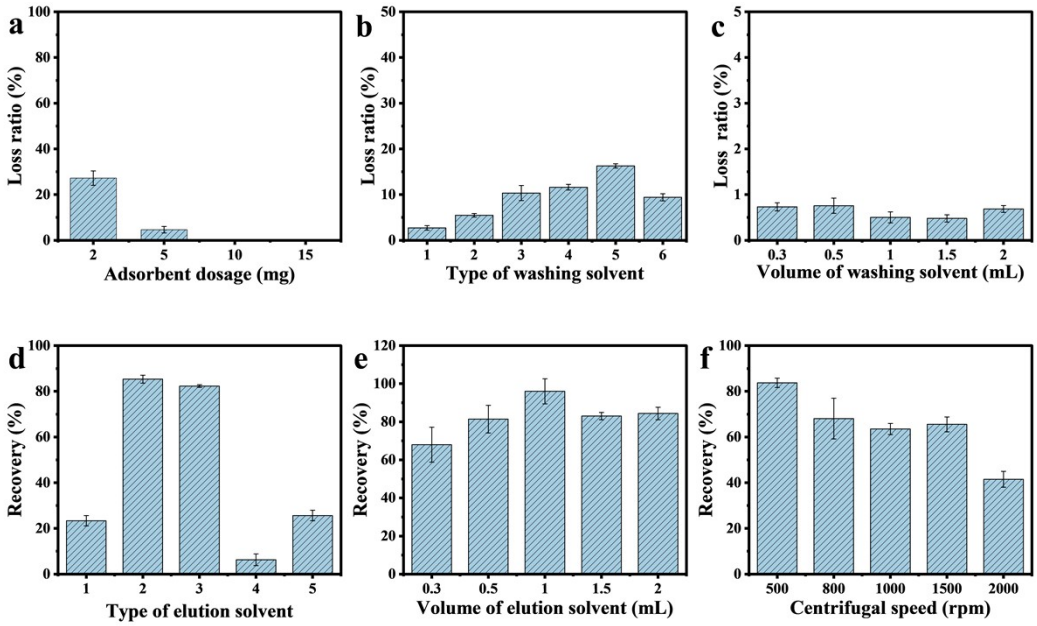

Fig. S5 Optimization of the extraction conditions. a: Adsorbent dosage; b: types of washing solvent (1: water; 2: methanol-water (1:9, v/v); 3: acetonitrile-water (1:9, v/v); 4: acetonitrile; 5: methanol-water (5:5, v/v); 6: methanol); c: the volume of washing solvent; d: types of elution solvent (1: acetonitrile-formic acid (9:1, v/v); 2: methanol-formic acid (9:1, v/v); 3: methanol-formic acid-water (8:1:1, v/v/v), 4: acetonitrile-water (9:1, v/v); 5: acetone-water (9:1, v/v)); e: volume of elution solvent; f: centrifugal speed.

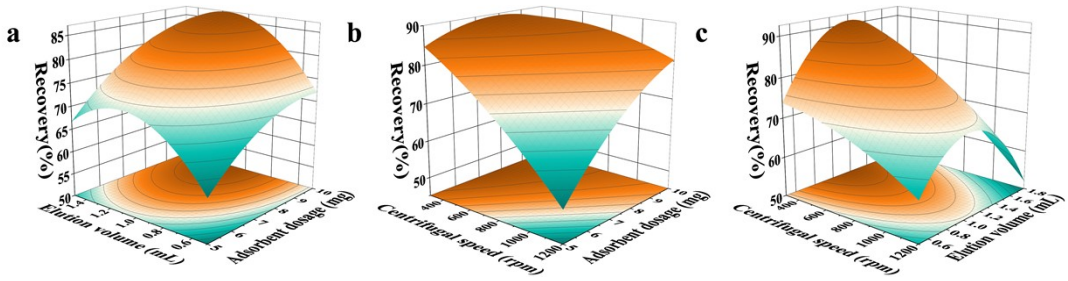

Fig. S6 Effect of adsorbent dosage, elution volume, centrifugal speed and their reciprocal 3D response interaction on the recovery of CGA. (a: effect of adsorbent dosage and elution volume, b: effect of adsorbent dosage and centrifugal speed, c: effect of elution volume and centrifugal speed).

