Supplementary information

Sustainable synthesis of nanoporous carbons from agricultural waste and their application for solid-phase microextraction of chlorinated organic pollutants

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The hydrothermal process could resolve OSRS into small fragments, forming oxygen-contained functional groups and increasing the porosity by hydrolysis of the lignin and hemicellulose. Then, remained crystalline cellulose was activated by KHCO$_3$ under the process of redox reactions between various decomposed potassium compounds with carbon precursor, blowing the melt carbon matrix with as-prepared H$_2$O and CO$_2$, intercalating into the carbon lattices of the carbon matrix with the formation of metallic K, and removing metallic K via acid washing.
**Fig. S2** Typical SEM (a, b) and TEM (c, d) images of the NPC-8.
Fig. S3 Typical TG and DSC results for the mixture of the hydrochar and KHCO$_3$ before and after activated.
Fig. S4 XRD patterns of the NPCs.
Fig. S5 Raman spectrum of the NPCs.
Fig. S6 FT-IR spectrum of the NPCs.
Fig. S7 Typical XPS spectra (a), C 1s XPS spectra (b) and N 1s XPS spectra (c) from the NPC-4.
Fig. S8 Effects of operation conditions on the extraction efficiencies of the NPC-coated fiber (NPC-8) towards CBs and PCBs, desorption temperature (1a, 1b), extraction temperature (2a, 2b) and extraction time (3a, 3b).
Table S1 Description of main contributions and respective calculation formula for the expanded uncertainty (U) following bottom-up approach.

| Uncertainty                  | Calculation                                                                 | Parameters                                                                 |
|------------------------------|------------------------------------------------------------------------------|----------------------------------------------------------------------------|
| Standard preparation         | \( \mu_{sp} = \left( \sum (\Delta m_i/m_i)^2 \right)^{1/2} \)             | \( \Delta m_i \): Error associated to the measurement of a given parameter  |
|                              |                                                                              | \( m_i \): Value measured in each of those actions                         |
|                              |                                                                              | SD_{xy}: Residual standard deviation in the determination of the sample     |
|                              |                                                                              | \( n \): Number of the measurements carried out for a given sample          |
| Calibration curve            | \( \mu_{cal} = (SD_{xy}/p) \left( \frac{1}{n} + \frac{1}{p} + \left( \frac{y_a - y_c}{b^2} \right)^2 \right)^{1/2} \) | \( p \): Number of the points included in the calibration curve            |
|                              |                                                                              | \( y_c \): Average value of the analytical signal                         |
|                              |                                                                              | \( b \): Slope of the calibration curve                                    |
|                              |                                                                              | \( S_{yi} \): Variance of the standards concentration                     |
|                              |                                                                              | SD: Standard deviation between duplicate samples                           |
|                              |                                                                              | \( n \): Number of the replications                                        |
| Precision                    | \( \mu_{pre} = SD/n^{1/2} \)                                               |                                                                           |
|                              |                                                                              | RSD: Relative standard deviation of the average percent recovery             |
|                              |                                                                              | \( n \): Number of the replications                                        |
| Accuracy                     | \( \mu_{ac} = RSD/n^{1/2} \)                                               |                                                                           |
|                              |                                                                              |                                                                           |
| Expanded uncertainty         | \( U_{k=2} = 2C(\mu_{sp}^2 + \mu_{cal}^2 + \mu_{pre}^2 + \mu_{ac}^2)^{1/2} \) | \( C \): Average concentration of the analyte                             |

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Table S2 Comparison of developed method with other analysis methods for determination of selected CBs and PCBs in water samples.

