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Supplementary information for

Water-compatible surface molecularly imprinted polymers with synergy of bi-functional monomers for enhanced selective adsorption of bisphenol A from aqueous solution

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Synthesis of porous graphene oxides (PGO). Graphene oxide was synthesized via Staudenmaier method. PGO was prepared by the method of Zhao's group.[1] Briefly, hard templates, silica nanospheres were synthesized by Stober method: ammonia solution (3 mL, 25%), distilled water (1 mL) and tetraethyl orthosilicate (2.3 mL) were mixed into 60 mL of ethanol. The mixed solution was reacted under vigorous stirring for 6 h at 25 ˚C. Then the solution was dialyzed for 48 h and then diluted to 75 mL with water. F108 (0.6 g), 1, 3, 5-trimethylbenzene (0.875 mL) and concentrated HCl (15 mL, 37%) were added into the diluted suspension and the reaction was continued for 48 h. Then ammonia solution was used to neutralize the suspension. Graphene oxide suspension (600 mL, 1.0 mg/mL) was mixed into the neutralized solution and the whole mixture was stirred for 12 h at room temperature. Then, the produced solid precipitate was collected by centrifugation at 4500 $r.min^{-1}$ and dried at 50 ˚C. The dried precipitate was calcined at 400 ˚C for 1 h under argon atmosphere. The sample was then washed by HF solution (5 wt%) three times to remove the silica template and PGO was obtained.

Adsorption capacity. The adsorption capacity of adsorbent (mg/g) at equilibrium q_e was calculated according to the following equation:

$$q_e = \frac{C_0 - C_e}{m} V \qquad (1)$$

where C_0 and C_e present the initial and equilibrium concentrations of BPA in the mixture solution (mg/L), respectively, V is the volume of solution (L), and m is the mass of adsorbent used (g).

Characterization. The morphologies of the parent PGO and functionalized PGO were characterized by transmission electron microscopy (TEM, JEOL-2100F). X-Ray energy dispersive spectroscopy (EDS) was used to obtain information about the chemical composition of the samples. Fourier-transform IR (FTIR) spectra were recorded on a Japan MODEL-8400s FTIR spectrometer using KBr pellet. Thermogravimetric (TG) analysis was carried out on a Netzsch TG 209 F3 instrument at a heating rate of 10℃/min under air atmosphere.

Table S1 The detailed monomer doses of MIPs with different monomer ratio (molar ratio).

AMPS:St / Monomer	5:0	4:1	3:2	2.5:2.5	2:3	1:4	0:5
AMPS (g)	0.8320	0.6656	0.4992	0.4160	0.3328	0.1664	-
St (μL)	-	92.0	184.0	230.0	276.0	368.0	460.0

