

Supplementary Material for
Boron-doping positively enhance the catalytic activity
of carbon materials for the removal of Bisphenol A

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The Supporting Information included:

6 Texts

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12 Pages

Text S1. List of materials and reagents

Bisphenol A (2,2-bis(4-hydroxyphenyl) propane, BPA), sodium persulfate (PS, $\geq 99\%$), ethanol (HPLC grade), 5, 5-dimethyl-1-pyrrolidine-N-oxide (DMPO, $\geq 97\%$) were purchased from Sigma-Aldrich Co., Ltd (Shanghai, China). Boric acid (H_3BO_3 , analytical grade), sodium bicarbonate, sulfuric acid (H_2SO_4 , analytical grade) and sodium hydroxide (NaOH, analytical grade) were obtained from Kelong Chemical Co., Ltd (Chengdu, China). Fullerene (C_{60} , $\geq 99.9\%$) were obtained from Tanfeng Science and Technology Ltd. Commercial multi-walled carbon nanotubes (CNTs, $\geq 98\%$ purity) was obtained from Chengdu Organic Chemicals Co., Ltd (Chengdu, China). Commercial grapheme (G) and multi-layer grapheme (MLG) were purchased from Tanfeng Tech. Inc (Suzhou, China). Pure nitrogen gas (N_2 , $\geq 99.99\%$) were stored in gas cylinders. The water used for the preparation of the reagents and reaction system was purified by a Milli-Q (18.25 M Ω cm). The solution pH was adjusted by H_2SO_4 and NaOH solution. All reagents and chemicals were of analytical reagent grade and were used as received without further purification.

Text S2. Experimental procedures

For adsorption, a certain amount of carbon materials was immersed in a beaker (250 mL) with a total solution volume of 250 mL of ultrapure water containing 0.02 mmol/L BPA; for adsorption and oxidation, a certain amount of carbon materials was immersed in a beaker (250 mL) with a total solution volume of 250 mL of ultrapure water containing 0.02 mmol/L BPA and 2.0 mmol/L PS. The mixture was stirred under a constant rate (850 rpm) for 60 min or 15 min at 25 ± 1 °C. 1.0 mL samples were filtered by a PTFE filter (pore size: 0.22 μm) at defined time intervals and quenched immediately by 20 μL of 0.5 M sodium thiosulfate solution. Then the residual samples concentration in the filtered solution were determined using a HPLC chromatography. The experiments were operated open to the air. Control experiments were conducted and the interaction between the filter and BPA was excluded. The various water matrix were collected at Sichuan University. And all the experiments were carried out in duplicate.

Test S3. Conventional analytical methods

The pH values of solutions were measured by the pH-meter (FiveEasy Plus, METTLER TOLEDO, Shanghai). The concentration of BPA in aqueous solution was analyzed by a HPLC chromatography (Waters, e2695) equipped with a 2489 UV-vis detector (Text S2) and the detection wavelength and binary phase composition were as follows: 276 nm and methanol/0.1% formic acid (70:30, v/v) for BPA. The flow rate of these binary phases was 1 mL/min and the temperature of liquid chromatographic column was 35 °C. After filtration with a cellulose ester membrane of 0.45 μm pore size and freeze vacuum drying in turn, the residual BCs after reaction

(reaction time 60 min) were prepared. The surface properties of the materials were characterized by the thermogravimetric analysis instrument (TGA and DTG, STA 449 F3 (DSC/DTA-TG)), the scanning electron microscopy (SEM, FEI Inspect F50(FSEM)) equipped with an energy dispersive X-ray spectrometer (EDX, FEI Inspect F50 (FSEM)), the X-ray photoelectron spectroscopy (XPS, Escalab 250Xi), the Brunauer–Emmett–Teller (BET, Micromeritic ASAP2460) and the Fourier transform infrared spectroscopy (FT-IR, Nicolet iS 10). The intermediates in the BPA degradation were examined using a liquid chromatograph linked to a mass spectrometer (LC–MS, TSQ quantum ultra (MS)).

Test S4. EPR measurement

It is common knowledge that EPR spectroscopy with the spin-trapping reagent of DMPO was conducted to directly detect the generation of $\cdot\text{OH}$ or $\text{SO}_4^{\cdot-}$ and TMP was adopted as a spin-trapping agent to capture the $^1\text{O}_2$. The ESR spectrum was measured under the following conditions: a center field of 3505.40 G; a sweep width of 150.00 G, a microwave frequency of 9.84 GHz, a microwave attenuator of 20.00 dB, a microwave power of 2.00 mW, and a sweep time of 10.53 seconds.

