Effects of Inherent/Enhanced Solid Acidity and Morphology of Diatomite Templates on the Synthesis and Porosity of Hierarchically Porous Carbon

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Material synthesis and acidity measurement: Dt-T was prepared by heating Dt at 923 K for 3 h. Dt-A was prepared by the following steps: (i) 15 mL hydrochloric acid solution (2 mol/L) was mixed with 1 g of Dt and kept at 378 K for 4 h; (ii) the mixture was stirred for 1 h at room temperature and dried at 333 K; (iii) the dried product was heated at 823 K for 5 h in the muffle furnace. Here, the Al, derived from the montmorillonite, was introduced the surface (or implanted to the structure) of

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20   diatom shell to increase the solid acid sites. All chemicals and reagents used in this

21   work were of analytical grade and used as received.

22   Porous carbon products were prepared as following: templates and furfuryl alcohol

23   were mixed in ceramic boats with a ratio of solid : liquid=1 g:5 mL and stirred for 1.5

24   h at room temperature, followed by heating at 368 K for 24 h. After that, the mixture

25   was further heated at 423 K under vacuum condition for 1 h to promote cross-linking.

26   The resultant was transferred into a tubular oven and heated at 973 K for 3 h under N_2

27   atmosphere (99.999%) for complete carbonization. The obtained product was

28   dissolved in HF solution (40%) for 12 h to remove diatomite template (1 g solid in 20

29   mL aqueous HF solution). C/FA was prepared using oxalic acid (5 mg/mL furfuryl

30   alcohol) as the catalyst following the above steps without the addition of any

31   template.

32   The acidity of the template was determined by the titration method following the

33   procedure previously described by Benesi et al.[1] The suspension of 0.3 g template in

34   20 mL dry solvent petroleum ether was stirred for 5 min, and then three drops of

35   dimethyl yellow-benzene solution (0.1%) was added. The resultant red-colored

36   mixture was stirred for 20 min. Then the *n*-butylamine solvent petroleum ether

37   solution was added dropwise from the microburet into the above mixture and stopped

38   until the color of mixture turned yellow. The volume of consumed *n*-butylamine

39   solvent petroleum ether solution was converted into the surface acid sites of templates

40   by the equation (1).

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$$A = \frac{C*V}{M}*10^{-3} \tag{1}$$

42 Where A is the acid amount, mmol/g; C is the concentration of solution, C=0.1 mol/L;

43 V is the volume of consumed n-butylamine, mL; M is the quality of catalysts, g.

44 **Element analysis and SEM/TEM characterization**: Element analysis was

45 performed on a Rigaku 100e X-ray fluorescence spectrometer (XRF). The chemical

46 composition of Dt is: SiO_2 (86.18, wt%), Al_2O_3 (3.08%), Fe_2O_3 (1.47%), K_2O (0.51%),

47 CaO (0.37%), MgO (0.33%) and Na_2O (0.06%), and the loss on ignition (L.O.I) is

48 8.00%.

49 Scanning electron microscopy (SEM) micrographs were obtained using a 5 kV

50 FEI-Sirion 200 field emission scanning electron microscope (FESEM) attached an

51 Oxford INCA energy dispersive X-ray spectroscopy (EDS).

52 Transmission electron microscopy (TEM) images were obtained on a JEOL

53 JEM-2100 electron microscope operating at an acceleration voltage of 200 kV. The

54 specimens for TEM observation were prepared by the following procedure. The

55 sample was ultrasonically dispersed in ethanol for 5 min, and then a drop of sample

56 suspension was dropped onto a carbon-coated copper grid, which was left to stand for

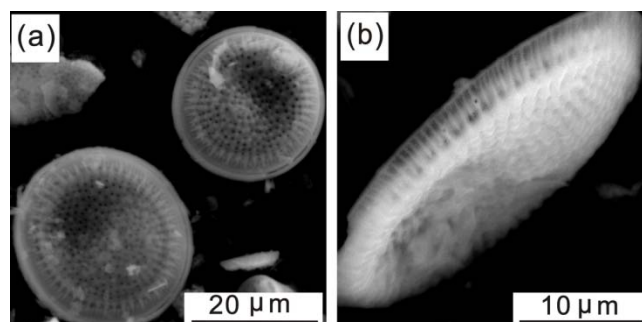57 10 min and transferred into the microscope.