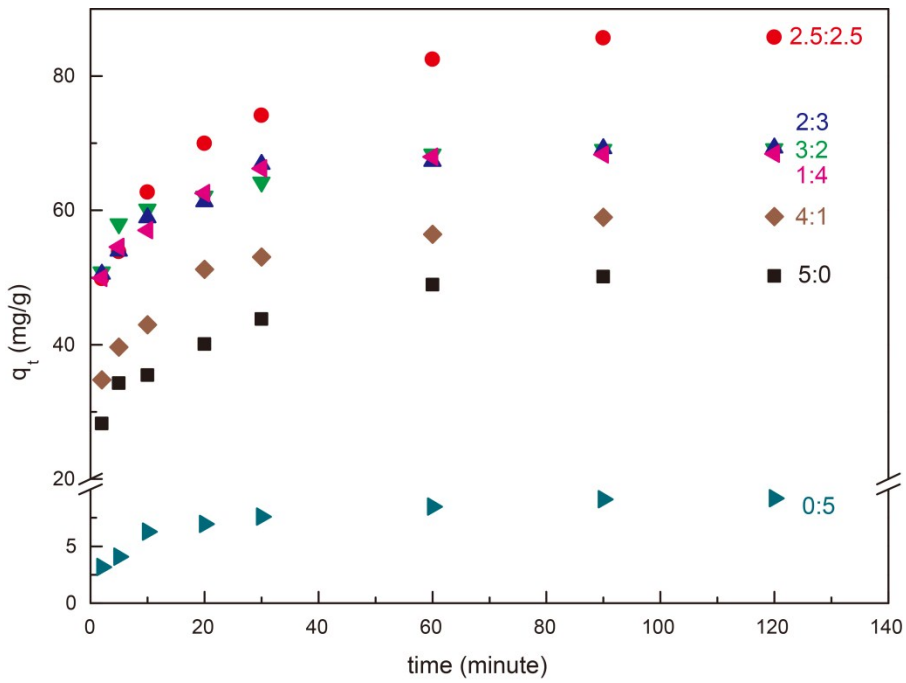

Fig. S1 Effect of contact time on the adsorption of MIPs with different molar ratio of AMPS to St (20 mg of each MIPs in 40 mL of 50 mg/L BPA solution at 293 K).

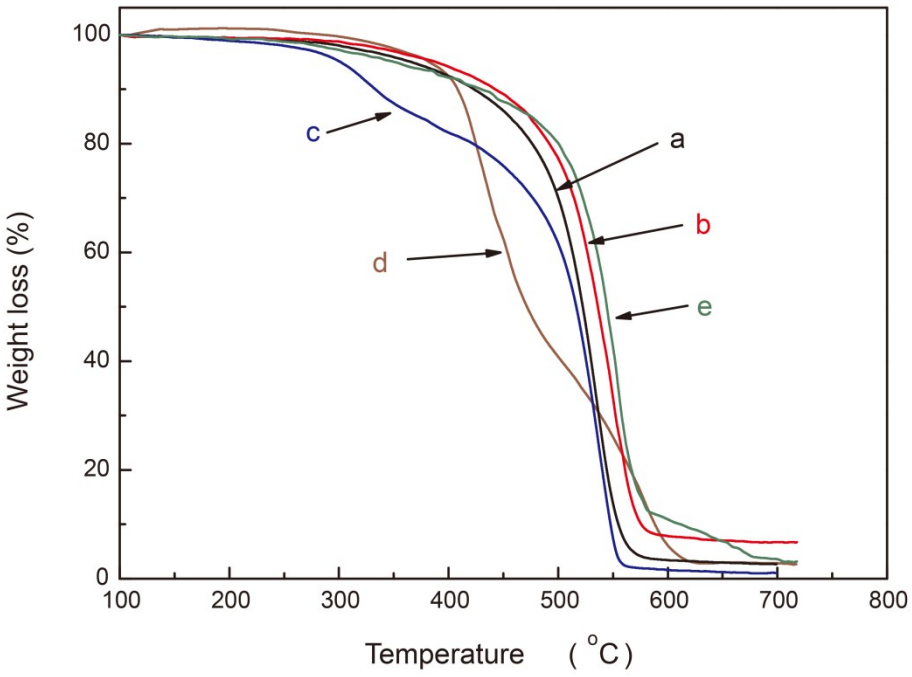

Fig. S2 TG curves of (a) PGO, (b) silanized PGO, (c) AMPS/MIPs, (d) St/MIPs and (e) AMPS-St/MIPs.

Adsorption kinetics studies of AMPS-St/MIPs

Two conventional kinetics models (pseudo-first-order and pseudo-second-order) were applied to analyze the experimental data.

The pseudo-first-order model can be described as:

$$\ln(q_e-q_t)=\ln q_e-k_1 t \qquad (2)$$

where k_1 is the rate constant of the pseudo-first-order model of adsorption (1/min), q_e and q_t (mg/g) are the adsorbed BPA amounts on AMPS-St/MIPs at equilibrium and at

various times t, respectively. The values of q_e and k_1 can be determined from the intercept and slope of the linear plot of $\ln(q_e - q_t)$ versus t.

