Supporting Information

Microscopic Insights into Water Adsorption in Carbon Nanopore –

The Role of Acidic and Basic Functional Groups and their Configurations

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2D density distribution and 2D compressibility distribution

For 2D density distribution with respect to *xz* plane (side view), the volume of the pore is divided into bins in the *x*- and *z*-directions, and the 2D-density of the bin located at (*x*, *z*) is calculated as $\rho(z,x)=\frac{\langle \Delta N(z,x) \rangle}{L_y \Delta z \Delta x}$, where $\Delta N(z,x)$ is the number of molecules whose centres of mass are in this bin bounded by [*z*, *z* + Δ*z*] and [*x*, *x* + Δ*x*]; L_y is the length of the pore in the *y*-direction. Likewise, for 2D density distribution with respect to *xy* plane (top view), the volume of the pore is divided into bins in the *x*- and *y*-directions, and the 2D-density of the bin located at (*x*, *y*) is calculated as $\rho(x,y)=\frac{\langle \Delta N(x,y) \rangle}{L_z \Delta x \Delta y}$, where $\Delta N(x,y)$ is the number of molecules whose centres of mass are in this bin bounded by [*y*, *y* + Δ*y*] and [*x*, *x* + Δ*x*]; L_z is the length of the pore in the *z*-direction. Note that L_z is different for the micropore and mesopore sections. The bin dimensions Δ*x*, Δ*y* and Δ*z* are a fraction of the collision diameter of oxygen atom, and in our work we chose $\Delta x = \Delta y = \Delta z = 0.1\ \sigma_O$.

Compressibility is defined as the negative of the relative volume change with respect to pressure at constant temperature. In GCMC, local compressibility can be expressed in terms of the corresponding particle number fluctuation F_k, as

$$\kappa = -\frac{1}{V}\frac{\partial V}{\partial \rho} = \frac{1}{kT\langle \rho_k \rangle}\frac{f\left(N_k, N_k\right)}{\langle N_k \rangle} = \frac{F_k}{kT\langle \rho_k \rangle}$$

where ρk is the density of bin k, and F_k is the local fluctuation of number of molecules.

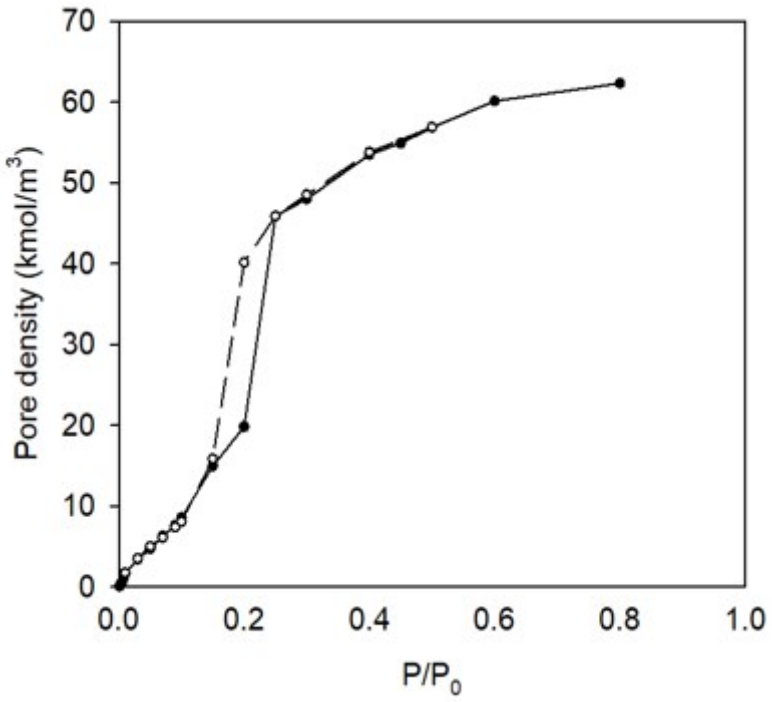

Figure S1. Simulated isotherms for water adsorption at 298 K in a 1.6 nm pore with 14 rows of FGs located at *A*-*G* and *A′*-*G′*. Dashed lines: desorption.

