

Surface Modification of Ordered Mesoporous Carbons via 1,3-Dipolar Cycloaddition of Azomethine Ylides

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Ordered mesoporous carbons (OMCs) have recently attracted considerable attention because of their unique features, such as high surface area, narrow pore size distribution, large pore volume, as well as good chemical and thermal stabilities.¹ Such properties make OMCs ideal for many applications in separation, adsorption, catalysis, and energy storage.² OMCs were usually prepared via a nanocasting process (hard-templating route) using ordered mesoporous silicas (OMSs)³ or colloidal silica nanoparticles⁴ as hard templates. Recently, we⁵ and others⁶ have developed an alternative soft-templating route for preparation of OMCs via self-assembly of phenolic resins and block copolymers. So far, OMCs with different structural symmetries^{1,5,6} and various morphologies^{5b,7} have been prepared. In addition to the control of pore structures and morphologies, surface modification of OMCs is also crucial for many applications, such as catalysis and separation.^{1,2,8} Furthermore, surface modification can be utilized to tune the hydrophobicity and hydrophilicity of OMCs, which enables their wide applications in different solvent media.

Preparation from heteroatom-containing carbon precursors represents a direct way to integrate functionalities into OMCs. For example, N-doped, S-doped, F-doped, and pyridine-containing OMCs have been reported; however, the types

and densities of functionalities are usually limited.⁹ As a simple method, oxidation of OMCs and the subsequent reaction of generated carboxylic groups allows grafting of many functional groups on the carbon surface.¹⁰ But the intrinsic drawbacks of this method lie in the deterioration of carbon structures because of the harsh oxidation conditions (e.g., very strong acids).¹⁰ In seeking new routes to modification, we and others recently applied the diazonium chemistry for covalent attachment of ortho-substituted aryl groups [Ar-R, R = Cl, COOCH₃, C(CH₃)₃, (CH₂)₃CH₃, SO₃H] on the surface of OMCs via chemical reduction of aryl diazoniums.¹¹

As an efficient methodology, Prato's reaction,¹² which is based on the 1,3-dipolar cycloaddition of azomethine ylides, has been applied to organic modification of fullerenes,¹³ carbon nanotubes,¹⁴ and carbon nanohorns.¹⁵ Herein we for the first time report the functionalization of OMCs via 1,3-dipolar cycloaddition of azomethine ylides, generated by thermal condensation of an α -amino acid and an aldehyde. The cycloaddition reaction leads to the formation of pyrrolidines attached on the surfaces of OMCs (Scheme 1). The effect of carbon wall characteristic (amorphous or graphitic) of OMCs on the efficiency of functionalization was investigated both experimentally and computationally.

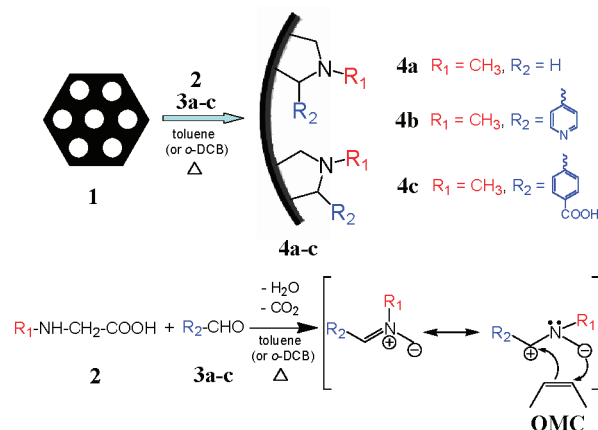
Hexagonal OMC C-ORN-1 (**1**) and highly graphitic mesoporous carbon (**1-G**, the graphitic feature was indicated by the XRD pattern, see Figure S1 in the Supporting Information) were synthesized via self-assembly of block copolymers and phenolic resins under acidic conditions as described in our previous reports.⁵ Surface modification of **1** was carried out by heating a mixture of *N*-methylglycine (**2**, 160 mg, 0.45 mmol) and an aldehyde (**3a–c**, 0.3 mmol) at reflux in a solvent (120 mL) in the presence of C-ORN-1

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Scheme 1. Functionalization of OMC



(**1**, 180 mg) (see details in the Supporting Information). The reaction was allowed to proceed for 18 h, and the modified samples (**4a–c**) were then recovered by filtration; washed thoroughly with toluene, CH_2Cl_2 , and THF; and finally dried in a vacuum oven at 120 °C overnight.

