

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

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The inherent or enhanced solid acidity of raw or activated diatomite is found to have significant effects on the synthesis of hierarchically porous diatomite-templated carbon with high surface area and special porous structure. The solid acidity makes raw/activated diatomite a catalyst for the generation of porous carbon, and the porous parameters of the carbon products are strongly dependent on the solid acidity of diatomite templates. The morphology of diatomite also dramatically affects the textural structure of porous carbon. Two types of macroporous structures in the carbon product, the partially solid pillars and the ordered hollow tubes, derive from the replication of the central and the edge pores of diatom shell, respectively. The hierarchically porous carbon shows good capability for the adsorption of solvent naphtha and H₂, enabling potential applications in adsorption and gas storage.

Porous carbon-based materials with high specific surface area are attracting significant interest because of their increasing applications in various industrial fields, such as adsorption and purification. The templating method has been widely reported as a well-established route for the preparation of porous carbon.^{1–4} In this route, various organic or inorganic templates with porous structures are used to produce carbon with a microporous, mesoporous, macroporous, or hierarchical porous framework.^{5–10} The basic method to produce the templated carbon involves filling the void space of a template with a polymer precursor which is then polymerized using the acid catalyst followed by carbonization under an inert atmosphere and finally dissolution of the template.^{1,3,8}

Consequently, to find templates which have not only desirable porous structure but also economical viability is of high significance

for the production of porous carbon. Among the inorganic templates previously reported,^{11–20} natural diatomite is one of the few templates for the preparation of macroporous carbon. Diatomite is mainly composed of the mineralized exoskeletons of diatoms, which have various macroporous structures with pore sizes extending from the nanometric to the micrometric domains.^{19,21–23} In the preparation of diatomite-based porous

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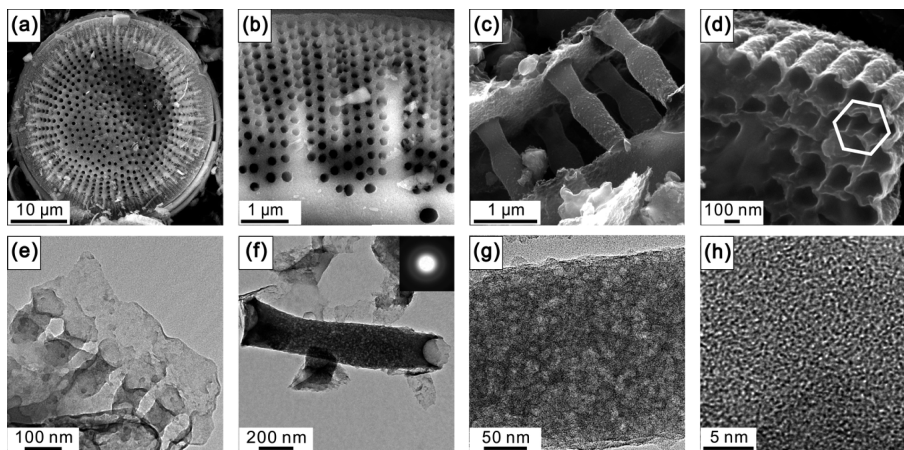


Figure 1. Scanning electron microscopy (SEM) images of (a) diatom shell; (b) edge macropores of the diatom shell; (c) cross-sectional view of carbon pillars; (d) ordered macropores of carbon product. Transmission electron microscopy (TEM) images of (e) ordered macropores of carbon product; (f) carbon pillar (inset: selected area electron diffraction (SAED) pattern); (g) mesopores in the carbon pillar; (h) micropores of the carbon wall.

carbon, sulfuric acid was always used as the catalyst to catalyze the carbon precursor.^{19,22} However, the addition of sulfuric acid is potentially harmful to the environment and also increases the cost of the preparation. In our previous study, we have found that diatomite itself contains solid acid sites: the Brønsted acid sites are sourced from some H-bonded silanols, and the Lewis acid sites result from very small clay mineral particles strongly adhered to the diatom shells.²⁴ Therefore, it should be very interesting to utilize these inherent acid sites of diatomite instead of the additive acid to catalyze the carbon precursor, and to further investigate the key effects of the solid acidity on the final structure of porous carbon.

Here we report the preparation of hierarchical porous carbons by using diatomite and its activated derivatives as both template and catalyst and the effects of inherent solid acidity on the pore structure of carbon products. A diatomite sample from Changbai deposit, Jiling Province was selected for the preparation. The dominant diatom of this sample is genus *Coscinodiscus* Ehrenberg (Centrales), which is disk-shaped and has highly developed porous structure. The diatom shells are relatively uniform in diameter (20–40 μm) and thickness (1.2–1.8 μm) (see the Supporting Information). This feature, better than many commercially available samples where a variety of frustules are present and have already undergone thermal treatment, is expected to promote homogeneous structure in the final porous carbon.

