Micro- and Mesoporous Carbons Derived from KOH Activations of Polycyanurates with High Adsorptions for CO2 and Iodine

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Supporting Information

ABSTRACT: The adsorption ability of porous carbons toward contaminants is closely related to the porous structures and the working functional groups. In this aspect, two porous carbons, with the potential use as adsorbents for CO2 and iodine, were prepared from polycyclotrimerizations (PCTs) of flexible bisphenyl A dicyanate (BPAC) and rigid binaphthylphenyl dicyanate (BNC) cyanate ester monomers. Primarily, PCT reactions of BPAC and BNC generated the respective nonporous c-BPAC and c-BNC precursors, which contain high amounts of nitrogen and oxygen heteroatoms. Further KOH activations of c-BPAC and c-BNC produced the respective porous a-BPAC and a-BNC carbons, which mainly contain oxygen heteroatoms. The a-BNC derived from rigid BNC contains both micro- and mesopores and is high in adsorbing both CO2 (6.3 mmol/g) and iodine; in contrast, the microporous a-BPAC is lower in adsorbing CO2 (3.9 mmol/g) and iodine. The effects of molecular flexibility of the starting cyanate ester on the micro- and mesopore distribution as well as the CO2 and iodine adsorption behaviors of the porous carbons are therefore probed in this study.

INTRODUCTION

The immense scientific and commercial value of porous organic polymers is illustrated by their ubiquity as key materials in several potential application fields, such as heterogeneous catalysis,1,2 sensors,3 organic electronics,4 and gas storage5,6 and separation.7,8 The interconnected porous structures endowed the polymers with the capability of an accommodating guest molecule and meanwhile, tailored modifications through inherent functional groups, which offered porous carbons the specific binding sites for targeted recognition. Among various family members9−19 of porous organic polymers, nitrogen-doped porous carbons (NPCs)20,21 have been under considerable research studies for the past three decades ever since the finding that the basic nitrogen heteroatoms22 can interact strongly with the acidic CO2 gas to result in the enhanced adsorption capacity.

Radioiodine (129I and 131I) has been identified as one of the most hazardous species in terms of detrimental radiological effects on health and environment in the case of accidental release. Previously, several porous polymers23−36 with a microporous structure had been developed and demonstrated as efficient absorbents for iodine. Among them, a charged porous aromatic polymer25 was shown to exhibit an excellent uptake of 2760 mg/g, as one of the highest values reported to date, due to the high affinity of its inherent ionic bond, phenyl ring, and triple bond toward iodine. Moreover, two NPCs37,38 also were characterized to be good adsorbents for iodine in view that the beneficial polar interaction between nitrogen-containing functional groups and iodine.

Mesoporous carbons with a pore size in between 2 and 50 nm are of great interest regarding their potential application in adsorbing large organic molecules; in contrast, microporous carbons with an enlarged specific surface area are more suitable for the adsorption of volatile organic molecules, hydrogen storage, and CO2 capture. In this aspect, micropores39−41 are crucial for maximizing CO2 uptake at ambient conditions, and microporous carbons42 with small (< 0.8 nm) and large micropores, by activation of the polymeric materials with KOH, were reported to adsorb CO2 with high capacity (4.6 mmol/g) at 23 °C. The combination of meso- and micropores is nevertheless necessary for some applications in considering that mesopores can be beneficial in transporting and accommodating larger adsorbate molecules, whereas micropores are essential for adsorption of small molecules. In this regard, KOH activation33 was employed to develop microporosity and to increase the surface area of mesoporous carbons. Therefore, micro- and mesoporous carbons43,44 having the specific surface area, total pore volume, and volumes of micropores and mesopores were synthesized, using different phenolic molecules and formaldehyde as precursors.
through carbonization and the high-temperature KOH activation process.

The polycyclotrimerization (PCT) reaction of aromatic cyanate esters is unique in considering that the reaction brings three cyanate (−OCN) groups together to form a one-sixth-electron \( s^6 \)-triazine ring as a cross-linking point in the resulting cross-linked network of polycyanurates (PCs). In the presence of small-mass porogens or polymeric templates, a variety of porous PCs with the desired pore sizes had been prepared and identified as adsorbents for CO\(_2\). PCT of bisphenol E dicyanate in the presence of inert porogen afforded mesoporous PCs after carbonization at elevated temperature. Meso- and macroporous PC networks also were fabricated through copolymerization of cyanate esters with different soft block copolymer templates, which can be hydrolytically and thermally removed afterward. More recently, microporous PCs with pore sizes less than 2 nm were successfully prepared through the uses of specially designed rigid cyanate ester. Thus, the first microporous PC with a Brunauer–Emmett–Teller surface area \( S_{\text{BET}} \) over 530 m\(^2\)/g was constructed from tetrafunctional tetrakis(4-cyanatophenyl)silane cyanate ester through high-temperature solution condensation. To implement this design strategy, two micro- and macroporous PCs with tetrahedral and triangular