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60 Figure S1. SEM images of the original diatomite: (a) planform and (b) side view.

61   Fig. S1 shows the SEM images of Dt. The diatom shell has disc-like morphology

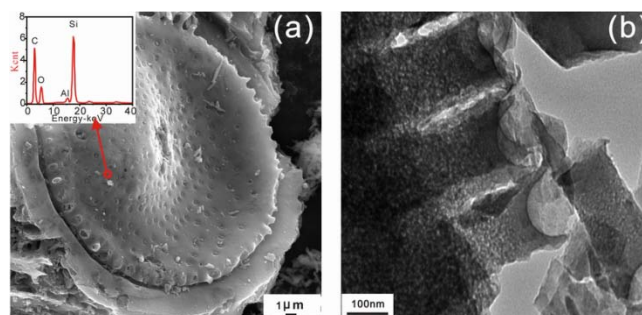62   and highly developed macroporous structure (Fig. S1.a and b).

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65   Figure S2. (a) SEM and (b) TEM images of the template-carbon composites;

66   Insert image of (a): EDS analysis result.

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68   Fig. S2.a displays the SEM image of the template-carbon composite (C/Dt),

69   which exhibits the thin carbon film coated on the surface of diatom shell. The EDS

70   analysis shows Si, Al, C and O elements coexist in the template-carbon composites

71   with a Si/C molar ratio near to 0.12. The TEM image shows a fragment of the

72   composite (Fig. S2.b), which consists of the diatomite framework and the filled

73   carbon.

74   **Powder X-ray diffraction characterization:** The powder X-ray diffraction (XRD)

75   patterns were taken on a Bruker D8 Advance diffractometer with Ni filter and CuKa

76   radiation ($\lambda = 0.154$ nm) using a generator voltage of 40 kV and a generator current of

77   40 mA, and a scan rate of 1º (2θ)/min was applied for the determination.
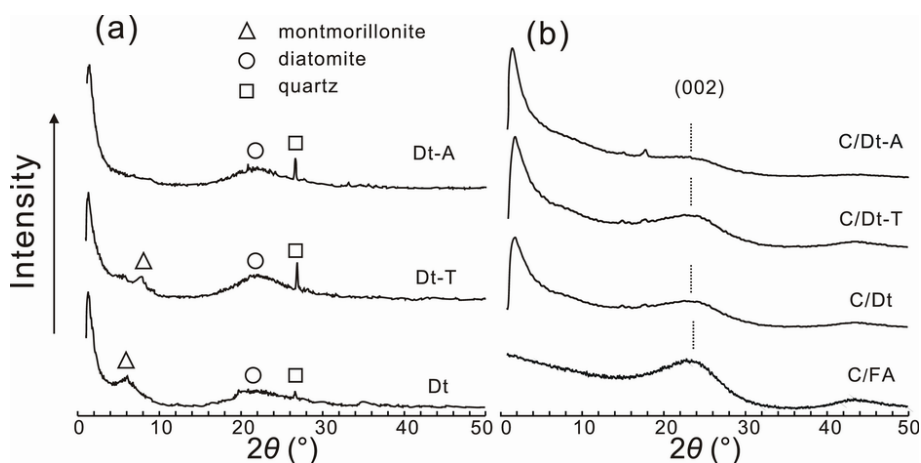
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Figure S3. XRD patterns of: (a) the diatomite templates and (b) the carbon products.

Fig. S3.a presents the XRD patterns of Dt, Dt-T and Dt-A. The XRD patterns of all diatomite templates exhibit one broad peak centered at about 22º (2θ) attributed to the reflection of amorphous diatomaceous SiO_2. Moreover, a sharp peak appears at about 1.2-1.4º in the XRD patterns of all the diatomite templates. This sharp XRD peak in the low 2θ angle region is an indicator of the long-range ordered macro/mesoporous structure, as what happened in some ordered porous solids.[2-3] Here it should be attributed to the edge macropores which has a repeated spatial arrangement model of hexagonal array.