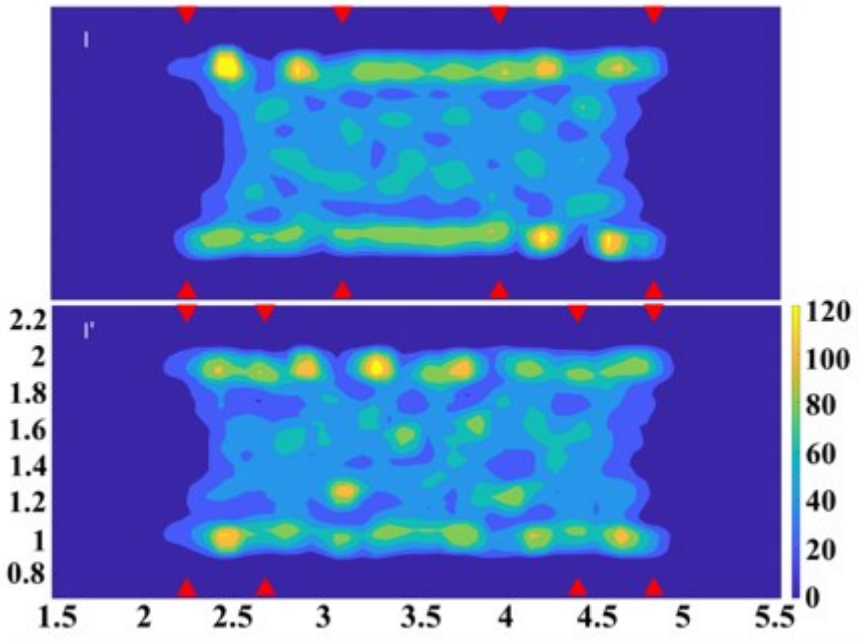

Figure S2. 2D density distributions of s for selected points marked in the water isotherm at 298 K in Figure 5. Red triangles are indicative of the positions of FGs in x-direction.

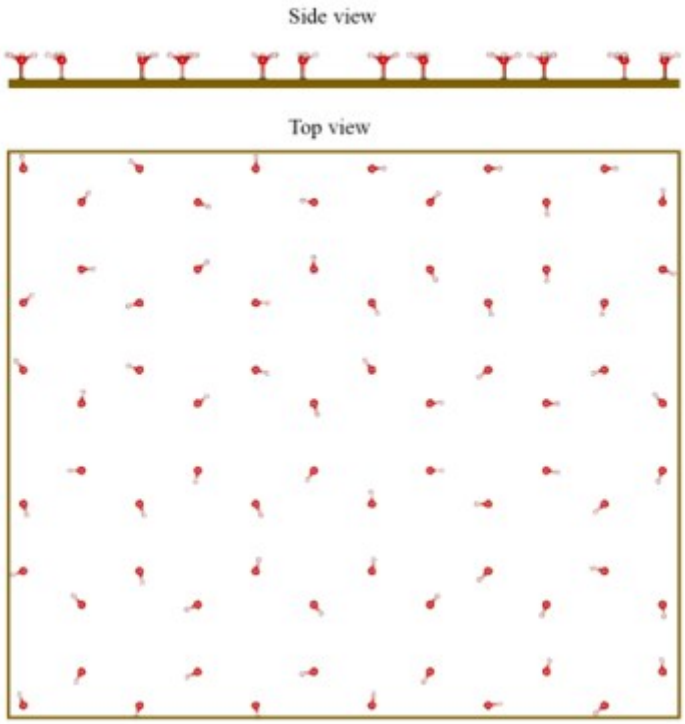

Figure S3. Configurations of FGs on a graphitic surface.