![Scheme 1. Syntheses of Cyanate Esters of BPAC, BNC, and PFC for the Subsequent PCT and KOH Activation To Obtain the Respective Cured and Activated Products](image)

![Figure 1. DSC thermograms of (a) BPAC and (b) BNC (heating rate = 10 °C/min) and FTIR spectra of (c) BPAC and (d) BNC after cumulative heating at different curing temperatures for 2 h.](image)
Pyramidal shapes were synthesized. Moreover, the use of ionic liquid porogens during PCTs resulted in porous carbons with pore sizes in between 20 and 180 nm. As the member of NPC family, porous PCs are promising materials for CO$_2$ capture in considering the favorable dipole–quadrupole interaction between nitrogen and CO$_2$ molecules.

Table 1. EA and XPS Results of the Cured and Activated Products

| Sample   | C (%) | N (%) | H (%) | O (%) | C (%) | N (%) | O (%) |
|----------|-------|-------|-------|-------|-------|-------|-------|
| c-BPAC   | 73.37 | 5.07  | 10.07 | 11.49 | 68.18 | 14.29 | 17.53 |
| c-BNC    | 76.04 | 3.07  | 7.61  | 13.29 | 69.82 | 17.31 | 12.87 |
| a-BPAC   | 45.62 | 3.69  | 3.13  | 28.53 | 57.85 | 5.97  | 36.18 |
| a-BNC    | 59.81 | 3.14  | 1.93  | 30.09 | 58.34 | 1.83  | 39.83 |

**RESULTS AND DISCUSSION**

The starting cyanate ester of BPAC (or BNC) was prepared from the substitution reaction between BPA (or BN) and BrCN (Scheme 1) in the presence of triethyl amine as the acid scavenger. To eliminate spurious impurities, the crude products of BPAC and BNC were needed to be purified by recrystallization from cyclohexane. Chemical structures of BPAC and BNC were identified by $^1$H NMR (Figure S1), FTIR (Figure S2), and EA.

Primarily, BPAC and BNC were subjected to cumulative thermal curing at each designated temperature for 2 h, forming cross-linked PCs of c-BPAC and c-BNC, respectively. The thermal curing behavior of BPAC and BNC can be successfully identified by DSC and FTIR spectra (Figure 1). The DSC scan of pure BPAC (Figure 1a) resulted in a broad curing exotherm in the temperature range from 210 to 345 °C with a curing enthalpy of 304 kJ/mol. The curing enthalpy of BPAC decreased as the curing temperature increased from 150 to 215 °C, and eventually, the exothermic peak completely disappeared for BPAC after the final curing stage at 290 °C, which suggested that the curing reaction of BPAC was completed by the cumulative curing process. FTIR spectra (Figure 1c), recorded after 2 h of heating at each designated temperature, also correlate with the DSC results. By the cumulative curing process, the −OCN stretching peak at 2258 cm$^{-1}$ gradually disappeared, and at the same time, the characteristic absorption peaks of the s-triazine ring at 1568 and 1369 cm$^{-1}$ gained their intensities along the curing process.

In contrast, the DSC thermogram of BNC is not so informative as that of BPAC because its curing exotherm (Figure 1b) was partially overlapped with the melting endotherm to result in lowering the curing enthalpy (114 kJ/mol). Despite the inconclusive DSC results, the corresponding FTIR spectra (Figure 1d) can be used to demonstrate the success of the curing reaction. After the final curing stage at 240 °C, the FTIR spectrum exhibited the characteristic absorption of the s-triazine ring at 1560 and 1365 cm$^{-1}$ and no sign of the cyanate −OCN stretching peak at 2224 cm$^{-1}$.

The Raman spectra of a-BPAC and a-BNC (Figure 6a) contain two strong peaks of a D-band at 1350 cm$^{-1}$ and a G-band at 1595 cm$^{-1}$. The D-band is typically originated from the disorder and imperfect structures in the turbostratic carbon layers, whereas the G-band is due to vibrations of in-plane displaced carbon atoms in the graphite crystallites. The intensity ratio of the D and G bands provides information regarding the degree of graphitization of the carbon materials. The higher one is the I$_D$/I$_G$ ratio, and the lower one is the degree of graphitization. With a lower I$_D$/I$_G$ value (0.96), a-BNC should also be higher in the degree of graphitization than a-BPAC with a higher I$_D$/I$_G$ value (1.05).