The XRD peaks at about 6.1º and 27.3º in Dt and Dt-T are attributed to montmorillonite and quartz, respectively. The mineral composition was determined as diatomite 92.46 (wt%), montmorillonite 4.86% and quartz 2.68%, based on a semi-quantitatively calculation by use of deconvolution of XRD peaks. The diffraction peak of montmorillonite disappeared in Dt-A after acid activation (Fig. S3.a). The very weak XRD peaks at about ~15.2º and ~17.8º in C/Dt, C/Dt-T and C/Dt-A should be attributed to carbon fluoride.

As shown in Fig. S3.b, a sharp reflection exists at about 1.4-2.0° (2θ) in the XRD pattern of each templated carbon product, but does not appear in that of C/FA. It confirms that the long-range ordered structure of templated carbon product is resulted from the reproduction of diatom shell, instead of the carbonization of the precursor itself. According to the line width of the (002) peak, the sizes of graphite microcrystal in the c-direction (L_c), calculated by the Debye-Sherrer equation (Equation 2), were C/Dt: 0.34 nm; C/Dt-T: 0.37 nm; and C/Dt-A: 0.45 nm, respectively. These sizes are slightly smaller than those (~0.6 nm) of clay-templated carbons.[4]

$$L_c = k\lambda / \beta \cos\theta \tag{2}$$

Where λ is incident wavelength for CuKa: λ=0.154 nm; k is the shape coefficiency: k=0.9; β is the full width at half maximum (FWHM); θ is the diffraction angle.

Nitrogen adsorption characterization: N_2 adsorption–desorption isotherms were measured on a Micromeritics ASAP 2020 analyzer (Micromeritics Co. Norcross, USA) at liquid nitrogen temperature. The samples were outgassed at 423 K for 12 h at the degas port and then transferred to the analysis port to degas further for 6 h below a relative pressures of 0.01 before measurement. The specific surface area, S_{BET}, was calculated by using the multiple-point Brunauer–Emmett–Teller (BET) method and the total pore volume, V_{pore}, was evaluated from nitrogen uptake at a relative pressure of about 0.99. Micropore volume was estimated by the DA methods. Pore size distributions (PSDs) from 0.35 to 5 nm were determined by the adsorption branch of the N_2 isotherm , using non-local density functional theory (DFT).
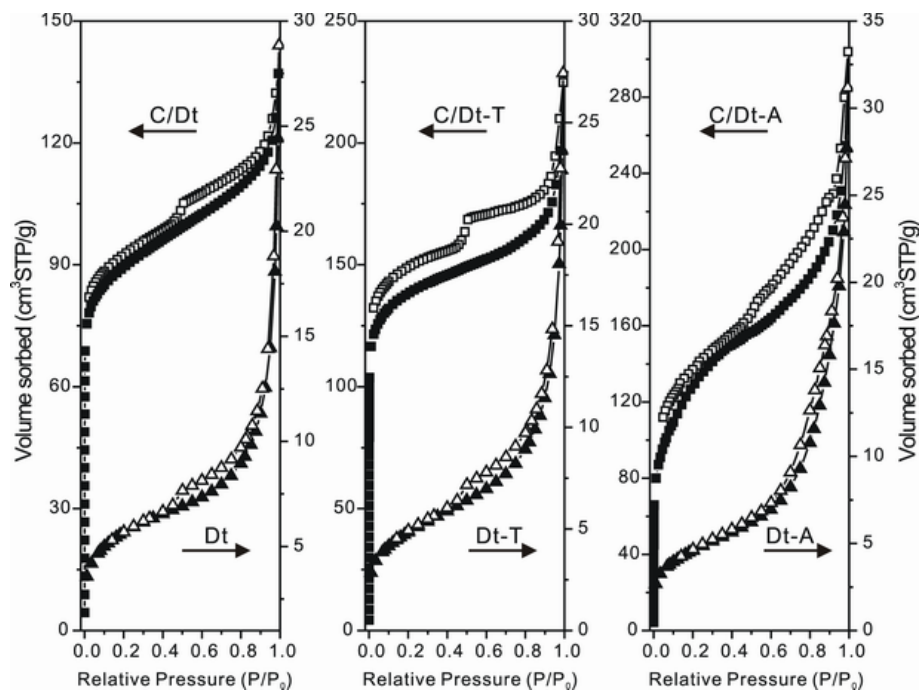
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Figure S4. N$_2$ adsorption isotherms of templates and carbon products at 77 K.