Test S5. The methods of PS concentrations detection

The concentration of PS was tested by the iodometric titration method using a UV-vis spectrometer (Mapada UV-1800). 0.5g potassium iodide, 0.1g sodium bicarbonate and 2.5mL Milli-Q water were mixed to create a stock solution. Then 2.5mL filtered

PS sample was added to above stock solution. After 21 min the concentration of PS was detected by a UV-vis spectrometer at 352nm¹.

Test S6. Electron transfer experiments

The electrochemical analysis of BCs and Cs were performed with a CHI660E electrochemical workstation (CH instrument, Inc. USA), which includes a working electrode (glassy carbon electrode of 5.0 mm diameter), a reference electrode (Ag/AgCl) and a platinum counter electrode.

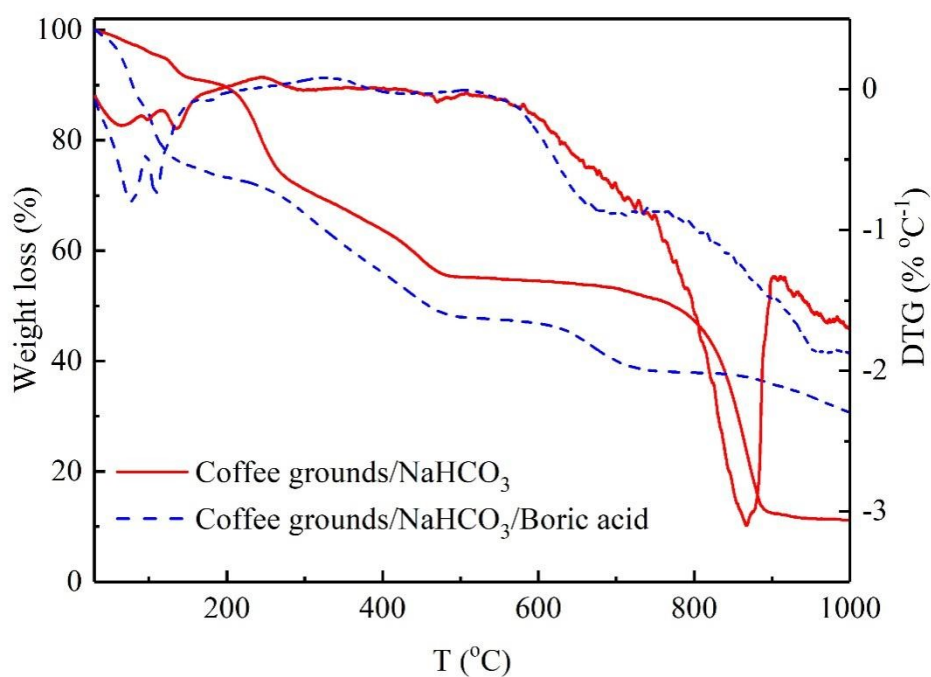


Fig. S1. TGA and DTG curves of the precursors heated under an N₂ atmosphere.