X-ray diffraction spectra of a-BPAC and a-BNC (Figure 6b) resembled to each other with both exhibit two broad, diffuse bands at 2θ = ~24° and 43°. These two bands are typical of a well-developed graphitic structure that the stacking peak at 2θ corresponds to the (002) plane of graphene while the peak at 43° is due to the (100) plane of graphite. Results from Raman and XRD spectra indicate the graphitic nature of the porous a-BNC and a-BPAC.

Without the participation of porogen during PCT reactions, the cured c-BPAC and c-BNC are essentially nonporous materials (Figure S7a) with low capture capacity toward CO$_2$ (<0.6 mmol/g at 25 °C, Figure S7b). In contrast, KOH activation of the cured PCs resulted in porous a-BPAC and a-BNC, which own superior capture capability (>3.9 mmol/g at 25 °C) and varied heteroatom contents. Heteroatom contents of the cured and porous carbons were evaluated from EA.
Nitrogen sorption analysis was conducted at −195 °C to resolve the sorption isotherms (Figure 3a) of the activated carbons. The sorption isotherm of a-BPAC (Figure 3a) exhibited a steeper rise of nitrogen uptake, beginning at the low relative pressure range of P/P₀ < 0.01, than the sorption isotherm of a-BNC, which may be due to a higher micropore content of a-BPAC compared to a-BNC. Anyway, unambiguous determination can be obtained from CO₂ sorption at −78 °C (inset, Figure 3b). The porous parameters, including the BET surface area (S_BET) and total pore volume (V_total), calculated from the nitrogen isotherms indicated that a-BPAC owns higher values of S_BET and V_total compared to those of a-BNC (S_BET, 1136.5 m²/g vs 1080.2 m²/g; V_total, 0.58 cm³/g vs 0.51 cm³/g). The pore size distribution (Figure 3b) evaluated from nitrogen sorption at −195 °C was combined with the results from CO₂ sorption at −78 °C (inset, Figure 3b) with the purpose of evaluating the structural difference between a-BNC and a-BPAC. The most noticeable observation in Figure 3b is that a-BNC contains both micropores and well-defined mesopores, with pore sizes of 7.3 and 11.7 nm, respectively, whereas a-BPAC contains a large fraction of micropores, which resulted in its high V_total value.

The CO₂ capture behaviors of the cured (Figure S7b) and activated products (Figure 4) were measured up to 1.0 atm at 25 °C. The cured c-BPAC and c-BNC are nonporous materials, and thus, they are inferior in CO₂ capture (<0.6 mmol/g) to the porous a-BPAC and a-BNC. The CO₂ capture capability of a-BNC is extremely high at 6.3 mmol/g, which is higher than most of the reported values. Even for the less efficient a-BPAC, the resolved CO₂ capture is still high at 3.9 mmol/g. In considering the beneficial parameters of S_BET and V_total, a-BPAC should be superior in CO₂ capture to a-BNC. Nevertheless, the CO₂ capture capability of a-BPAC is dramatically behind a-BNC (6.3 mmol/g vs 3.9 mmol/g). Accordingly, we suggested that pore size distribution is the key factor controlling the CO₂ capture ability. In contrast to the predominant microporous a-BPAC, a-BNC contains both micropores and mesopores. The large mesopores present in a-BNC are therefore responsible for the efficient adsorption of CO₂ gas, rendering an excellent CO₂ capture value of 6.3 mmol/g.

Presumably, the micro- and mesopore formations of the activated carbons are closely related to thermal stability of the PC precursors. Previous study⁸³ concluded that micropores are more stable and more sustainable to high-temperature treatment compared to mesopores. Therefore, more stable PCs are more sustainable to the high-temperature KOH activation process, which should generate stable microporous carbons, whereas less stable PCs tend to form less stable mesoporous carbons after KOH activation. TGA analyses (Figure S5) provided valuable information regarding thermal stabilities of the cured and activated products. As judged from the on-set decomposition temperature and the residual char yield at 800 °C, the cured c-BPAC is much more stable than the cured c-BNC. After KOH activation, this stable c-BPAC

Table 2. Deconvolution Results of XPS Spectra of a-BPAC and a-BNC

| sample | C species | O species |
|--------|-----------|-----------|
|        | C−C | C−O | C≡O | O−C≡O | quinone | C≡O | C−O | C−OH | H₂O |
| a-BPAC | 44.72 | 36.30 | 11.38 | 7.60 | 22.49 | 60.72 | 13.39 | 3.40 |
| a-BNC  | 55.42 | 27.17 | 11.08 | 6.33 | 17.04 | 26.71 | 21.35 | 30.54 | 4.36 |
tends to form microporous a-BPAC, whereas the less stable c-BNC results in porous a-BNC containing both meso- and microporous structures.