Fig. S4 shows the adsorption-desorption isotherms of diatomite templates and carbon products. All the isotherms have hysteresis loops which belong to the H3 type and imply the existence of micropores, mesopores and macropores. The H3 type loop of carbon product is corresponding to the narrow slit-like pores which may be given by the stacking of platy carbon microparticles. The increase of N$_2$ adsorption below the relative pressures of 0.1 of the carbon products is steeper than that of their diatomite counterparts (Fig. S4), indicating the amount of micropores in the former is larger than the latter. This is strongly supported by the results of the micropore volumes (Table S1).

Table S1. Porous parameters of the diatomite-templated carbons.

Carbon products	Dt	Dt-T	Dt-A	C/Dt	C/Dt-T	C/Dt-A	C/FA

BET surface area $(m^2/g)^a$	19	17	16	270	406	426	10
Total pore volume$(cm^3/g)^a$	0.045	0.042	0.048	0.212	0.348	0.470	0.009
Micropore volume $(cm^3/g)^a$	0.003	0.003	0.003	0.127	0.195	0.153	0.007
Macropore volume $(cm^3/g)^b$	2.21	2.55	2.73	1.66	1.71	5.66	—
Mean macropore diameter $(nm)^b$	686	575	565	551	423	422	—

^{a}measured by N_2 adsorption, ^{b}measured by mercury intrusion method.

The BET surface areas and the total pore volumes of the different carbon products follow an order of C/Dt-A > C/Dt-T > C/Dt (Table S1), which is in accordance with the order of the acid sites concentratation in the diatomite templates.

Fig. S5 shows the PSDs of the carbon products. It shows that micropores and mesopores coexist in the structure of the carbon products. There are dramatic peaks in the micropore region, and the size of the micropores is centered in about 0.6-0.8 nm. However, the size of mesopores exhibits a much wider distribution.
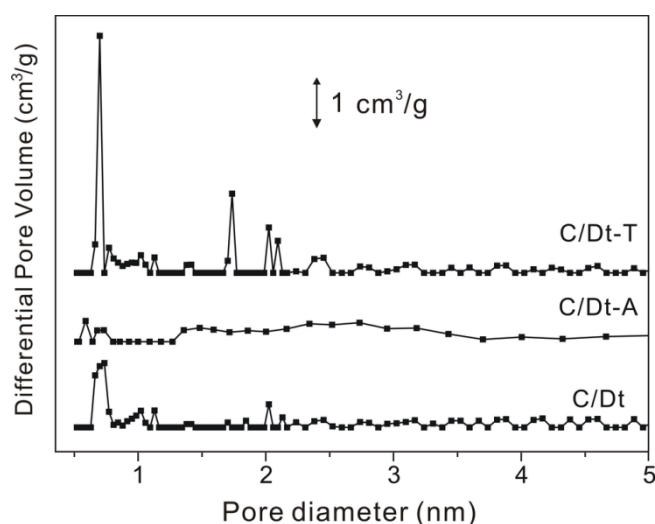

Figure S5. Pore size distributions of carbon products by DFT method.

146   **Mercury Intrusion Porosimetry characterization**: Macropore volumes and

147   size distributions were determined by the mercury intrusion method using a

148   Micromeritics Autopore IV 9500 porosimeter. Products were subjected to a pressure

149   cycle starting at approximately 0.5 psia, increasing to 60000 psia in predefined steps

150   to give the information of macropore volumes/sizes.

