Host-guest Inclusion Complexes Derived Heteroatom-doped Porous Carbon Materials

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Abstract: A facile and efficient strategy for the synthesis of heteroatom-doped carbon materials was developed, in which host-guest inclusion complexes were employed as versatile precursors. Inclusion of heteroatom containing guest molecules in the cavity of host molecules (such as cyclodextrins and cucurbit[n]urils) not only doped the carbon frameworks with heteroatoms (for instance, nitrogen, sulfur, boron, fluorine and iron), but also highly improved the carbonization yield. Since the chemical structure (composition) of host-guest inclusion complexes can be finely tuned at molecular level, they are ideal small molecular precursors for heteroatoms doped carbon materials. A nitrogen-doped porous carbon material derived from inclusion complexes exhibited a high performance as supercapacitors electrode with a high specific capacitance (348 F g^{-1}) at a current density of 1 A g^{-1} in 6 M KOH aqueous solution and good cycling stability over 5000 cycles, demonstrating its potential application in energy storage.

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1. Introduction

Carbon materials (CMs) have exhibited significant performance as supports for separation, catalysis, and energy conversion/storage due to their excellent electric and thermal conductivity, and high chemical stability.^[1-4] Recently, extensive efforts have been made to prepare the CMs with desirable microstructures and heteroatom doping via the carbonization of C-containing precursors. It has been shown that most small molecular organic compounds are not excellent precursors because they are volatile or decomposed into gas before/during the carbonization.^[5] Despite polymers^[6] and ionic liquids^[7, 8] have been successfully used as precursors of CMs, the tedious synthetic procedures and high cost of polymers and ionic liquids may complicate the manufacture and hinder their large-scale production. Particularly, doping of heteroatoms (such as nitrogen, boron, sulfur, and phosphorus elements)^[9-12] into carbon frameworks has been demonstrated to be an effective way for enhancing the surface wettability and electronic conductivity of CMs.^[13] Although both post-treatment and in situ synthesis have been successfully applied for the synthesis of heteroatoms-enriched CMs,^[14, 15] the traditional approach is difficult and complicated to achieve the specific atoms-doped CMs. As a consequence, developing new, efficient and facile strategy to prepare high yielding and various heteroatoms doped CMs is highly desirable.

During the past couple of decades, supramolecular assemblies based on the host-guest molecular recognition have attracted considerable interest because the confined spaces of host compounds (such as crown ethers, cyclodextrins (CDs), and cucurbit[n]urils(CBs)) offer an opportunity to investigate and manipulate the properties of encapsulated small molecules.^[16, 17] In addition, the chemical composition of the supramolecular assemblies can be easily adjusted by simply changing the guest molecules. For example, CDs have a hydrophobic cavity and hydrophilic exterior.^[18] Such a chemical structure endues CDs to form inclusion complexes with the hydrophobic guest molecules.

Herein, we report a facile and efficient strategy for the direct and large-scale synthesis of heteroatom

doped CMs, using host-guest inclusion complexes as small molecular organic precursors. The host compound, β -cyclodextrin (β -CD) or cucurbituril[6] (CB6), acted as the carbon precursor, while a series of heteroatom-containing small molecules, such as p-aminoazobenzene (P-AZO), amantadine (Ad-NH₂), 1-dodecylimidazole (DIM), ferrocene (Fc), and multiple heteroatom containing (nitrogen, sulfur, boron and fluorine et. al.) ionic liquids were selected as the guest molecules, which provided both the carbon and heteroatom sources. Inclusion of these guest molecules in the cavity of host not only implanted the carbon frameworks with heteroatoms, but also highly improved the carbonization yield. Such an efficient method allows the synthesis of CMs with desired heteroatoms.