Disregarding the potential influence of the chemical structure, a densely packed cross-linked network should be regarded as the more stable structure compared with the loosely packed cross-linked network. In this aspect, we attempted to assess the preformed c-BPAC and c-BNC network structures by computer simulations using Materials Studio software. The models were constructed by connecting \( \text{\textsuperscript{1}} \text{N}_{3} \text{H}_{6} \text{N}_{3} \) rings with three neighboring bisphenyl A or three binaphthalenyl substituents without considering the mutual penetration of the networks. After successive geometry and molecular mechanic optimizations, the energy-minimized structures of the preformed c-BPAC and c-BNC networks are presented in Figure 6a,b, respectively. In the case of c-

Figure 3. (a) \( \text{N}_{2} \) adsorption isotherms recorded at \(-195^\circ\text{C}\) and (b) mesopore (determined from \( \text{N}_{2} \) sorption at \(-195^\circ\text{C}\)) and micropore (inset, determined from \( \text{CO}_{2} \) sorption at \(-78^\circ\text{C}\)) size distributions of a-BPAC and a-BNC.

![Figure 3](image)

Figure 4. \( \text{CO}_{2} \) capture using a-BNC and a-BPAC samples (at \(25^\circ\text{C}\) and 1 atm).

![Figure 4](image)

Figure 5. TGA thermograms of the cured and activated products.

Figure 6. Energy-minimized preformed network structures of (a) c-BPAC within a unit cell of \( a = 5 \text{ nm}, b = 5 \text{ nm}, \) and \( c = 5 \text{ nm} \) and (b) c-BNC within a unit cell of \( a = 10 \text{ nm}, b = 10 \text{ nm}, \) and \( c = 10 \text{ nm} \). In the case of c-

BPAC, it takes four monomeric subunits to form a cycle with a size of \( \sim 1.97 \text{ nm} \), but for c-BNC, a larger cycle with a size of \( \sim 7.42 \text{ nm} \) and 19 monomeric subunits was resolved. The results suggested that the simulated preformed structure of c-BPAC is a densely packed preformed network consisting of 27 monomeric subunits within a unit cell of \( a = 5 \text{ nm}, b = 5 \text{ nm}, \) and \( c = 5 \text{ nm} \), whereas the simulated c-BNC structure contains a loosely packed network consisting of 63 monomeric subunits within a larger unit cell of \( a = 10 \text{ nm}, b = 10 \text{ nm}, \) and \( c = 10 \text{ nm} \). The distinctive network structures of c-BNC and c-BPAC are associated with the molecular flexibility of starting cyanate esters used to construct the network. When connect with each other to form a cycle, the rigid BNC monomers can only adopt minute adjustment on their molecular orientation, which takes more monomeric subunits to construct the cyclic building motifs of the loosely packed c-BNC network. In contrast, the flexible BPACs can take a higher degree of molecular adjustment, thus taking less monomeric subunits to form a small cycle in the densely packed c-BPAC network. In consequence, molecular flexibility of the cyanate esters directly
affects packing density and thermal stability of the cured PCs, which in turn determines the porous structures formed in the KOH-activated porous carbons.

■ IODINE ADSORPTION OF A-BNC AND A-BPAC

The iodine adsorption was measured by using porous adsorbents (30 mg) immersed in different amounts (3 and 10 mL) of iodine solution in hexane (2 mg/mL). When iodine was dissolved in the nonpolar hexane solvent, the solution became violet in color (Figure 7a), but further treatment of a-BNC turned the solution into colorless, which indicated that iodine in the solution had been consumed by the a-BNC adsorbent. A quantitative view can be obtained from tracing the UV-vis absorption peak of iodine at 523 nm (Figure 7b). The absorbance of the peak at 523 nm decreased significantly within the initial 1/2 h, which correlated with the efficient iodine adsorption by a-BNC. Actually, removal efficiencies of a-BNC and a-BPAC (Figure 7c) reached their maxima within the initial 2 h, and after that, the removal efficiencies remained at constant values for the rest of the experimental period. Removal efficiency of the high iodine-loaded (10 mL) solution is lower than that of the low iodine-loaded solution (3 mL). Overall, a-BNC is a better adsorbent for iodine than a-BPAC (Figure 7d) in considering that a-BNC is higher in maximum adsorption capability with a value of 489.05 mg/g than a value of 331.33 mg/g for a-BPAC. The large mesopores of a-BNC are suggested to be more efficient in accommodating iodine molecules than the small micropores of a-BPAC, which resulted in the higher iodine adsorption capacity of a-BNC compared to a-BPAC.