Three types of diatomite materials, Dt, Dt-T, and Dt-A, were used as the templates. Dt-T and Dt-A are the thermally and acid activated products resulting from the original diatomite (Dt), respectively. Porous carbon products, C/Dt, C/Dt-T, and C/Dt-A, corresponding to the three templates, respectively, were obtained via the templating preparation route by using furfuryl alcohol as the carbon source in the absence of any additional catalysts (see the Supporting Information).

Electron microscopy characterization indicates that there exists a highly morphological dependency between all the three diatomite templates and their porous carbon counterparts. As shown in Figure 1a, the SEM image of Dt, there exist macropores that are not so regularly arrayed in the center of the diatom shell. However, the pores at the edge region show a highly ordered hexagonal array, and their diameters (100–250 nm) are much smaller than those (300–800 nm) in the central region (Figure 1b).

Porous structures resembling these two types of pores universally exist in all the final porous carbon products, as revealed by SEM/TEM observation (Figure 1c–h, herein take C/Dt as an example). Figure 1c exhibits a cross-sectional view of a porous carbon particle, which consists of two carbon platforms connected by some carbon pillars. This structure results from the reproduction of the original porous structure in the center of the diatom shell, because the diameter (250–750 nm) of the carbon pillar and the pillar height (1.2–1.6 μm) correspond very well with the size of the central pores and the thickness of the shell, respectively. The macroporous structure derived from the edge pores presents an ordered array, composing of regular hollow carbon tubes interconnected by thin carbon walls (Figure 1d). The tube diameter (80–200 nm) is in good agreement with the original size of the edge pores.

TEM images (Figure 1e) give further clear evidence for the hollow structure of the ordered pores corresponding to the edge pores. However, the carbon pillars derived from the central pores are mostly solid but hollow at both ends (Figure 1f). These pillars were presumed to be completely hollow tubes based on SEM observation in the previous report on the diatom-based porous carbon.²³ Our result herein indicates that TEM is indispensable for an accurate estimation on the inner structure of porous carbon. The partially solid structure should be generated in the process of the polymerization: the central pores of diatom shell are deep enough to confine most of the already filled furfuryl alcohol molecules and lead them to “in situ” polymerize at the middle part of the pillars; however, the furfuryl alcohol molecules filled in both openings of the channels were mostly evaporated under high temperature. In contrast, the ordered edge pores are too shallow to prevent the filled furfuryl alcohol from evaporating, thus resulting in a completely hollow macroporous structure. A related schematic representation is shown in Figure 2.

The carbon wall of the hollow tube and the solid part of the carbon pillar are composed of graphite microcrystals, which lead to faint and consecutive diffraction rings in the corresponding selected area electron diffraction (SAED) pattern (Figure 1f, inset). The stacking of the carbon species results in the formation of the mesopores (Figure 1g). At a higher magnification, a wormhole-like structure²⁵ (Figure 1h) was observed. This structure consists of disorderly interconnected micropores, mainly

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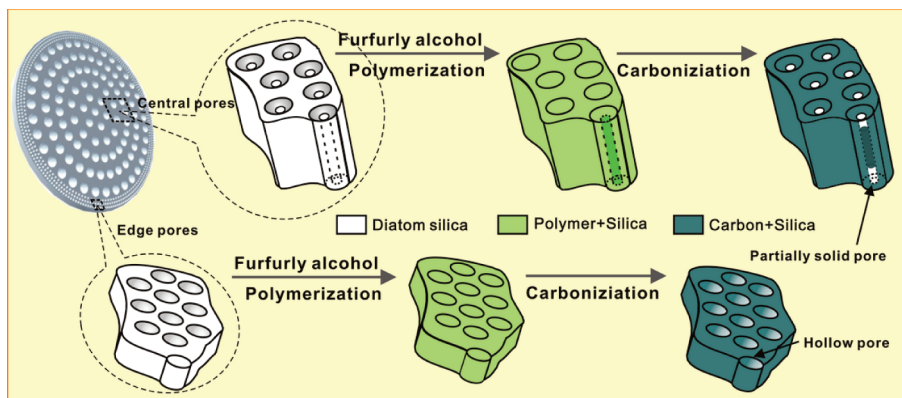


Figure 2. Schematic representation of the possible formation mechanism of the hierarchically porous carbon.

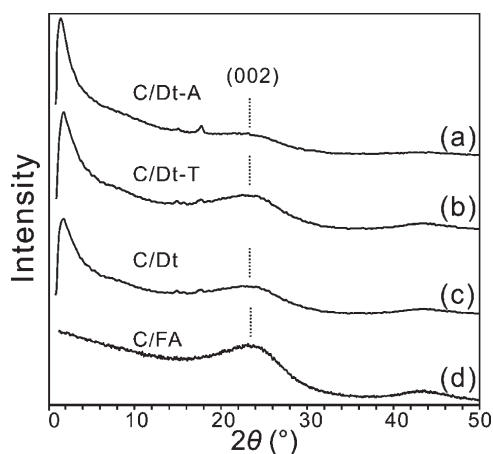


Figure 3. XRD patterns of the carbon products.

generated by the breaking of the carbon film,⁸ which occurred universally during the removal of the diatom template.