2. Experimental Section

2.1. Chemicals

β -Cyclodextrin (β -CD), cucurbituril[6], ethanol, and potassium hydroxide were purchased from Sinopharm Chemical Reagent Co.,Ltd. Hydrochloric acid (HCl) and N,N-dimethylformamide (DMF) were acquired from ChinaSun Specialty Products Co.,Ltd. Polytetrafluoroethylene (PTFE) solution, potassium hexafluorophosphate and sodium tetrafluoroborate were purchased from Aladdin chemistry Co. Ltd. P-aminoazobenzene, ferrocene and amantadine were bought from Beijing InnoChem Science & Technology Co.,Ltd and used as received. Lithium bis-(trifluoromethanesulfonyl)imide (LiTFSI) was kindly provided by Rhodia and used as received. 1-Dodecylimidazole was obtained from Alfa Aesar. 1-Propyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl) imide (PMITFSI), 1-butyl-3-methylimidazolium hexafluorophosphate (BMIPF₆) and 1-butyl-3-methylimidazolium tetrafluoroborate (BMIBF₄) were synthesized according to the previous reports.^[19, 20] Acetylene black and nickel foam were used as purchased. All other reagents were commercially available and used without further purification. Distilled deionized water was used throughout the experiments.

2.2. Materials synthesis

2.2.1. Synthesis of β -CD-derived carbon ($C_{\beta\text{-CD}}$)

A mixture containing β -CD (2 g) and deionized water (10 g) was sealed in a 50 mL Teflon-lined stainless steel autoclave, and reacted at 180 °C for 24 h. After the autoclave was cooled down to room temperature, the pre-carbonized material was collected and washed with deionized water by means of centrifugation. The obtained dark powder was dried in a vacuum oven at 100 °C, and then carbonized in a ceramic crucible up to 800 °C under a nitrogen atmosphere at a heating rate of 5 °C min⁻¹ and then held at the setting temperature for 1 h. The resulting black solid was washed with distilled water, and then dried at 100 °C under vacuum.

2.2.2. Synthesis of β -CD-derived activated carbon ($C_{\beta\text{-CD-A}}$)

The $C_{\beta\text{-CD-A}}$ was prepared by carbonizing the pre-carbonized $C_{\beta\text{-CD}}$ with KOH (weight $\text{KOH/C} = 2:1$) at 800 °C for 1 h with a heating rate of 5 °C min⁻¹ under nitrogen atmosphere. The $C_{\beta\text{-CD-A}}$ was obtained by washing with 1 M HCl solution and distilled water, and then dried at 100 °C under vacuum.

2.2.3. Synthesis of the inclusion complex of P-AZO and β -CD-derived carbon ($C_{\beta\text{-CD/P-AZO}}$)

A mixture of β -CD (2.0 g, 1.8 mmol) and P-AZO (0.35 g, 1.8 mmol) was dissolved in N, N-dimethylformamide (5 mL). After be ultrasonicated for about 2 h, 100 mL deionized water was added. The precipitate was filtered and washed with water and then be sealed in a 50 mL Teflon-lined stainless steel autoclave with 10 g deionized water, and reacted at 180 °C for 24 h. The pre-carbonized material was collected and washed with deionized water by means of centrifugation. The dark powder was dried in a vacuum oven at 100 °C, and then carbonized in a ceramic crucible up to 800 °C under a nitrogen atmosphere at a heating rate of 5 °C min⁻¹ and then held at the setting temperature for 1 h. The resultant black solid was washed with 1 M HCl solution and distilled water, and then dried at 100 °C under vacuum.

2.2.4. Synthesis of the inclusion complex of P-AZO and β -CD-derived activated carbon ($C_{\beta\text{-CD/P-AZO-A}}$).

The $C_{\beta\text{-CD/P-AZO-A}}$ was prepared by carbonizing the pre-carbonized $C_{\beta\text{-CD/P-AZO}}$ with KOH (weight $KOH/C=2:1$) at 800 °C for 1 h under nitrogen atmosphere. The $C_{\beta\text{-CD/P-AZO-A}}$ was obtained by washing with 1 M HCl solution and distilled water, and then dried at 100 °C under vacuum.

2.2.5. Synthesis of other carbon materials ($C_{\beta\text{-CD/Ad-NH}_2}$, $C_{\beta\text{-CD/DIM}}$, $C_{\beta\text{-CD/PMITFSI}}$, $C_{\beta\text{-CD/BMIPF}_6}$, $C_{\beta\text{-CD/BMIBF}_4}$, $C_{\beta\text{-CD/Fc}}$, $C_{CB6/Fc}$)

A mixture of host (1.8 mmol) and respective guest (1.8 mmol) was dissolved in deionized water (10 g). After be ultrasonicated for about 2 h, the solution was sealed in a 50 mL Teflon-lined stainless steel autoclave, and reacted at 180 °C for 24 h. The pre-carbonized material was collected and washed with deionized water by means of centrifugation. The dark powder was dried in a vacuum oven at 100 °C, and then carbonized in a ceramic crucible up to 800 °C under a nitrogen atmosphere at a heating rate of 5 °C min⁻¹ and then held at the setting temperature for 1 h. The resultant black solid was washed with 1 M HCl solution and distilled water, and then dried at 100 °C under vacuum.