151   **Thermogravimetric analysis characterization**: Thermogravimetric (TG)

152   analysis was performed on a Netzsch STA 449C instrument. Approximately 50 mg of

153   finely carbon product was heated in an open corundum crucible from 303 to 1273 K

154   at a heating rate of 10 K/min under highly pure air atmosphere (20 cm^3/min).
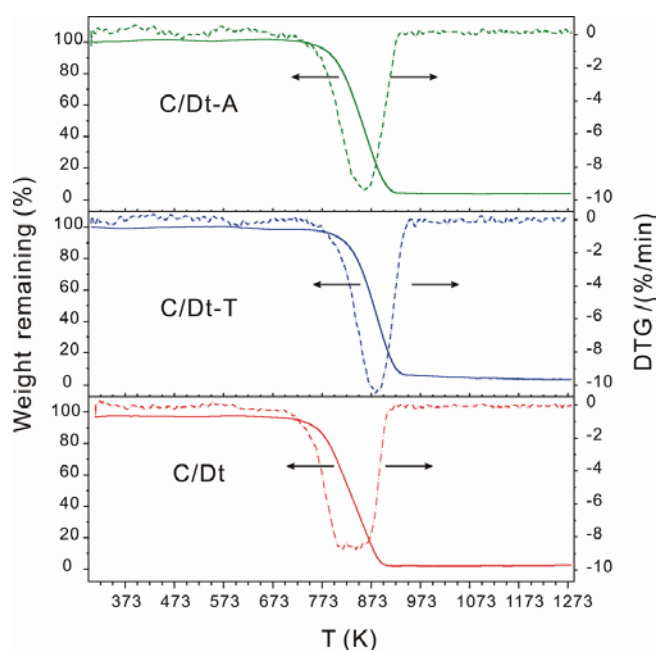
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157   Figure S6. TG and DTG curves of carbon products.

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159   TG analysis results reveal that very few inorganic residues (< 5, wt%) in carbon

160   products existed after the calcination under air atmosphere, which indicates almost all

161 the diatomite templates had been removed by HF washing and the carbon product was

162 nearly homogenous.

163   **Application performance tests**: The capacity of the carbon product for solvent

164 naphtha (predominantly consisting of aromatic hydrocarbons and long-chain alkanes,

165 density: 0.78 cm^3/g) adsorption was determined by comparing the carbon materials'

166 weight before and after the adsorption.[3] The packed carbon product was dipped into

167 solvent naphtha and kept at 293 K for 10 h in an airtight weighing bottle to avoid

168 volatilization of solvent naphtha. The carbon product was then pulled out from

169 solvent naphtha and hung in the air for 3 h. The total increased mass of carbon

170 materials was due to the adsorption of solvent naphtha. The adsorption capacity of

171 solvent naphtha is expressed by the g of solvent naphtha per gram of carbon product.

172 A paralleling test for the purpose of comparison was performed by changing the

173 sorbent to commercial activated carbon which has a surface area of 1013.2 m^2/g. The

174 adsorption capacity of solvent naphtha in commercial activated carbon is 3.2 g/g.

175   Hydrogen sorption isotherm was measured using a Micromeritics ASAP 2020

176 analyzer (Micromeritics Co. Norcross, USA) and 99.999% pure H_2 at 77 K. C/Dt-A

177 was heated at 423K under vacuum condition for 12 h and the free space was measured

178 using helium (99.9999% purity). The hydrogen adsorption amount (Δm, wt%) was

179 expressed by the ratio of the increased mass to the total mass of the sample and the
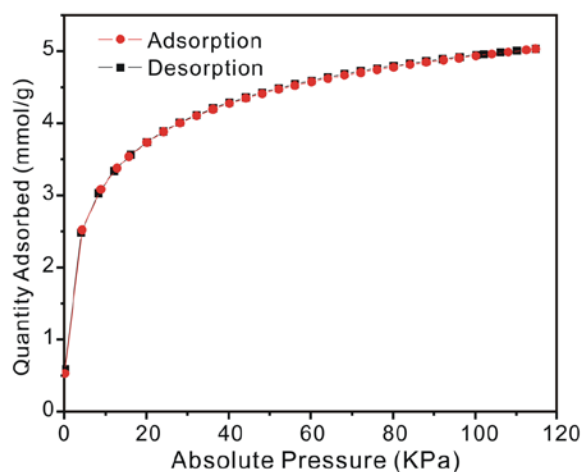
180 adsorbed hydrogen.

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Figure S7. H_2 adsorption isotherms of C/Dt-A at 77 K.

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