Figure 1 shows the N_2 sorption isotherms and the BJH pore size distribution plots of C-ORNL-1 before and after surface modification. One can see that all modified samples (**4a–c**) exhibit an isotherm shape similar to that of pristine C-ORNL-1 (**1**), indicating the maintenance of highly ordered mesostructure after surface modification (see also a high-resolution SEM image in Figure S2 in the Supporting Information). Because of the relatively low grafting densities (see below), the presence of functional groups may not cause an obvious decrease in pore diameter but likely block the microporosity, and thus lead to a significant decrease in BET surface area (Table 1). A similar observation has been reported on primary amine-functionalized ordered mesoporous carbons.¹⁶

Figure 2 shows the TGA profiles of the unmodified and modified samples under a N_2 atmosphere. The pristine C-ORNL-1 exhibited a slight weight loss, which could be attributed to the chemically/physically adsorbed species, such as H_2O , CO_2 , and the release of some oxygen-containing functional groups, whereas the major weight losses for all

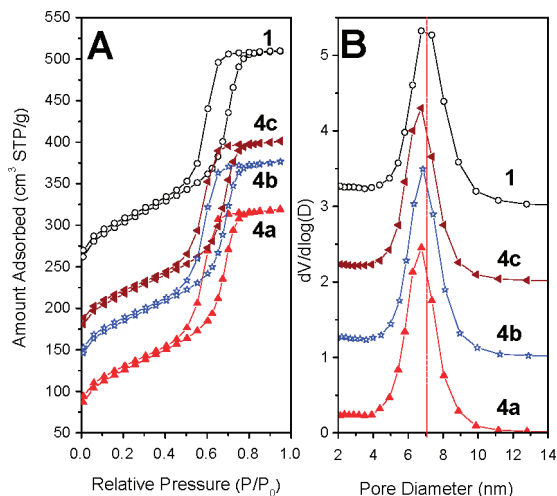


Figure 1. (A) N_2 sorption isotherms and (B) pore size distribution plots of C-ORNL-1 before (**1**) and after functionalization (**4a–c**). For clarity, the isotherms of **4b**, **4c**, and **1** are offset vertically by 50, 100, and 150 cm^3/g , respectively.

Table 1. Textural Properties of Carbons^a

material	S_{BET} (m^2/g)	w (nm)	V (cm^3/g)	weight loss (%)	grafting density (mmol/g)
1	712	7.0	0.76	0.8	
4a	420	6.9	0.49	4.9	0.72
4b	446	6.9	0.51	3.7	0.22
4c	392	6.9	0.47	5.9	0.29
1-G	262	9.2	0.46		
4a-G	260	9.2	0.46	~0	~0

^a S_{BET} , BET surface area; w , pore diameter; V , total pore volume; weight loss was determined from the TGA profiles between 200 and 500 °C; grafting density was estimated from the weight loss, from which a weight loss due to the chemically/physically adsorbed species (0.8%) was subtracted.

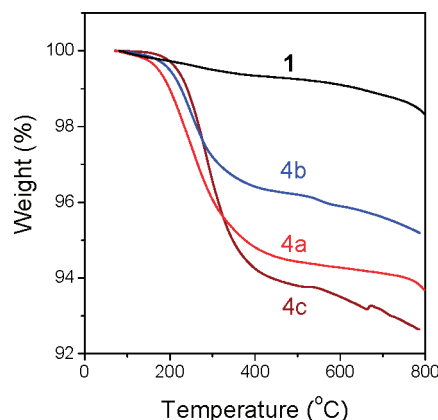


Figure 2. TGA curves of the pristine (**1**) and modified C-ORNL-1 (**4a–c**) under a N_2 atmosphere.

three modified samples took place in the temperature range of 200–500 °C, suggesting that the organic groups were covalently attached on the carbon surface.^{11,15} The weight losses in this range due to the decomposition of pyrrolidines¹⁵ were 4.9% (**4a**), 3.7% (**4b**), and 5.9% (**4c**), respectively. The grafting densities were estimated to be 0.22–0.72 mmol/g, which are smaller than those of modified mesoporous carbons through diazonium chemistry.¹¹ The presence of functional groups on the modified carbon samples can also be confirmed by X-ray photoelectron spectroscopy (XPS) measurement.¹⁶ The XPS spectra (see Figure S3 in the Supporting Information) show the N 1s peak for all of the modified samples (**4a–c**) but no N 1s signal was observed for the pristine C-ORNL-1 (**1**). It is worth noting that increasing the concentration of reactants (**2** and **3**) or prolonging the reaction did not increase grafting density significantly, as indicated by no obvious change in the results of N_2 sorption and TGA analyses. In addition, the solvent-thermal stability of the modified samples was investigated by refluxing the samples in organic solvents. For example, sample **4a** was found solvent-thermally stable in some organic solvents, such as THF and CH_2Cl_2 , as suggested by the results of N_2 sorption analysis (see Figure S4 in the Supporting Information).