2.3. Materials' Characterization

2D NOESY NMR spectroscopy was measured by BRUKER AVANCE III 400. Thermal gravimetric analyzer (TGA) 4000 from PerkinElmer was used for the investigation of the thermal properties of the samples. Energy-dispersive X-ray fluorescence (EDX) measurements were performed with a spectrometer attached to Hitachi Model S-4700 field-emission scanning electron microscopy (SEM) system. The microstructure of obtained carbon materials was detected by Tecnai G220 transmission electron microscopy (TEM) with CCD imaging system. X-ray photoelectron spectra (XPS) were conducted through an XPS-7000 spectrometer (Rigaku) with an excitation source of Mg K α radiation. X-ray powder diffraction (XRD) pattern was tested on a Philips X'Pert PRO diffractometer with nickel-filtered Cu K α radiation. Raman spectra were obtained with the LabRAM

HR800 from JY Horiba. Nitrogen sorption analysis was carried out on an ASAP 2020 accelerated surface area and porosimetry instrument (Micromeritics), equipped with automated surface area, at 77 K using Brunauer-Emmett-Teller (BET) calculations for the surface area. The pore size distribution plots were recorded from the desorption branch of the isotherms based on the Barrett-Joyner-Halenda (BJH) model.

2.4. Electrochemical measurements

All the electrochemical measurements were carried out on a CHI660c electrochemical workstation (Shanghai Chenhua Instruments Co.) at room temperature in a three-electrode system collocating with Pt sheet as the counter electrode and Hg/HgO as the reference electrode. The working electrodes were prepared by mixing the carbon material with carbon black (conductive agent) and PTFE (binder) at the mass ratio of 8:1:1 to viscous slurry before pressing it onto a nickel foam current collector at 15 MPa. The obtained electrodes with an area of 1.0 cm² were dried at 100 °C in a vacuum oven overnight. The quality of carbon material loaded on the prepared electrode was about 5.0 mg for each other. The tests were proceeded in 6 M KOH aqueous solution. Cyclic voltammetry curves were obtained in the potential range of -1.0-0 V vs Hg/HgO by varying the scan rate from 5 to 100 mV s⁻¹. Charge/discharge measurements were worked at galvanostatically from 0.5 to 30 A g⁻¹, over a voltage range of -1.0-0 V vs Hg/HgO. Electrochemical impedance spectroscopic (EIS) was conducted at the frequency range of 10 KHz and 0.01 Hz with an alternate current amplitude of 5 mV. The long-term stability was cycled on a LAND-CT2001A instrument (Wuhan Land Electronics Co. Ltd.). The specific capacitances were calculated from the discharge curves by the following equation:

$$C = \frac{I\Delta t}{m\Delta V} \quad (1)$$

Where I (A), ΔV (V), m (g), Δt (s) represent the discharge current, the potential window within the discharge time Δt , the mass of active material on the electrode and the discharge time, respectively.