■ CONCLUSIONS

Porous carbons of a-BPAC and a-BNC, as efficient adsorbents for CO₂ and iodine, were prepared from PCTs of the flexible BPAC and the rigid BNC, respectively, through carbonization and KOH activation. PCTs of BPAC and BNC can be driven to complete by a cumulative heating process according to the results from DSC and FTIR analyses.

The KOH-activated a-BPAC and a-BNC have their functional groups and porous structures essentially different from the c-BPAC and c-BNC precursors. KOH activation converted the nonporous PC precursors into porous carbons with a high oxygen content. Both a-BPAC and a-BNC exhibit high $S_{BET}$ (1136.5 m²/g for a-BPAC and 1080.2 m²/g for a-BNC) and $V_{total}$ (0.58 cm³/g for a-BPAC and 0.51 cm³/g for a-BNC). Owing to the inherent mesoporous structure, a-BNC exhibits excellent adsorption ability (6.3 mmol/g) to CO₂, which is comparatively higher than that (3.9 mmol/g) of the microporous a-BPAC. The mesopores in a-BNC also make a-BNC superior in an iodine adsorbent to the microporous a-BPAC. The influence of molecular flexibility of the starting cyanate ester on the micro- and mesopore distribution, and CO₂ and iodine adsorption behaviors of the porous carbons were therefore assessed in this study.

■ EXPERIMENTAL SECTION

Materials. Bisphenol A (BPA), 1,1-bi-2-naphthol (BN), phenol, formaldehyde, oxalic acid catalyst, cyanogen bromide (BrCN), and iodine were purchased from Sigma-Aldrich Chemical and were used directly. Tetrahydrofuran (THF) was refluxed over sodium and benzenophene under a nitrogen
atmosphere for more than 2 days before distillation use. Triethylamine was distilled from CaH₂ under a nitrogen atmosphere before use.

**Synthesis of BPAC and BNC.** Synthesis of BPAC and BNC followed the same procedures, and the selected atmosphere before use.

32 scans at a spectral resolution of 4 cm⁻¹. FTIR spectrophotometer and a typical KBr disk method with spectra of all samples were recorded using a Bruker Tensor 27 FTIR spectrophotometer and a typical KBr disk method with.

BPAC: 1H NMR (500 MHz, DMSO-d₆): 7.37 (s, 4H, H₄), 1.65 (s, 6H, H₆) (Figure S1, Supporting Information); anal. calcd for C₁₇H₁₄N₂O₂: C, 73.37; H, 5.07; N, 11.74%. BNC: 1H NMR (500 MHz, DMSO-d₆): 7.86–7.83 (m, 4H, H₄), 7.32–7.30 (d, 2H, H₂), 7.24–7.14 (m, 4H, H₆), 6.94–6.92 (d, 2H, H₂) (Figure S1, Supporting Information); anal. calcd for C₁₇H₁₄N₂O₂: C, 76.83; H, 3.95; N, 10.29%.

**Preparation of Cured c-BPAC and c-BNC.** Thermal PCT reactions of BPAC and BNC were carried out by cumulative heating at each of the designated temperatures for a period of 2 h. The designated temperatures are 150, 215, and 290 °C for BPAC and are 140, 175, and 240 °C for BNC.

**Synthesis of Activated Carbons: a-BPAC and a-BNC.** Carbonizations of a-BPAC and a-BNC were carried out using c-BPAC and c-BNC, respectively, as starting PC precursors to work with. The c-BPAC and c-BNC precursors were mixed with aqueous KOH solution (200 g/L) with a weight ratio of 1:4, and the whole solution mixtures were further stirred at room temperature overnight. The resulting solution mixtures were then distilled to remove the solvent, and the brown residue was dried in vacuum at 70 °C for 24 h. Carbonization of the c-BPAC/KOH and c-BNC/KOH mixtures was carried out in a nickel crucible placed within a tube furnace by heating the mixtures to the target temperatures of 600 °C with a heating rate of 5 °C/min and held for 2 h at 600 °C under nitrogen gas flow. After cooling down to room temperature, the black residues were washed with distilled water to remove excess KOH. Further purification of the activated carbons was carried out by washing with distilled water and acetone. The resulting activated carbons were dried in vacuum at 80 °C for 24 h.