| Analytes        | Limits of detections, ng L$^{-1}$ | LLE-DSPE- GC-ECD | SPNE- GC-ECD | SBSE- GC-MS | SPME- GC-MS | HS-SPME- GC-ECD | SPME- GC-ECD | HS-SPME- GC-MS |
|-----------------|-----------------------------------|------------------|--------------|-------------|-------------|-----------------|--------------|----------------|
|                 | This study                         | 1                | 2            | 3           | 4           | 5               | 6            | 7              |
| 1,3,5-TCB       | 0.34                              | —                | —            | —           | —           | 2.25            | —            | —              |
| 1,2,3-TCB       | 0.19                              | —                | —            | —           | —           | 0.94            | —            | —              |
| 1,2,3,4-TeCB    | 0.09                              | —                | —            | —           | —           | 0.32            | —            | —              |
| 1,2,3,5-TeCB    | 0.28                              | —                | —            | —           | —           | —               | —            | —              |
| PeCB            | 0.64                              | —                | —            | —           | —           | 0.50            | —            | —              |
| HCB             | 0.30                              | —                | —            | —           | —           | 0.69            | 0.64         | —              |
| PCB-8           | 0.29                              | —                | —            | 0.36        | —           | —               | —            | —              |
| PCB-9           | 0.22                              | —                | —            | —           | —           | —               | —            | —              |
| PCB-18          | 0.21                              | —                | —            | —           | —           | —               | —            | 0.03           |
| PCB-20          | 0.08                              | —                | —            | —           | —           | —               | —            | —              |
| PCB-28          | 0.13                              | 0.25             | 1.40         | 0.50        | —           | —               | 0.1          | —              |
| PCB-52          | 0.12                              | 0.30             | 3.10         | 0.27        | —           | —               | 0.1          | 0.03           |
**Table S3** Comparison of partly detected COPs from water samples with others in the literatures.

| Analytes | Detected concentration (ng L⁻¹) |
|----------|---------------------------------|
|          | This study | Rainwater | lake water¹ | pond water | lake water² | well water |
| 1,3,5-TCB | 0.45 | — | — | — | nd | 0.6 |
| HCB      | 5.88 | 11.7 | 17.5 | 14.8 | nd | 0.3 |

*nd: not detected; rainwater: collected from in Guangzhou, China, on May 21st, 2014; lake water1: collected from the surface water of Pearl River, Guangzhou, China; pond water: collected from the surface water of pond located in Sun Yat-sen University, China; lake water2: collected from the surface water of Xuan Wu Lake, Nanjing, Jiangsu, China; well water: none.*
### Table S4: Advantages and drawbacks of diverse protocols for the determination of COPs from water.

| Techniques     | Advantages                                      | Drawbacks                                      |
|----------------|------------------------------------------------|------------------------------------------------|
| LLE-DSPE-GC-ECD | High sensitivity                                | Complex procedure                              |
|                | Short extraction time consuming: 10 min         | Uses organic solvents: methanol, n-hexane, dichloromethane |
|                | Multiple analytes at the same run: 7            | Consumes large quantities of solvents: 100 mL  |
|                | Low cost of analysis instrument                 | Large sample volume: 1000 mL                   |
| SPNE-GC-ECD    | Short extraction time consuming: 9.5 min        | Complex procedure                              |
|                | Consumes small quantities of solvents: 0.1 mL   | Moderate sensitivity                           |
|                | Multiple analytes at the same run: 7            | Uses organic solvents: n-hexane                |
|                | Low cost of analysis instrument                 |                                                |
|                | Small sample volume: 1 mL                       |                                                |
| SBSE-GC-MS     | Easy and simple procedure                       | Long extraction time consuming: >24 h          |
|                | High sensitivity                                | High cost of analysis instrument               |
|                | Non-toxic solvents                              | large sample volume: 200 mL                   |
|                | Multiple analytes at the same run: 77           |                                                |
|                | Environmental friendly, benign                  |                                                |
| HS-SPME-GC-ECD | Easy and simple procedure                       | Long extraction time consuming: 24.5 min       |
|                | High sensitivity                                |                                                |
|                | Non-toxic solvents                              |                                                |
|                | Multiple analytes at the same run: 12           |                                                |
|                | Environmental friendly, benign                  |                                                |
|                | Low cost of analysis instrument                 |                                                |
|                | Small sample volume: 10 mL                      |                                                |
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