All the diatomite-based carbon products exhibit a broad peak at ca. 24° (2θ) in the powder X-ray diffraction (XRD) patterns (Figure 3a–c), attributed to the (002) reflection of the graphite microcrystals.²⁰ The graphite microcrystals are produced from the carbonization of carbon precursor, evidenced by the XRD pattern (Figure 3d) of the carbonized product (C/FA) of pure purpuryl alcohol where one similar reflection is shown. Each of the diatomite-based carbon products also has a sharp XRD peak in the low 2θ angle region (Figure 3a–c). This feature, first reported here, should be attributed to the ordered porous structure of carbon, which is a replica of the original ordered structure of the edge pores. This result gives strong support to the above-mentioned SEM observation on the ordered porous structure of carbon.

All of the obtained carbon materials exhibit specific Brunauer–Emmett–Teller (BET) surface areas: C/Dt, $270 \text{ m}^2/\text{g}$; C/Dt-T, $406 \text{ m}^2/\text{g}$; C/Dt-A, $426 \text{ m}^2/\text{g}$; which are tens of times greater than the original diatomite ($16\text{--}19 \text{ m}^2/\text{g}$) and C/FA ($10 \text{ m}^2/\text{g}$), and the value of C/Dt-A is much higher than those (169^{23} and $312 \text{ m}^2/\text{g}^{19}$) of the diatom/diatomite-templated carbon prepared by using additive acid as the catalyst. The acidity values of Dt, Dt-T, and Dt-A were determined as 0.09, 0.17, and 0.31 mmol/g, respectively. There is a dramatically positive correlation between the acidity of the diatomite templates and the resulting surface area and pore volume of the carbon products (Figure 4). The reason is that more acid sites lead to higher extent of the polymerization of furfuryl alcohol and the generation of stacked graphite microcrystals, which further increases the break points of the carbon

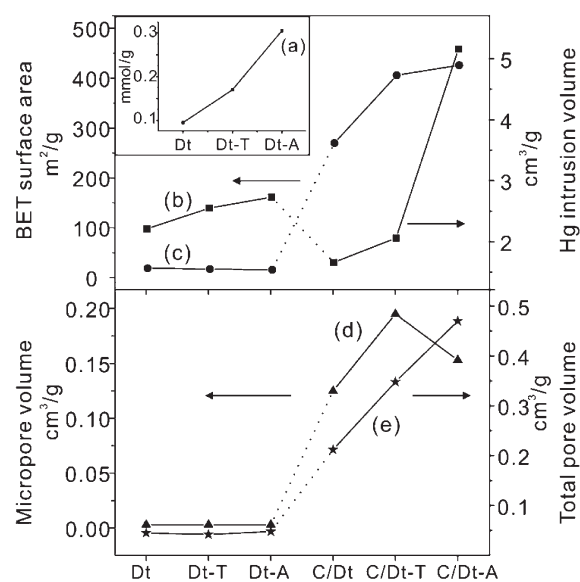


Figure 4. Acidity and porous parameters of the diatomite templates and carbon products: (a) acidity of the templates; (b) mercury intrusion volume; (c) BET surface area; (d) total pore volume; (e) micropore volume.

film and produces more micropores and mesopores. However, the exact catalytic mechanism, such as the roles of the Brønsted and the Lewis acid sites, still needs further investigation.

This diatomite-based hierarchically porous carbon enables use not only in the catalysis field by loading catalytically active centers using already developed techniques, but also in applications of absorption and gas storage. In our preliminary tests, the adsorption amount of solvent naphtha on C/DT-A was shown to be 5.5 g/g, nearly 1.7 times greater than that of a commercial activated carbon with much higher specific surface area ($1013.2 \text{ m}^2/\text{g}$), and the H_2 adsorption capacity was 1.0 wt % at 77 K (see the Supporting Information), which is also higher than the reported microporous carbon with similar BET surface area.²⁶

Herein, we have demonstrated that the inherent or the enhanced solid acidity not only makes raw or activated diatomite the catalyst to prepare the hierarchically porous diatomite-templated carbon, but also has significant effects on the textural structure of the carbon product. The porous framework of the obtained carbon is dramatically dependent on the morphology

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and acidity of the diatomite template. The diatomite-templated carbons have high surface areas and pore volumes, as well as partially ordered macroporosity and disordered mesoporosity/microporosity, enabling potentially versatile applications in catalysis, adsorption, and gas storage.

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Supporting Information Available: Characterization methods, data analysis, Figures S1–S7, and Table S1. This material is available free of charge via the Internet at <http://pubs.acs.org>.