**Characterization.** 1H NMR spectra were recorded by an Inova 500 instrument using DMSO-d₆ as the solvent. FTIR spectra of all samples were recorded using a Bruker Tensor 27 FTIR spectrophotometer and a typical KBr disk method with 32 scans at a spectral resolution of 4 cm⁻¹. The dynamic thermal curing behavior of the samples was monitored at elevated temperatures using a cell mounted in the temperature-controlled compartment of the FTIR spectrophotometer. The dynamic curing behavior of all samples (5–7 mg) was also studied by DSC using a TA Q-20 DSC apparatus, with a heating scan from 30 to 350 °C at 20 °C/min under a nitrogen atmosphere. The thermal stabilities of all samples were measured using a TA TQ-50 TGA apparatus, with heating from 30 to 800 °C at 20 °C/min under a nitrogen atmosphere. Raman spectra were recorded at room temperature using a Jobin–Yvon T6400 micro-Raman apparatus with a He–Cd laser as the excitation source (325 nm). XPS was obtained from Thermo Scientific Theta Probe using Mg Kα radiation from the double anode at 50 W. The related binding energies of all samples in the high-resolution spectra were calibrated by using the C 1s peak at 284.6 eV. EA was measured using Thermo Flash 2000 to determine the C, H, N, and O contents. The N₂ adsorption isotherms were determined using an ASAP 2020 analyzer at −195 °C, whereas the CO₂ adsorption isotherm was evaluated at −78 °C. The CO₂ uptake isotherms were determined using an ASAP 2020 analyzer at 1 bar and 25 °C. The samples of porous carbons were degassed at 150 °C for 8 h prior to measurement. The BET method was used to measure the specific surface areas, pore size distributions, and pore volumes from the adsorption branches of the isotherms. UV–vis spectra were obtained from Jasco Model V-770. Removal efficiency was calculated from the following equation:

\[
\text{efficiency removal} = \frac{(A_o - A_t)}{A_o}
\]

where \(A_o\) and \(A_t\) are the absorbance of the iodine peak at 523 nm at the beginning and time \(t\) after reacting with the adsorbent, respectively.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00901.

**Notes**

The authors declare no competing financial interest.

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**REFERENCES**

(1) Roese, J.; Kailasam, K.; Thomas, A. Covalent triazine frameworks as heterogeneous catalysts for the synthesis of cyclic and linear carbonates from carbon dioxide and epoxides. *ChemSusChem* 2012, 5, 1793–1799.
(22) Gomes, R.; Bhaumik, A. A new triazine functionalized luminescent covalent organic framework for nitroaromatic sensing and CO2 storage. RSC Adv. 2016, 6, 28047−28054.
(23) Chen, Y.; Sun, H.; Yang, R.; Wang, T.; Pei, C.; Xiang, Z.; Zhu, Z.; Liang, W.; Li, A.; Deng, W. Synthesis of conjugated microporous polymer nanotubes with large surface areas as sorbents for iodine and CO2 uptake. J. Mater. Chem. A 2015, 3, 87−91.
(24) Ali, I.; Aboul-Enein, H. Y. Taylor & Francis Group: Photocatalytic degradation of atrazine by heteropolyoxoanatages. New York 2006.
(25) Chojnacka, K. Biosorption and bioaccumulation—the prospects for practical applications. Environ. International 2010, 36, 299−307.
(26) Pruden, W. Mordubility & Morttality Weekly Report. Survey of green building water systems reveals elevated water age and water quality concerns. J Prev Med Public Health 1985, 34, 66.
(27) Rice, K. M.; Walker, E. M.; Jr.; Wu, M.; Gillette, C.; Blough, E. R. Environmental mercury and its toxic effects. J Prev Med Public Health 2014, 47, 74−83.
(28) Blumenthal, N. C.; Cosma, V.; Skylar, D.; LeGeros, J. The effect of cadmium on the formation and properties of hydroxyapatite In vitro and its relation to cadmium toxicity in the skeletal system. M. Calcif Tissue Int 1995, 56, 316−322.
(29) Ali, I. Speciation of arsenic and chromium metal ions by reversed phase high performance liquid chromatography. H. Y. Chemosphere 2002, 48, 275−278.
(30) Matlock, M. M.; Howerton, B. S.; Atwood, D. A. Chemical precipitation of heavy metals from acid mine drainage. Water Res. 2011, 45, 4757−4764.
(31) Chen, Y.; Pan, B.; Li, H.; Zhang, W.; Lv, L.; Wu, J. Selective removal of Cu(II) ions by using cation-exchange resin-supported polyethyleneimine (PEI) nanoclusters. Environ. Sci. Technol 2010, 44, 3508−3513.
(32) Salehi, E.; Darai, P.; Shamsabadi, A. A. A review on chitosan-based adsorptive Membranes. A Carbohydrate Polymers 2016, 152, 419−432.
(33) Feng, C.; Sugita, N.; Shimada, S.; Maekawa, T. Development of a high performance electrochemical wastewater treatment system. Journal of Hazardous Materials B 2003, 103, 65−78.
(34) Wang, J.; Liu, H.; Yang, S.; Zhang, J.; Zhang, C.; Wu, H. Physicochemical characteristics and sorption capacities of heavy metal ions of activated carbons derived by activation with different alkal phosphate triesters. Appl. Surf. Sci. 2014, 316, 443−450.
(35) Sun, H.; La, P.; Yang, R.; Zhu, Z.; Liang, W.; Yang, B.; Li, A.; Deng, W. Innovative nanoporous carbons with ultrahigh uptakes for capture and reversible storage of CO2 and volatile iodine. J. Hazard. Mater. 2017, 321, 210−217.
(36) Qian, X.; Zhu, Z.-Q.; Sun, H.-X.; Ren, F.; Mu, P.; Liang, W.; Chen, L.; Li, A. Capture and Reversible Storage of Volatile Iodine by Novel Conjugated Microporous Polymers Containing Thiophene Units. ACS Appl. Mater. Interfaces 2016, 8, 21063−21069.
(37) Sigen, A.; Zhang, Y.; Li, Z.; Xia, H.; Xue, M.; Liu, X.; Mu, Y. Highly Efficient and Reversible Iodine Capture using a metalloporphyrin-Based Conjugated Microporous polymer. Chem. Commun. 2014, 50, 8495−8498.
(38) Yan, Z.; Yuan, Y.; Tian, Y.; Zhang, D.; Zhu, G. Addendum: Highly Efficient Enrichment of Volatile Iodine by Charged Porous Aromatic Frameworks with Three Sorption Sites. Angew. Chem., Int. Ed. 2015, 54, 14215−14215.
(39) Ma, H.; Chen, J. J.; Tan, L.; Bu, J. H.; Zhu, Y.; Tan, B.; Zhang, C. Nitrogen-Rich Tripyrene-Based Porous polymer for Gas Storage and iodine Enrichment. ACS Macro Lett. 2016, 5, 1039−1043.
(40) Shen, Y. M.; Chen, D. Z. An Explorer of Chemical Biology of Plant Natural Products in Southwest China, Xiaojiang Hao. Nat. Prod. Bioprospect. 2018, 8, 217.
(41) Hu, X.; Radosz, M.; Cychosz, K. A.; Thommes, M. CO2-Filling Capacity and Selectivity of Carbon Nanopores: Synthesis, Texture, and Pore-Size Distribution from Quenched-Solid Density Functional Theory (QSDFT). Environ. Sci. Technol. 2011, 45, 7068−7074.
(42) Lu, X.; Jin, D.; Wei, S.; Wang, Z.; An, C.; Guo, W. Strategies to enhance CO₂ capture and separation based on engineering absorbent materials. J. Mater. Chem. A 2015, 3, 12118–12132.

