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Activated carbon efficient atomistic model construction that depicts experimentally-determined characteristics

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ABSTRACT

Construction of large-scale atomistic representations of activated carbon aids exploration of structure–property relationships. The construction approaches for existing structures are limited in the control over the distribution of structural features. Here, an initial atomistic representation of a lignite-based activated carbon was constructed using a construction strategy that allows control over the distributions of stacking, degree of orientation, and pore size. Fringe3D was used to produce a collection of 42 molecules within 25 stacks comprised of graphene sheets with control over their length, orientation, and stack height. Vol3D populated the specified 100 × 100 × 100 Å cuboid volume with an assumed Gaussian distribution of stack width, without changing orientation and thus retaining regional organization. Eight of these were combined to create a large-scale structure. The pore size distribution was captured due to smaller microporosity caused by packing inefficiencies of the stacks and by inclusion of additional desired porosity. To demonstrate the control over the extent of curvature, three 200 × 200 × 200 Å structures overall were constructed with varying extent of curvature. The construction protocols were efficient producing large-scale structures (~330,000 atoms) constructed far more rapidly than traditional strategies using a personal computer.

1. Introduction

Activated carbon is extensively utilized in water and gas treatment due to its adsorption ability and low-cost. Determining the chemical and physical structure helps facilitate optimization in matching desired properties with application. These data also allow construction of large-scale atomistic representations that can be helpful in exploring structure–property relationships and adsorption phenomena. High resolution transmission electron microscopy (HRTEM)

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[1–6] revealed significant structural information, showing that activated carbons were composed of randomly arranged Basic Structural Units (BSUs), which formed from stacks determined as groups of parallel planar graphene sheets ranging from one to four layers depending on the precursor. Several authors have produced molecular representations [7–21], however due to limited data quantifying the distribution of structural features and limitations in construction techniques, the majority of these models were of small-scales (~100's to 5000's of atoms) while the construction protocols are either very simplistic or require high computational expense. Although these representations are helpful, an easier, more accurate, and less expensive approach will allow more frequent and improved explorations.

Computer power has evolved rapidly, making it possible to quantitatively construct activated carbon models and perform molecular simulations of sorption. This provides insight regarding structure–property relationships [15,18,22–25]. The proposed models spanned the simplistic slit-like structures [11–13] to comprehensive representations that host spatial and chemical complexity [14–17]. Among the latter, the virtual porous carbon models have been used to study adsorption [18–20,23–25]. However, there has been a challenge in relating these structures to real systems, as the construction process has often involved simply fitting a model to the average Brunauer–Emmett–Teller surface area, and/or total pore volume. Often there is reliance on matching the pair distribution function using computationally intense approaches. These approaches lack an ability to control the distribution of structural features such as regional variations in the extent of ordering.

Pore size distributions have been captured via geometric methods [21,23,24,26,27] to mimic their adsorption properties. For example, Kowalczyk et al. [21] compared experimental versus atomistic structures of carbon molecular sieve films synthesized from liquid cellulose. They discerned that "theoretical and experimental N_2 adsorption isotherms at 77 K was excellent over 4 orders of magnitude in relative pressure", i.e., from 10^{-4} p/p_0, which corresponded to "about 5 mmol/g adsorbed N_2". These comparisons were conducted with a carbon molecular sieve for which they determined that N_2 adsorption was primarily within a very narrow slit-shaped pore width of 5.5 Å [21,28]; while the modeled pore width distribution ranged from 0 to 6 Å.

An alternative structure generation approach has utilized Fringe3D software that has employed image analysis from high-resolution transmission electron microscope (HRTEM) lattice fringe micrographs, to directly recreate slice models of aromatic moieties in coal [29–31]. Specifically, the image analysis have provided information of the Cartesian location of each fringe and the distributions of length, orientation, interlayer spacing, and stacking number. Fringe3D has enabled duplication of those fringes features simply and accurately, while also rapidly capturing the stacking and orientations as determined by good agreement with pair distribution function and structural anisotropy for coals [30,32]. Mathews et al. [29–37] have successfully demonstrated this construction protocol for coal and coal char atomistic representations capturing a broad range of structural diversity (aromatic, aliphatic, heteroatom, moisture components, porosity, density, etc.); and they have constructed large-scale (>50,000 atoms) and continuum molecular representations (100–2850 Da) in a 3D cross-linked network consistent with experimental data [36]. The resulted models have demonstrated applicability for simulating the behavior of solvent interaction, pyrolysis, and combustion for char [31,37–40].

In that approach, the distribution of polycyclic aromatic hydrocarbons (PAH) molecules was achieved and a molecular weight distribution created by cross-linking and the addition of functional groups via scripting. The final structure being constructed using the amorphous builder in Materials Studio. This approach is reasonable in those cases with limited stacking and orientations but is not appropriate for more ordered crystalline materials such as heat-treated coal where the structural distributions observed by HRTEM showing alignment and organization. Thus a robust and rapid construction approach (Vol3D), where there is control over the full range of structural features such as the stack distribution, orientation domains, and pore size distribution, was adopted [39–41]. Here we have sought to experimentally characterize and model a complex three-dimensional lignite-based activated carbon that exhibits a broader distribution of pore sizes with a more rapid construction approach.

1.1. *Objective and modeling approach*

The objective here is to (a) adapt the team's previously derived coal and coal char modeling technique to activated carbon; (b) to represent activated carbon in a manner that captures the distributions of graphene sheet width, stacking extent, orientation, and pore size from experimentally-derived characteristics; and (c) to provide a new construction strategy to create 3-dimensional atomistic representation for use in simulations exploring lignite-based activated carbon behavior regarding sorption and reaction. The approach may also assist as the starting point for more computationally intense construction strategies that would be more suited to extensive undulating structures.

Here the approach used for coal [29–36] was applied to activated carbon – specifically a thermally tailored lignite-based activated carbon that has been well-characterized [42–46]. To allow large-scale and improved atomistic representations, a perl script (Fringe3D) was utilized to create individual files that contained stacks, while controlling the distributions of graphene sheet width, orientation, and extent of stacking. Vol3D populated the specific cubic (or otherwise defined) volume from a collection of PAH stacks and pores [39]. This was conducted in an iterative manner, so as to match the modeled pore size distribution to the experimental data; thus captured some of the structural diversity for this specific activated carbon.

2. Experimental characterization and model-input methodology

2.1. *Experimental parameters for activated carbon*

Here we devise an atomic-scale model of a well-characterized activated carbon that would appropriately depict the