3. Results and Discussion

Fig. 1

The synthetic route for the synthesis of heteroatom doped CMs is shown in **Fig. 1a**. All the host/guest inclusion complexes were synthesized in water (or DMF) and subsequent removal of the solvent. The produced inclusion complexes were then carbonized at 800 °C. It has already been well studied that heteroatom containing compounds (chemical structures see **Fig. 1b**), including P-AZO,^[21] Ad-NH₂,^[18, 22] DIM,^[23] Fc,^[24] and room temperature ionic liquids 1-propyl-3-methylimidazolium bis((trifluoromethyl) sulfonyl)imide (PMITFSI),^[25, 26] 1-butyl-3-methylimidazolium hexafluorophosphate (BMIPF₆) and 1-butyl-3-methylimidazolium tetrafluoroborate (BMIBF₄)^[27] are able to form host-guest complexes with β -CD under suitable experimental conditions. To get the detailed insights into the nature of β -CD/guest complex system, NMR spectroscopy analysis was first carried out. **Fig. S1a** shows the 2D NOESY NMR spectroscopy of β -CD/P-AZO complex formed in DMSO-*d*₆. It can be seen that the β -CD/P-AZO complexes display two nuclear Overhauser enhancement (NOE) cross-correlation peaks (marked with green circles), which derived from the inner CD protons at 3.5 ppm and the azobenzene protons (7.5-7.7 and 6.7 ppm), respectively. These NOE correlation points confirmed the close spatial proximity of azobenzene moiety and the inner β -CD protons, indicating the successful formation of β -CD/P-AZO host-guest complexes.^[28] In addition, all the formed segmental inclusion complexes can be observed by the NOE cross-correlation peaks in 2D NOESY NMR (see **Fig. S1b-e**) as well as the peak shifts of fluorine atoms in ¹⁹F NMR spectroscopy (see **Fig. S2**).

Fig. 1c shows the thermal gravimetric analysis (TGA) curves measured for host or guest compounds. As can be seen that β -CD showed a weight loss step at around 382 °C, representing the destruction of cyclic oligosaccharides. The residual mass of 8.6% and 21.1% were obtained for β -CD and CB6 at 800 °C, respectively. However, no carbon residue was achieved for the attempted

carbonization of guest compounds, indicating that these guest compounds (except PMITFSI, carbon yield: 6.1%) can not produce CMs. For example, the decomposition temperature of P-AZO was determined to be 175 °C, however, no char residue above 316 °C was obtained, indicating that P-AZO itself can not be used as the carbon precursor directly.

Fig. 1d shows the TGA curves of host/guest inclusion complexes, and all the data were summarized and listed in **Table 1**. Compared with pure β -CD, CB6 or guest compounds, the carbon yields of all the host-guest inclusion complexes (except β -CD/Fc) were highly increased (varied from 13.6% to 31.2% at 800 °C, see **Table 1**). **Fig. S3** shows the TGA curves of β -CD/P-AZO inclusion complexes. Two weight loss steps peaking at about 180 and 382 °C were ascribed to the decomposition of P-AZO and β -CD, respectively. It should be noted that the residual mass of CMs was about 16.3%, which was much higher than those obtained from either β -CD or P-AZO. These results demonstrated that the host-guest interactions between β -CD and P-AZO could prevent the exclusion of P-AZO from the nano-cavity of β -CD, and thus P-AZO was carbonized within the cavity of β -CD. Furthermore, the β -CD/P-AZO complex at a molar ratio of 1:1 exhibited the highest yield (16.3%), while the lower or higher ratio of β -CD/P-AZO lowered carbonization yields (12-13%). These results further confirmed that P-AZO was successfully encapsulated into the cavity of β -CD through the host-guest interactions with the molar ratio of 1:1. The only exception that we found are β -CD/Fc inclusion complexes, which exhibited the carbonization yield of only 3.9% at 800 °C (**Fig. 1d**). Such an extremely low carbonization yield was probably due to the low association constant of β -CD/Fc ($K_a = 17 \times 10^3 \text{ M}^{-1}$), which is unable to prevent the sublimation of Fc during the carbonization process.^[29] However, a higher carbonization yield of 31.2% at 800 °C was obtained for CB6/Fc inclusion complexes (**Fig. 1d**) probably due to the relatively higher association constant of CB6/Fc ($K_a = 1.3 \times 10^{12} \text{ M}^{-1}$).

It should be noted that the initial decomposition temperatures of host-guest inclusion complexes are slightly higher (or almost unchanged) (see **Table S1**) than those of guest compounds (including P-AZO, Ad-NH₂, DIM and Fc), indicating that encapsulation into the cavity of β -CD could slightly

improve the thermal stability of the guest compounds. In contrast, the β -CD/ionic liquid (such as BMIBF₄, BMIPF₆, and PMITFSI) inclusion complexes exhibit relatively lower decomposition temperature than those of ionic liquid guest compounds. The host-guest interactions between β -CD and ionic liquids increase the distance between cations and anions. The steric congestion and the geometry distortion of the components may make inclusion compounds unstable.^[30] The total energies of cations and anions are higher than those of the original ion pairs, which lead to the lower decomposition temperature of the host-guest complexes.^[31] As the carbon precursors, host-guest inclusion complexes allow the chemical compositions to be adjusted at molecular level because various guest molecules can be included in the cavity of β -CD through various noncovalent interactions.^[32] Therefore, we expected that the heteroatoms of guest compounds could be retained during the carbonization of β -CD/guest inclusion complexes.