(43) Presser, V.; McDonough, J.; Yeon, S. H.; Gogotsi, Y. Effect of pore size on carbon dioxide sorption by carbide derived carbon. Energy Environ. Sci. 2011, 4, 3059–3066.

(44) Wickramaratne, N. P.; Jaroniec, M. Importance of small micropores in CO₂ capture by phenolic resin-based activated carbon spheres. J. Mater. Chem. A 2013, 1, 112–116.

(45) Wang, J.; Kaskel, S. KOH activation of carbon-based materials for energy storage. J. Mater. Chem. A 2012, 22, 23710–23725.

(46) Choma, J.; Zubrowska, A.; Gorka, J.; Jaroniec, M. Adsorption properties of phenolic resin-based mesoporous carbons obtained by using mixed templates of Pluronic F127 and Brij 58 or Brij 78 polymers. Adsorption 2010, 16, 377.

(47) Chang, B.; Tian, Y.; Shi, W.; Liu, J.; Xi, F.; Dong, X. Magnetically separable porous carbon nanospheres as solid acid catalysts. RSC Adv. 2013, 3, 20999–21006.

(48) Hamerton, I. The Status and Trend of Inter Layer Insulating Materials for Semiconductor Packages. BLACKIE 1994, 5, 128.

(49) Grande, D.; Grigoryeva, O.; Gusakova, K.; Fineleib, A. Novel mesoporous high-performance Films derived from polycyanurate networks containing high-boiling temperature Liquids. Eur. Polym. J. 2013, 49, 2162–2171.

(50) Grigoryeva, O.; Gusakova, K.; Fineleib, A.; Grande, D. Nanopore generation in hybrid polycyanurate/poly(e-caprolactone) thermostable networks. Eur. Polym. J. 2011, 47, 1736–1745.

(51) Grande, D.; Grigoryeva, O.; Fineleib, A.; Gusakova, K.; Lorthioir, C. Porous thermosts via hydrolytic degradation of poly(e-caprolactone) fragments in cyanurate-based hybrid networks. Eur. Polym. J. 2008, 44, 3588–3598.