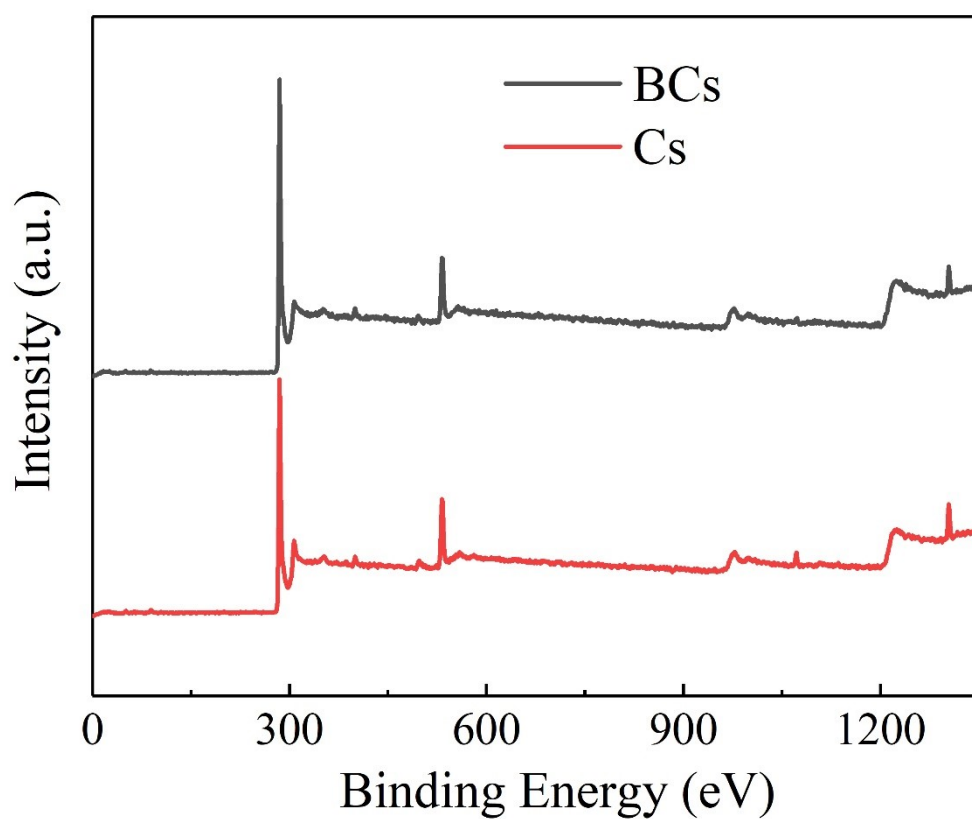


Fig. S2. XPS survey spectra.

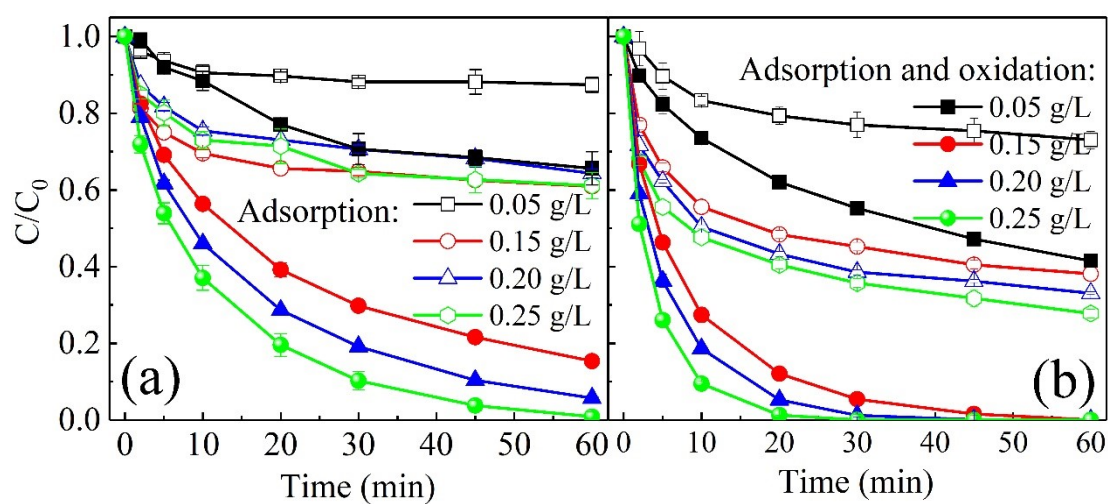
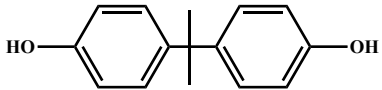
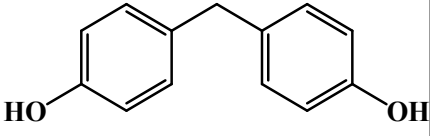
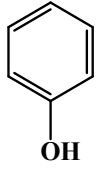

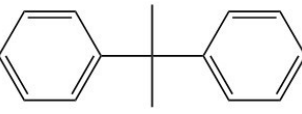

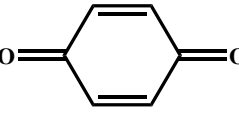
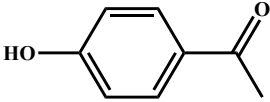
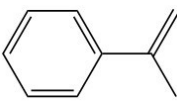
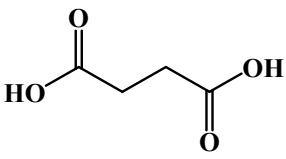
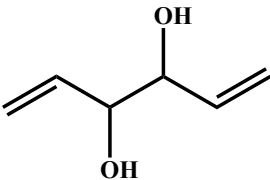


Fig. S3. BPA removal efficiency at varying BCs and Cs dosage. ($[BPA]_0 = 0.02$ mM, $T = 25 \pm$

1 °C, $[BCs]_0 = [Cs]_0 = 0.05 - 0.25$ g/L, $[PS]_0 = 2$ mM, $pH_0 = 4.0 \pm 0.1$)

Table. S1. Several intermediates detected by LC-MS and the m/z values.