Here, the chemical composition of the resultant CMs were characterized by both energy dispersive X-ray (EDX) and X-ray photoelectron spectra (XPS). The results were summarized and listed in **Table 1** and **Table S2**. As confirmed by elemental analysis, it can be seen that various heteroatoms (such as nitrogen, sulfur, boron and fluorine) were successfully doped into the framework of prepared CMs by simply changing the guest molecules. It is also feasible to prepare multi-heteroatoms doped CMs through prudently screening of guest molecules, such as BMIBF₄, BMIPF₆, and PMITFSI. Therefore, it can be concluded here that inclusion of heteroatom containing guest molecules in the cavity of β -CD can not only dope the heteroatoms into the carbon frameworks, but also highly improve the carbonization yield, as compared with that of either β -CD or guest molecules as precursors.

Table 1

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were applied to studying the morphology of the obtained CMs. **Fig. 2a,b** show the SEM of CMs derived from β -CD (denoted as C _{β -CD}) and β -CD/P-AZO complexes (denoted as C _{β -CD/P-AZO}). Carbon spheres with the average diameter of about 1 μ m were obtained for C _{β -CD} (**Fig. 2a**). Similar carbon spheres, however,

with bigger size (4-5 μm in diameter), were obtained for $\text{C}_{\beta\text{-CD/P-AZO}}$ (**Fig. 2b**), probably due to the residues of $\text{C}_{\text{P-AZO}}$ remained in the cavity of $\text{C}_{\beta\text{-CD}}$ which enlarge the framework of carbon spheres. The same phenomenon is observed from **Fig. S4a-e**. **Fig. S4f and g** shows the morphology of C_{CB6} and $\text{C}_{\text{CB6/FC}}$, respectively. In order to further enhance the electrochemical performance of the obtained CMs, KOH activation was performed on prepared CMs (denoted as $\text{C}_{\beta\text{-CD-A}}$ and $\text{C}_{\beta\text{-CD/P-AZO-A}}$, respectively). As can be seen that the surface of obtained carbon spheres are destroyed and become rough (**Fig. 2c,d**). The morphology of $\text{C}_{\beta\text{-CD-A}}$ and $\text{C}_{\beta\text{-CD/P-AZO-A}}$ were further characterized by TEM (**Fig. 2e-g**). **Fig. 2f** takes on different sizes of vesicles. In addition, the consecutive distribution of abundant nanopores are clearly observed from **Fig. 2g**. Both $\text{C}_{\beta\text{-CD}}$ and $\text{C}_{\beta\text{-CD/P-AZO}}$ exhibit relatively low surface areas at around $290 \text{ m}^2 \text{ g}^{-1}$, which were increased to $929.2 \text{ m}^2 \text{ g}^{-1}$ and $989.4 \text{ m}^2 \text{ g}^{-1}$ for $\text{C}_{\beta\text{-CD-A}}$ and $\text{C}_{\beta\text{-CD/P-AZO-A}}$ (**Fig. S5** and **Table S3**), respectively. The pore volume of $\text{C}_{\beta\text{-CD/P-AZO-A}}$ was improved from 0.17 to $0.53 \text{ cm}^3 \text{ g}^{-1}$ after the chemical activation. This spatial structure provided available access to delivering and permeating the ions of electrolyte to the surface of the electrode, contributing to fast ions transmission.^[33-35]