(52) Fineleib, A.; Gusakova, K.; Grigoryeva, O.; Starostenko, O.; Grande, D. Synthesis, morphology, and thermal stability of nanoporous cyanate ester resins obtained upon controlled monomer conversion. Eur. Polym. J. 2015, 73, 94–104.

(53) Hedrick, J. L.; Russell, T. P.; Hedrick, J. C.; Hilborn, J. G. Microporous polycyanurate networks. J. Polym. Sci., Part A: Polym. Chem. 1996, 34, 2879–2887.

(54) Zhang, B.; Wang, Z. Building ultramicropores within organic polymers based on A thermosetting cyanate ester resin. Chem. Commun. 2009, 5027–5029.

(55) Yu, H.; Shen, C.; Wang, Z. Micro- and Mesoporous Polycyanurate Networks Based on Triangular Units. Chemplaschem 2013, 78, 498–505.

(56) Yu, H.; Shen, C.; Tian, M.; Qu, J.; Wang, Z. Microporous Cyanate Resins: Synthesis, Porous Structure, and Correlations with Gas and Vapor Adsorptions. Macromolecules 2012, 45, 5140–5150.

(57) Katsoulidis, A. P.; Dyar, S. M.; Carmili, R.; Malliakas, C. D.; Wasielowski, M. R.; Kanatzidis, M. G. Copolymerization of terephthalaldehyde with pyrrole, indole and carbazole gives microporous POFs functionalized with unpaired electrons. J. Mater. Chem. A 2013, 1, 10465–10473.

(58) Nugent, P.; Belmabkhout, Y.; Burd, S. D.; Cairns, A. J.; Luebke, R.; Forrest, K.; Pham, T.; Ma, S.; Space, B.; Wojtas, L.; Eddaoudi, M.; Zaworotko, M. J. Porous materials with optimal adsorption thermodynamics and kinetics for CO₂ separation. Nature 2013, 495, 80.

(59) Liu, J.; Thallapally, P. K.; McGrail, B. P.; Brown, D. R.; Liu, J. Progress in adsorption-based CO₂ capture by metal–organic frameworks. Chem. Soc. Rev. 2012, 41, 2308–2322.

(60) Li, P.; He, Y.; Guang, J.; Weng, L.; Zhao, J. C. G.; Xiang, S.; Chen, B. A Homochiral Microporous Hydrogen-Bonded Organic Framework for Highly Enantioselective Separation of Secondary Alcohols. J. Am. Chem. Soc. 2014, 136, 547–549.

(61) Nandi, M.; Okada, K.; Dutta, A.; Bhaumik, A.; Maruyama, J.; Derks, D.; Uyama, H. Unprecedented CO₂ uptake over highly porous N-doped activated carbon monoliths prepared by physical activation. Chem. Commun. 2012, 48, 10283–10285.
Surface-Energy Materials of polybenzoxazine. Macromol. Rapid Commun. 2008, 29, 1216–1220.

(81) Liu, J.; Ishida, H. Anomalous Isomeric Effect on the Properties of Bisphenol F-based Benzoxazines: Toward the Molecular Design for Higher Performance. Macromolecules 2014, 47, 5682–5690.

(82) Hao, G. P.; Li, W. C.; Qian, D.; Wang, G. H.; Zhang, W. P.; Zhang, T.; Wang, A.-Q.; Schuth, F.; Bongard, H.-J.; Lu, A. H. Structurally designed synthesis of mechanically stable poly-(benzoxazine-co-resol)-based porous carbon monoliths and their application as high-performance CO2 capture sorbents. J. Am. Chem. Soc. 2011, 133, 11378–11388.

(83) van der Voort, P.; Ravikovitch, P. I.; de Jong, K. P.; Benjelloun, M.; van Bavel, E.; Janssen, A. H.; Neimark, A. V.; Weckhuysen, B. M.; Vansant, E. F. A New Templated Ordered Structure with Combined Micro- and Mesopores and Internal Silica Nanocapsules. J. Phys. Chem. B 2002, 106, 5873–5877.

(84) Davies, J. M. R.; Hamerton, I.; Jones, J. R.; Povey, D. C.; Barton, J. M. Structure of 2,2?-bis(4-cyanatophenyl)isopropylidene. J. Crystallogr. Spectrosc. Res. 1990, 20, 285–289.

(85) Buttke, K.; Niclas, H.-J. Untersuchungen zur stereoselektiven elektrophilen Cyanierung. Journal für Praktische Chemie/Chemiker-Zeitung 1998, 340, 669–675.