Product	Detected m/z	Chemical structure	Detection mode	Ref
Bisphenol A	226.86		Positive	2-4
B1 (4-[4-(Hydroxymethyl) phenyl] phenol)	202.95		Negative	2
B2 (Phenol)	96.00		Negative	2
B3 (4-vinylphenol)	131.81		-	2, 4, 5
B4 (2,2-Bis(phenyl) propane)	197.00		Negative	6
B5 (Hydroquinone)	109.00		-	7
B6 (p-benzoquinone)	107.93		-	2, 3
B7 (4-hydroxyacetophenone)	134.98		Negative	2, 4, 5
B8 (1-methylethenylbenzene)	117.87		Positive	6
B9 (Succinic acid)	117.87		Positive	2
B10 (divinyloxyethane)	113.98		Positive	2, 4, 8

B11 (OEA)	128.93		Positive	²
B12 (Ethanedioic acid)	90.81		Positive	⁴
B13 (Ethylene glycol)	62.38		Negative	²

Note: “-” stands for undetected.

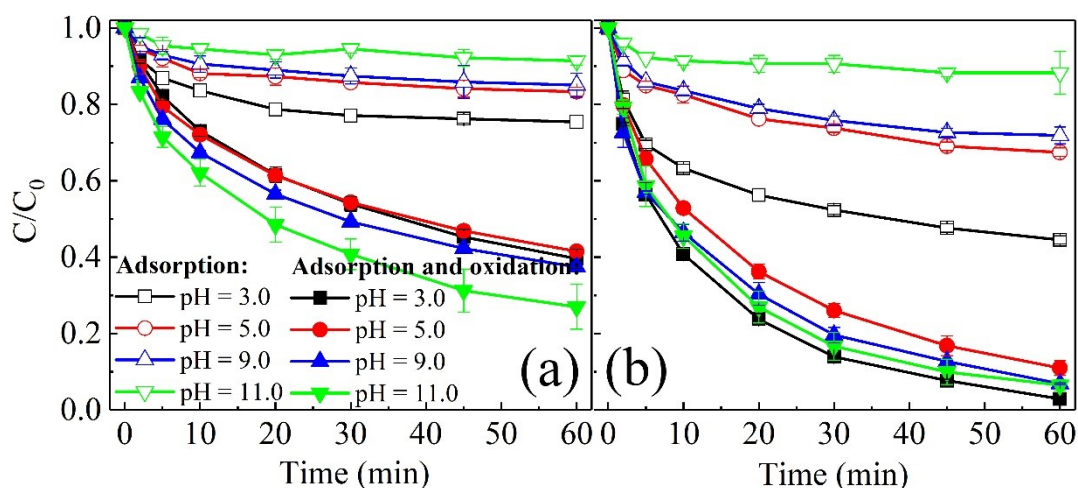


Fig. S4. BPA removal efficiency at varying initially pH regimes by Cs (a) and BCs (b). ($[BPA]_0 = 0.02$ mM, $T = 25 \pm 1$ °C, $[BCs]_0 = [Cs]_0 = 0.1$ g/L, $[PS]_0 = 2$ mM)

pH effects on BPA removal

Fig. S4 illustrated the effect of initially pH on adsorption and PS oxidation, where the pH values were 3.0, 5.0, 9.0 and 11.0. For adsorption, both Cs and BCs showed the adsorption activity increased with increasing the initially pH. However, when PS was added, the adsorptive and PS oxidized removal of BPA reach 97.1% in the PS/BCs system at pH 3, which was the highest removal rate. With pH increasing from 3.0 to

11.0 the BPA removal changed a little, which showed that the change of pH had little effect on the BPA removal performance, demonstrating a wide pH working range of this BCs.

Table. S2. Characteristics of various water matrices.

Water	DW	RW	JAW	LW	MYW
pH	5.77	8.16	8.01	7.51	7.79
TOC	-	0.60±0.04	1.13±0.10	1.78±0.05	1.80±0.42
F ⁻ (mg/L)	-	0.256	0.143	0.445	0.204
Cl ⁻ (mg/L)	-	7.111	3.778	8.077	6.936
NO ₂ ⁻ (mg/L)	-	4.380	5.300	4.075	5.240
NO ₃ ⁻ (mg/L)	-	2.521	3.246	0.792	0.930
Na ⁺ (mg/L)	-	3.308	5.004	8.566	7.594
NH ₄ ⁺ (mg/L)	-	1.054	1.419	1.082	1.607
K ⁺ (mg/L)	-	3.770	5.289	2.455	2.229
Mg ²⁺ (mg/L)	-	7.185	8.180	11.161	10.963
Ca ²⁺ (mg/L)	-	31.488	34.566	21.341	32.976
Sr ²⁺ (mg/L)	-	0.570	7.437	6.868	7.440

Note: “-” stands for undetected.