Fig. 2

Fig. S6 shows the XPS data of the $\beta\text{-CD/P-AZO}$ derived CMs. The XPS C1s spectra show four peaks, corresponding to C-C (284.7 eV), C-O/ C-N (285.4 eV), C=O/C=N (286.8 eV) and O=C-O (290.0 eV) functional groups.^[36] The XPS spectra of O1s show three peaks at 531.9, 532.9 and 533.8 eV, representing C=O, O-C-O, and O=C-O, respectively.^[37] Four types of N-containing groups, including pyridinic N (N-6 at 399 eV), pyrrolic N (N-5 at 400.1 eV), quaternary N (N-Q at 401.1 eV), and pyridinic N-oxide group (N-X at 402.4-403.3 eV) were confirmed from the N1s XPS spectra.^[38-40] The presence of quaternary N can enhance the electronical conductivity of the materials, which plays an important role in the supercapacitor performance.^[14, 41] **Fig. 3a** shows the wide-angle X-ray diffraction (XRD) curves of the obtained carbon materials. It can be clearly seen that the carbon materials have two distinct broad peaks at about 22.8° (002) and 43.8° (100), indicating the formation

of amorphous carbon frameworks.^[42, 43] The peak at 22.8° shows a well-developed graphitic stack, while the formation of a higher degree of intralayer condensation results in a peak appearing at 43.8°, which can strengthen the electronic conductivity to a certain extent.^[44] The formation of carbon materials were also confirmed by Raman spectra (**Fig. 3b**). Two peaks are obviously centered at 1330 and 1590 cm⁻¹, which reflect the characteristic D (defects and disorder) and G (graphitic) peaks of carbon materials, respectively.^[45, 46] The degree of structural order in regard to an excellent graphitic structure are determined by the D/G ratio of band intensities.^[47] The D/G intensity ratios of C_{β-CD/P-AZO-A}, C_{β-CD-A}, C_{β-CD/P-AZO}, C_{β-CD} were calculated to be 1.16, 1.13, 1.10 and 1.08, respectively. Heteroatom N in the graphite layer can serve as defect sites, resulting in intense D band.^[42] In addition, more disorder in graphitic structures can be fabricated through KOH activation.^[48] Therefore, both N doping and KOH activation probably increase the I_D/I_G value of C_{β-CD/P-AZO-A}.

Fig. 3

The electrochemical capacitive performances of these carbon materials were evaluated by cyclic voltammetry (CV) in 6 M KOH aqueous solution at room temperature (**Fig. 4**). It can be seen that both C_{β-CD/P-AZO-A} (**Fig. 4a**) and C_{β-CD-A} (**Fig. S7a**) behave a quasi-rectangular shaped voltammetry at a low scan rate of 5 mV s⁻¹ from -1.0 to 0 V, which indicate an ideal double-layer capacitance behavior and fast charge–discharge property.^[49, 50] These two carbon materials could also maintain a similar rectangular shape, exhibiting a highly capacitive nature and a rapid charge-discharge process when the scan rate was increased from 5 to 100 mV s⁻¹.^[51] Compared with C_{β-CD-A}, C_{β-CD/P-AZO-A} shows a higher current density at the scan rate of 5 mV s⁻¹ (**Fig. 4b**), benefiting from its higher specific surface area and nitrogen content. It should be noted that the Faradaic hump of C_{β-CD/P-AZO-A} was observed at ≈0.41 V in **Fig. 4b**, probably due to redox reactions of the doped heteroatoms such as pyridinic and pyrrolic nitrogen species.^[13] However, no rectangular shape CV curves were observed for both C_{β-CD} (**Fig. S7b**) and C_{β-CD/P-AZO} (**Fig. S7c**), suggesting the poor double-layer capacitance behaviors. The results might due to their poor specific surface area and pore volumes, which result in insufficient ion

channels. Therefore, these results may suggest that $C_{\beta\text{-CD/P-AZO-A}}$ possesses the most promising potential in supercapacitor electrode material among all the carbon materials prepared in this work.