Interestingly, attempts to modification of graphitic mesoporous carbon (**1-G**) using the same procedure did not result in an obvious change in N_2 sorption isotherm and weight loss in TGA profile (see Figure 3 and Table 1), suggesting the grafting on graphitic mesoporous carbon was unsuccessful.

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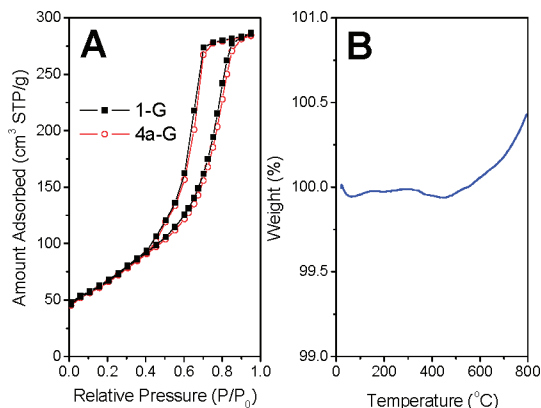


Figure 3. N₂ sorption isotherms (A) of unmodified (**1-G**) and modified (**4a-G**) graphitic mesoporous carbons and TGA curve (B) of **4a-G**. The observation of slight increase on the TGA curve could be due to the partial oxidation of graphitic carbon by O₂ impurity in a N₂ atmosphere.

Table 2. Energetics of Ylide Addition to Carbons^a

carbon	addition energy (kcal/mol)	structure
armchair edge	−28.4	Figure 4a
zigzag edge	−27.2	Figure 4b
graphene	16.8	Figure 4c
fullerene	−27.9	Figure 4d

^a Addition energy is defined as the energetic change for the reaction ylide + carbon → ylide-carbon.

ful. The sharp difference between **1** and **1-G** with respect to the addition of azomethine ylides must be related to their differences in geometric and electronic structures. The porous carbons obtained by pyrolyzing block copolymer-phenolic resin nanocomposite at 850 °C are considered to consist of discrete fragments of curved carbon sheets with plenty of edges, whereas the highly graphitic mesoporous carbon is typically composed of large graphene sheets/domains parallel to the pore surface.^{17,18}

To confirm the different reactivities of **1** and **1-G** regarding ylide cycloaddition, we employed density functional theory (DFT) to compute the energetic change for ylide cycloaddition.¹⁹ We used edge models to represent the active sites on amorphous mesoporous carbons such as **1** and a graphene sheet to represent graphitized mesoporous carbons such as **1-G**.²⁰ Table 2 displays the energetics and one can clearly see that the cycloaddition reaction is quite favorable for both zigzag and armchair edges in the same degree as for fullerene, whereas the reaction is unfavorable for graphene. These computational results agree very well with our experimental observation that **1** can be functionalized by ylide cycloaddition, whereas graphitized carbon (**1-G**) cannot.

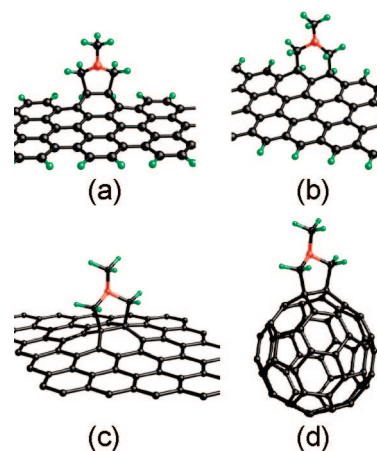


Figure 4. DFT-optimized structures for ylide-functionalized carbons: (a) armchair edge model, (b) zigzag edge model, (c) graphene, and (d) fullerene. C, black; H, green; N, red.

Although the grafting density of functional groups on OMCs is limited via the Prato's reaction, one of the unique advantages of such method is to integrate two functional groups (R1 and R2, see Scheme 1) simultaneously. In addition, a wide variety of α -amino acids and aldehydes are commercially available or readily prepared from commercial sources.^{12–15} Therefore, this method holds great promise in designing the advanced functional materials based on OMCs by integration of the functionalities of pyrrolidines and the unique structural features of OMCs. For example, this method would allow one to prepare OMC-based cooperative catalysts,²¹ in which two functional groups are intrinsically formed as a pair.

In summary, we successfully functionalized surfaces of ordered mesoporous carbons via 1,3-dipolar cycloaddition of azomethine ylides, yielding grafting densities of ca. 0.22–0.72 mmol/g. Although pore volume and surface area decreased after ylide addition, mesopore structures were well-maintained. Graphitic carbon showed little or no reactivity for ylide addition, which was confirmed by density functional calculations.

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Supporting Information Available: Experimental and computational details. XRD pattern, SEM image, N 1s XPS spectra, and coordinates for structures in Figure 4 (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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