Table S1 Parameters of the three kinetic models

Kinetic models	Parameters	SMIR/PGO	SNIR/PGO
Pseudo-first-order model	k_1 (min^{-1})	0.0273	0.0189
	Q_e (mg g^{-1})	8.9835	9.4164
	R^2	0.9869	0.9894
Pseudo-second-order model	Q_e (mg g^{-1})	39.6196	15.2835
	k_s (g·mg^{-1} min^{-1})	0.0149	0.0067
	R^2	0.9999	0.9960
Elovich model	a	27.0512	3.5292
	b	2.5058	2.0140
	R^2	0.9617	0.9409

Table S2 Parameters of Langmuir, Freundlich, and Temkin adsorption isotherms

Isotherm		Parameters	
Freundlich	SMIR/PGO	n	2.5445
		K_f (mL μg^{-1})	11.9676
		R^2	0.9144
	SNIR/PGO	n	2.7174
		K_f (mL μg^{-1})	4.2046
		R^2	0.8082
Langmuir	SMIR/PGO	Q_m (mg g^{-1})	101.3171
		K_l (mL μg^{-1})	0.0566
		R^2	0.9943
	SNIR/PGO	Q_m (mg g^{-1})	30.1296
		K_l (mL μg^{-1})	0.0985
		R^2	0.9948
Temkin	SMIR/PGO	B_T	13.9420
		A_T (L mg^{-1})	2.5908
		R^2	0.9852
	SNIR/PGO	B_T	5.06288
		A_T (L mg^{-1})	1.4214
		R^2	0.9182

Table S3 Experimental factors and levels in the central composite design

	Levels				
Factors	Low (–1)	Central (0)	High (+1)	-α	+α
A: Adsorbent dosage (mg)	5.0	7.5	10	3.3	11.7
B: Elution volume (mL)	0.5	1.0	1.5	0.16	1.84
C: Centrifugal speed (rpm)	500	750	1000	330	1170

Table S4 The central composite design with experimental results

Run	Adsorbent dosage (mg)	Elution volume (mL)	Centrifugal speed (rpm)	Recovery (%)
1	7.5	1.0	750	86.5
2	5.0	0.5	500	67.9
3	5.0	1.5	1000	55.9
4	10	1.5	500	85.5
5	11.7	1.0	750	82.4
6	5.0	1.5	500	75.9
7	7.5	1.0	750	86.5
8	7.5	1.0	1170	70.0
9	7.5	1.84	750	67.5
10	7.5	1.0	750	79.4
11	10.0	0.5	1000	73.6
12	7.5	1.0	330	87.7
13	5.0	0.5	1000	53.9
14	7.5	0.16	750	46.2
15	7.5	1.0	750	86.5
16	10	0.5	500	74.1
17	10	1.5	1000	79.5
18	7.5	1.0	750	78.6
19	3.3	1.0	750	58.4
20	7.5	1.0	750	78.7

Table S5 ANOVA for the response surface model

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	2663.80	9	295.98	20.59	< 0.0001	significant
A- Adsorbent dosage	724.40	1	724.40	50.39	< 0.0001	
B- Elution volume	291.66	1	291.66	20.29	0.0011	
C- Centrifugal speed	361.54	1	361.54	25.15	0.0005	
AB	6.66	1	6.66	0.4633	0.5115	
AC	94.53	1	94.53	6.58	0.0282	
BC	16.53	1	16.53	1.15	0.3088	
A^2	199.83	1	199.83	13.90	0.0039	
B^2	1045.34	1	1045.34	72.71	< 0.0001	
C^2	7.80	1	7.80	0.5426	0.4783	
Residual	143.77	10	14.38			
Lack of Fit	56.75	5	11.35	0.6521	0.6748	not significant
Pure Error	87.02	5	17.40			
Cor Total	2807.57	19				

Table S6 Parameters of the SMIR/PGO-CPTE-HPLC method

Analyte	*r*	Regression equation	Linearity (μg mL^{-1})	LOD (ng mL^{-1})	LOQ (ng mL^{-1})
CGA	0.9993	y = 0.524x + 0.1346	0.02–25.00	5.2	17.2

Table S7 Recovery of CGA

Analyte	0.5 μg mL^{-1}		5.0 μg mL^{-1}		25 μg mL^{-1}	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
CGA	91.5	5.5	95.4	4.6	84.4	2.5

Reference

1. A. Shrivastava and V. Gupta, *Chron. Young Sci.*, 2011, **2**, 21–25.