For the sake of further studying the performance of carbon materials, the galvanostatic charge/discharge experiments were carried out in a three-electrode system at different current densities (**Fig. 4c,d** and **Fig. S8**). Charge/discharge curves of $C_{\beta\text{-CD/P-AZO-A}}$ (**Fig. 4c,d**) and $C_{\beta\text{-CD-A}}$ (**Fig. S8a**) at different current densities exhibit equicrural triangle shape, suggesting an ideal capacitor behavior.^[52, 53] However, obvious voltage drops are observed from charge/discharge curves of $C_{\beta\text{-CD}}$ (**Fig. S8b**) and $C_{\beta\text{-CD/P-AZO}}$ (**Fig. S8c**), indicating the relatively poor capacitor behavior. The specific capacitance values of obtained carbon materials were also calculated. At a current density of 1 A g^{-1} , the specific capacitances of $C_{\beta\text{-CD}}$, $C_{\beta\text{-CD/P-AZO}}$ and $C_{\beta\text{-CD-A}}$ are calculated to be 75, 120 and 220 F g^{-1} , respectively. The specific capacitance of $C_{\beta\text{-CD/P-AZO-A}}$ at 1 A g^{-1} is about 348 F g^{-1} , which is comparable to the reported activated carbon-based supercapacitor electrodes under the same experimental conditions, such as 340 F g^{-1} of human hair-derived carbon flakes,^[44] 279 F g^{-1} of willow catkins-derived activated carbon,^[54] and 306 F g^{-1} of shiitake mushroom-based porous carbons.^[55] Although the specific surface area of $C_{\beta\text{-CD/P-AZO}}$ is lower than that of $C_{\beta\text{-CD}}$, a slightly higher specific capacitance was still obtained for $C_{\beta\text{-CD/P-AZO}}$, might due to the faradaic pseudo-capacitance caused by the nitrogen element doping of $C_{\beta\text{-CD/P-AZO}}$. The Coulombic efficiency of $C_{\beta\text{-CD/P-AZO-A}}$ and $C_{\beta\text{-CD/P-AZO}}$ are 1.03, 1.05 at a current density of 1 A g^{-1} , indicating the existence of faradaic pseudocapacitance. **Fig. 4e** clearly reveals that the specific capacitance of $C_{\beta\text{-CD/P-AZO-A}}$ is always higher than that of $C_{\beta\text{-CD-A}}$ at current densities from 0.5 to 30 A g^{-1} . A specific capacitance of 216 F g^{-1} can be maintained for $C_{\beta\text{-CD/P-AZO-A}}$, even at the high current density of 30 A g^{-1} , demonstrating a good performance stability.

Fig. 4f shows the electrochemical impedance analysis of the carbon materials obtained. In low frequency section, the nearly vertical line represents double-layer energy storage.^[56, 57] The slope of 45° obtained at middle frequency section implies Warburg impedance.^[58, 59] The short line at this region shows the low ion diffusion resistance in the aqueous electrolyte. The resistance of the

electrodes assembled by carbon materials and current collectors are obtained from the semicircle at high frequency region.^[60, 61] The inset graph shows a magnified high frequency section for C_{P-AZO/β-CD}-A. The equivalent series resistances of C_{β-CD/P-AZO-A}, C_{β-CD-A}, C_{β-CD/P-AZO}, C_{β-CD} are calculated to be 0.15, 0.18, 0.23, and 0.21 Ω, respectively.

Fig. 4

Fig. 5

The cyclic stability test was conducted at a current density of 1 A g⁻¹ by galvanostatic charge/discharge measurement (**Fig. 5**). About 95% of the initial specific capacitance can be reserved even over 5 000 cycles, demonstrating good cyclic stability. The excellent electrochemical stability could be resulted from the robust carbon frameworks for the transfer of electrolyte ions to the electrode surface.^[62] All the electrochemical tests indicate that C_{β-CD/P-AZO-A} owns the best electrochemical performance of the synthesised carbon materials.

4. Conclusions

In summary, we reported a facile and efficient strategy for large scale production of heteroatom-doped porous CMs via the carbonization of host-guest inclusion complexes and followed by chemical activation. Inclusion of guest molecules in the cavity of host molecules could not only dope the carbon frameworks with heteroatom elements, but also highly improve the carbonization yield. One of the resultant nitrogen containing porous carbon materials possessed a high specific capacitance performance. Since the composition of guest compounds can be finely tuned, this method provided guidance for efficiently design of multi-functional carbon materials with potential application ranges widely from supercapacitors to lithium ion batteries and gas uptake.

Acknowledgements

This work was supported by the National Science Foundation for Distinguished Young Scholars (No.

21425417), the Natural Science Foundation of China (No. 21274101), the National Basic Research Program of China (973 Program) (No. 2012CB825800), and the Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions.