The pseudo-second-order model comprises all the steps of adsorption including external film diffusion, adsorption, and internal particle diffusion, which is described as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (3)$$

where q_e and q_t are defined as in the above pseudo-first-order model and k_2 (mg/mg·min) is the rate constant of the pseudo-second-order model of adsorption, which can be obtained from the linear plot of t/q_t versus t.

The kinetic parameters and correlation coefficients of BPA adsorption by AMPS-St/MIPs are fitted with the above two models under three different temperatures by nonlinear regression and summarized in Table S2.

Table S2 Kinetic parameters for the adsorption of BPA by AMPS-St/MIPs

temperature	$q_{e,exp}$ (mg/g)	pseudo-first-order			pseudo-second-order		
		K_1 (1/min)	$q_{e,cal}$ (mg/g)	R^2	K_2 (1/min)	$q_{e,cal}$ (mg/g)	R^2
293K	85.7	0.3366	77.17	0.5688	0.00573	82.75	0.9576
298K	75.5	0.1922	70.01	0.7023	0.00367	74.27	0.9847
303K	69.6	0.1502	65.14	0.7911	0.00315	68.31	0.9889

Adsorption isotherm and thermodynamic studies of AMPS-St/MIPs

Two commonly used models, the Langmuir and Freundlich models were adopted to describe the adsorption isotherms of BPA on AMPS-St/MIPs.

The Langmuir model, which assumes the adsorption takes place on a homogeneous surface with monolayer coverage and uniform energies, is expressed as: [2-4]

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m K_L} \qquad (4)$$

where q_e represents the amount of adsorbed BPA on AMPS-St/MIPs (mg/g), C_e is the equilibrium concentration of BPA in solution (mg/L), q_m is the maximum adsorption capacity of the adsorbent (mg/g), and K_L is the Langmuir constant (L/mg), which is related to the affinity of the binding sites. The values of q_m and K_L are determined from the slope and intercept of the linear plot of C_e/q_e against C_e.

Freundlich model is an empirical model based on mutilayer adsorption on a heterogeneous surface. The equation of Freundlich model is given as follows: [5, 6]

$$lnq_e = \frac{1}{n} lnC_e + lnK_F \qquad (5)$$

where q_e and C_e are defined the same as in the Langmuir model, and K_F and n are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively. If n＞1, suggesting favorable adsorption, then adsorption capacity increases. K_F and n can be calculated by a linear plot of lnq_e versus lnC_e. The corresponding parameters calculated according to the Langmuir and Freundlich models are listed in Table S3.

Table S3 Isotherm parameters for the adsorption of BPA by AMPS-St/MIPs.

temperature	Langmuir			Freundlich		
	q_m(mg/g)	K_L(L/mg)	R^2	K_F	n	R^2

293K	84.06	0.05369	0.9893	10.8740	1.4847	0.9952
298K	73.64	0.05021	0.9849	9.4046	1.5472	0.99672
303K	67.33	0.03798	0.9738	7.5155	1.6782	0.9995

The $\Delta G°$, $\Delta H°$ and $\Delta S°$ are calculated from the following equations:

$$\Delta G^o = -RT\ln K^o \quad (6)$$

$$\ln K^o = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (7)$$

$$K_d = \frac{C_0 - C_e V}{C_e \quad m} \quad (8)$$

where R is the universal gas constant (8.314 J/K•mol), T is the absolute temperature (K), K_d is the distribution adsorption coefficient (g/L), C_0 is the initial concentration (mmol/L), C_e is the equilibration concentration of BPA in solution (mmol/L), V is the volume of the solution (L), and m is the mass of the adsorbent (g). The adsorption equilibrium constant, $K°$, can be calculated by plotting $\ln K_d$ versus C_e and extrapolating C_e to zero. The value of the intercept is $\ln K°$. The thermodynamic parameters calculated from equations (6)-(8) at three different temperatures are listed in Table S5

Table S4 Thermodynamic parameters of BPA adsorption on AMPS-St/MIPs.