Materials reusability

For the reusability test, first, the BCs was collected by a vacuum filtration after each 60 min reaction, then washed with deionized water for three times, and dried in Freeze Dryer.

The operational stability and reusability of BCs were explored by three consecutive experiments for the removal of BPA. As illustrated in Fig. S5 (a), for adsorption, the

prepared BCs can still maintain a high adsorption activity in three-time recycling. However, when PS was added, the BPA removal capacities were different. Specifically, as illustrated in Table S3, the SSA of BCs decreased from 518.200 m²/g (1st) to 131.112 m²/g and 116.826 m²/g after the 2nd and 3rd runs, respectively. Fig. S5 (b) demonstrated the reusability for the removal of BPA with the repeatability results. In the 2nd run, BCs contributed 24.4% (adsorption) and 40.5% (adsorption and PS oxidation) of BPA removal within 60 min. Moreover, only 13.6% (adsorption) and 14.0% (adsorption and PS oxidation) of BPA got removed in the 3rd run, which may result from the consumption of the functional groups on BCs or the carbon framework of BCs was destroyed.

Table S3. Pore structure of the used BCs.

BCs	BET (m ² /g)	Total pore Volume (cm ³ /g)	Average pore Diameter (nm)
2nd	131.112	0.388	4.175
3rd	116.826	0.301	4.098

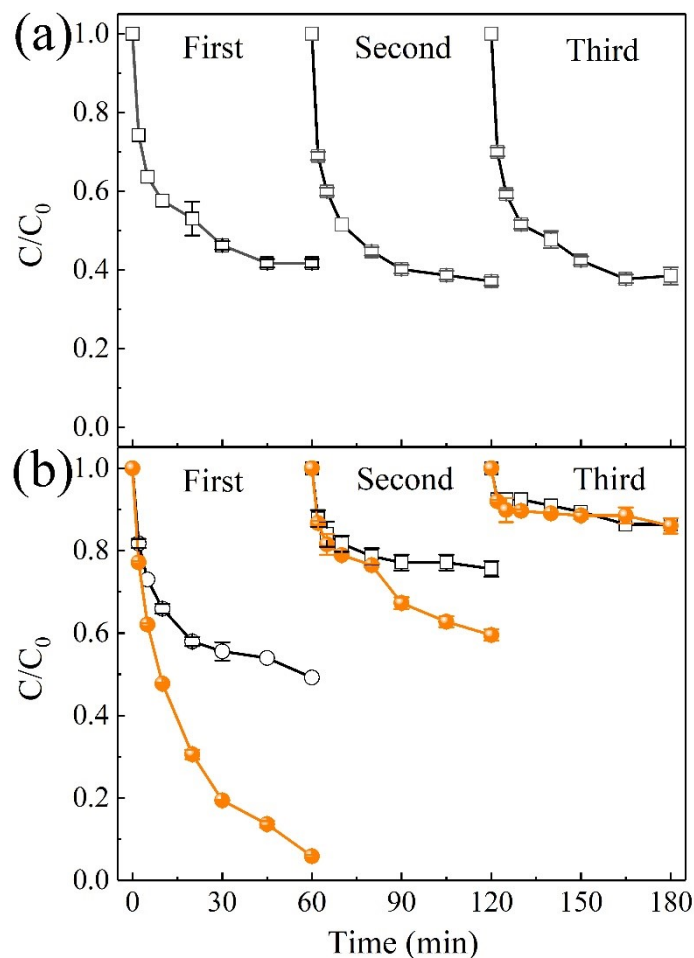


Fig. S5. Recycling test for the removal of BPA only with adsorption by BCs (a). ($[BPA]_0 = 0.02$ mM, $T = 25 \pm 1$ °C, $[BCs]_0 = 0.1$ g/L, $pH_0 = 4.0 \pm 0.1$) and with adsorption and PS oxidation by BCs (b). ($[BPA]_0 = 0.02$ mM, $T = 25 \pm 1$ °C, $[BCs]_0 = 0.1$ g/L, $[PS]_0 = 2$ mM, $pH_0 = 4.0 \pm 0.1$)

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