Appendix A. Supplementary data

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Figure captions

Fig. 1. a) Schematic procedure for the synthesis of heteroatom doped CMs derived from host-guest inclusion complexes; b) Chemical structures of guest compounds being investigated; c) Thermogravimetric analysis (TGA) of β -CD, CB6 and guest molecules; and d) TGA of host-guest complexes (1:1, molar ratio).

Fig. 2. Scanning electron microscopy (SEM) images of the prepared carbon materials, a) $C_{\beta\text{-CD}}$, b) $C_{\beta\text{-CD/P-AZO}}$, c) $C_{\beta\text{-CD-A}}$, and d) $C_{\beta\text{-CD/P-AZO-A}}$. Transmission electron microscopy (TEM) images of e) $C_{\beta\text{-CD-A}}$, f) $C_{\beta\text{-CD/P-AZO-A}}$, and g) high-resolution transmission electron microscopy (HR-TEM) images of $C_{\beta\text{-CD/P-AZO-A}}$.

Fig. 3. (a) Wide-angle X-ray diffraction (XRD) patterns and (b) Raman spectra of the synthesized carbon materials ($C_{\beta\text{-CD}}$, $C_{\beta\text{-CD/P-AZO}}$, $C_{\beta\text{-CD-A}}$ and $C_{\beta\text{-CD/P-AZO-A}}$). Two diffraction peaks were observed at 22.8° and 43.8° in (a), indicating the degree of graphitization. The peaks situated at around 1330 and 1590 cm^{-1} in (b) can be belonged to the characteristic D (defects and disorder) and G (graphitic) bands of the carbon materials.

Fig. 4. a) Cyclic voltammetry (CV) curves of $C_{\beta\text{-CD/P-AZO-A}}$ at different scan rates. b) CV curves of $C_{\beta\text{-CD-A}}$ and $C_{\beta\text{-CD/P-AZO-A}}$ at a scan rate of 5 mV s^{-1} . c,d) Charge-discharge curves of $C_{\beta\text{-CD/P-AZO-A}}$ at different current densities of $0.5\text{-}30\text{ A g}^{-1}$. e) Specific capacitances of $C_{\beta\text{-CD/P-AZO-A}}$ and $C_{\beta\text{-CD-A}}$ at different current densities. f) Electrochemical impedance spectra (EIS) plots of carbon materials under the influence of an ac voltage of 5 mV (inset: magnified $0.95\text{-}1.5\ \Omega$ region).

Fig. 5. Cyclic stability of $C_{\beta\text{-CD/P-AZO-A}}$ at a current density of 1 A g^{-1} by galvanostatic charge/discharge measurement for 5 000 cycles in 6 M KOH solution. The specific capacitance is retained approximately 95 % of the initial capacitance at 1 A g^{-1} .

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Table 1. The Composition and Yield of Carbon Materials Derived from Host/Guest Inclusion Complexes^a

Samples	C	N	O	F	S	B	P	Fe	Yield(%)
C _β -CD	90.5	-	9.5	-	-	-	-	-	8.6
C _β -CD/P-AZO	87.2	6.4	6.4	-	-	-	-	-	16.3
C _β -CD/Ad-NH ₂	90.3	4.7	5.0	-	-	-	-	-	16.1
C _β -CD/DIM	90.2	5.7	4.1	-	-	-	-	-	13.6
C _β -CD/PMITFSI	88.6	5.4	3.7	0.8	1.5	-	-	-	23.2
C _β -CD/BMIPF ₆	90.7	5.1	3.4	0.2	-	-	0.6	-	27.4
C _β -CD/BMIBF ₄	83.6	2.6	1.1	0.3	-	12.4	-	-	20.7
C _β -CD/Fc	89.9	-	10.08	-	-	-	-	0.02	3.9
C _{CB6}	71.2	16.7	12.1	-	-	-	-	-	21.1
C _{CB6} /Fc	16.2	1.8	42.8	-	-	-	-	39.2	31.2

^a Carbonized at 800 °C and characterized by energy dispersive X-ray (EDX, wt%)

Graphical abstract

Host-guest inclusion complexes-derived heteroatom-doped carbon materials were prepared and employed for high-performance supercapacitor electrode materials.