Thermodynamic constant	T(K)		
	293	298	303

lnK°	3.092	2.835	2.767
$\Delta G°$ (kJ/mol)	-7.39	-7.02	-6.97
$\Delta H°$ (kJ/mol)		-24.06	
$\Delta S°$ (J/mol•K)		-56.68	

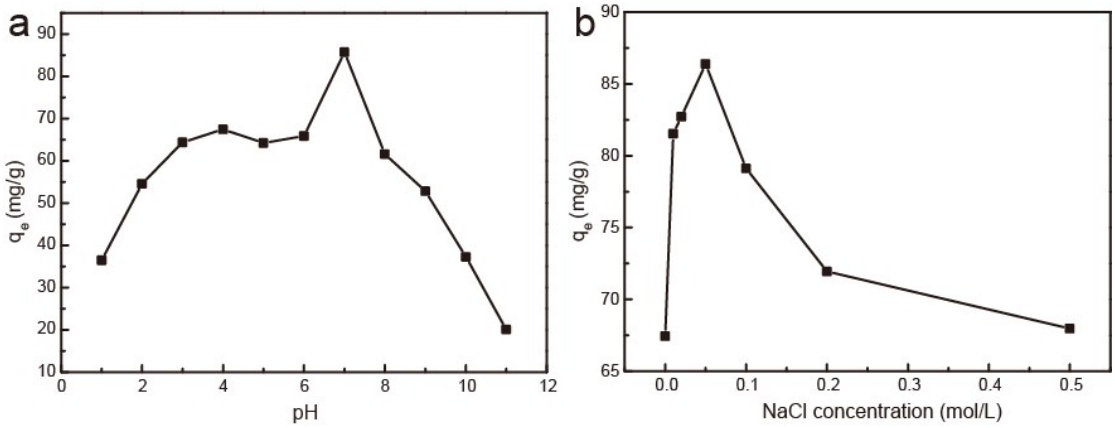

Fig. S3 (a) Effect of the solution pH (20 mg, BPA concentration: 50 mg/L, volume: 40 mL, adsorption time: 1.5 h, temperature: 293 K); (b) Effect of ionic strength (20 mg, BPA concentration: 50 mg/L, volume: 40 mL, adsorption time: 1.5 h, temperature: 293 K, pH 6.0) on the BPA adsorption by AMPS-St/MIPs.

REFERENCES

1. Huang, X.; Qian, K.; Yang, J.; Zhang, J.; Li, L.; Yu, C.Zhao, D., *Functional nanoporous graphene foams with controlled pore sizes*. Advanced Materials, 2012, **24** (32), 4419-4423.
2. Deng, H.; Gao, L.; Zhang, S.Yuan, J., *Preparation of a Copper Ion Selective Membrane by Surface-Modified Molecular Imprinting*. Industrial & Engineering Chemistry Research, 2012, **51** (43), 14018-14025.
3. Luo, J.; Jiang, S.Liu, X., *Efficient one-pot synthesis of mussel-inspired molecularly imprinted polymer coated graphene for protein-specific recognition and fast separation*. The Journal of Physical Chemistry C, 2013, **117** (36), 18448-18456.
4. Zhou, J.; Tang, C.; Cheng, B.; Yu, J.Jaroniec, M., *Rattle-type carbon–alumina core–shell spheres: synthesis and application for adsorption of organic dyes*. ACS applied materials & interfaces, 2012, **4** (4), 2174-2179.
5. Wang, X.; Pan, J.; Guan, W.; Dai, J.; Zou, X.; Yan, Y.; Li, C.Hu, W., *Selective removal of 3-chlorophenol from aqueous solution using surface molecularly imprinted microspheres*. Journal of Chemical & Engineering Data, 2011, **56** (6), 2793-2801.

6. He, X.; Male, K.B.; Nesterenko, P.N.; Brabazon, D.; Paull, B.Luong, J.H., *Adsorption and desorption of methylene blue on porous carbon monoliths and nanocrystalline cellulose*. ACS applied materials & interfaces, 2013, **5** (17), 8796-8804.