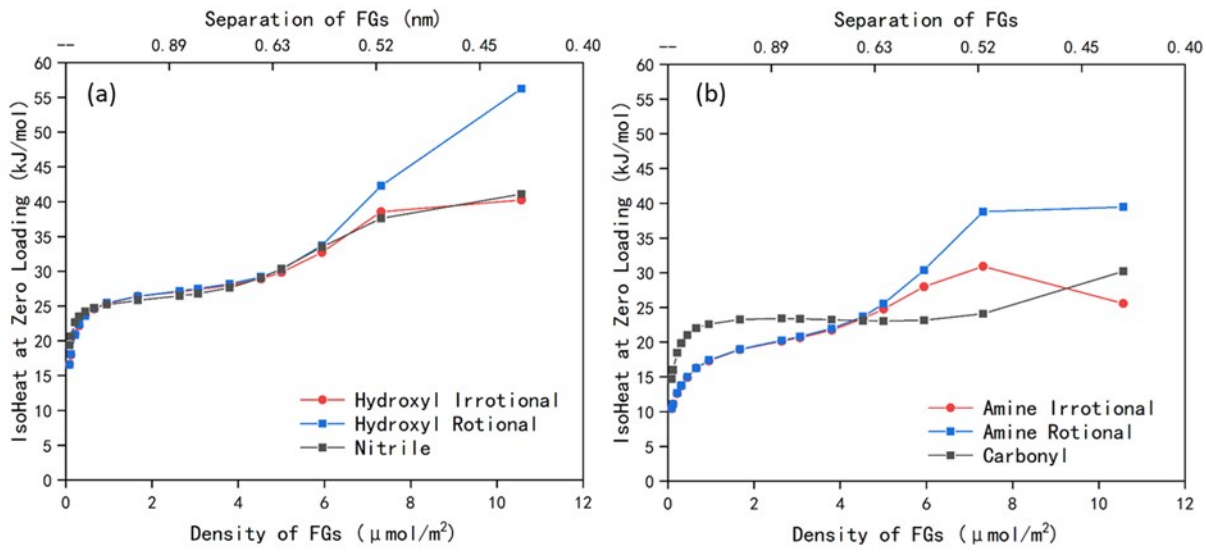

Figure S4. Isosteric heat at zero loading between water and multiple FGs. All FGs were embedded on an infinite graphite surface (modelled with 10-4-3 equation). (a) Hydroxyl and Nitrile groups and (b) amine and carbonyl groups.

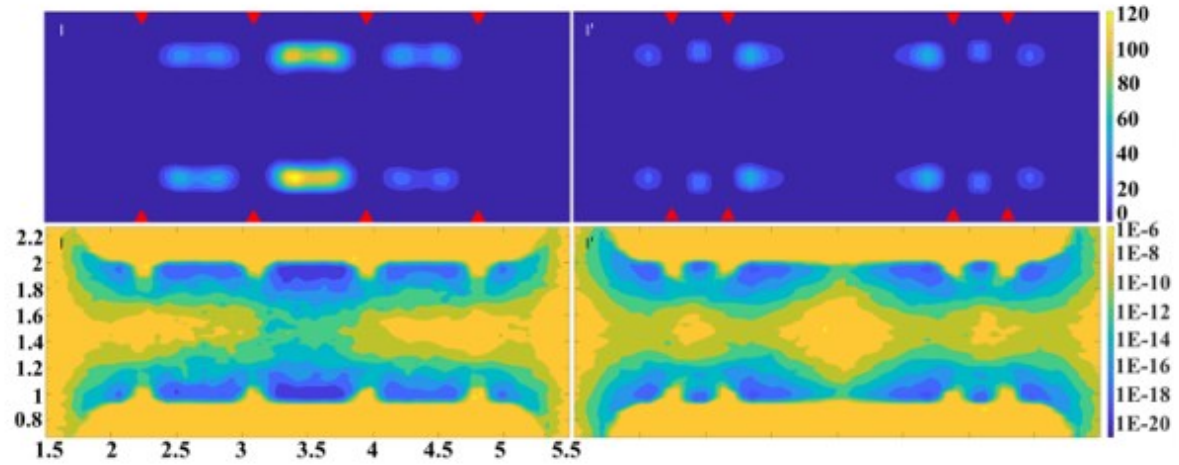

Figure S5. 2D density (top) and compressibility (bottom) distributions for selected points marked in the water isotherm at 298 K in Figure 8b for nitrile group. Red triangles are indicative of the positions of FGs in x-direction.

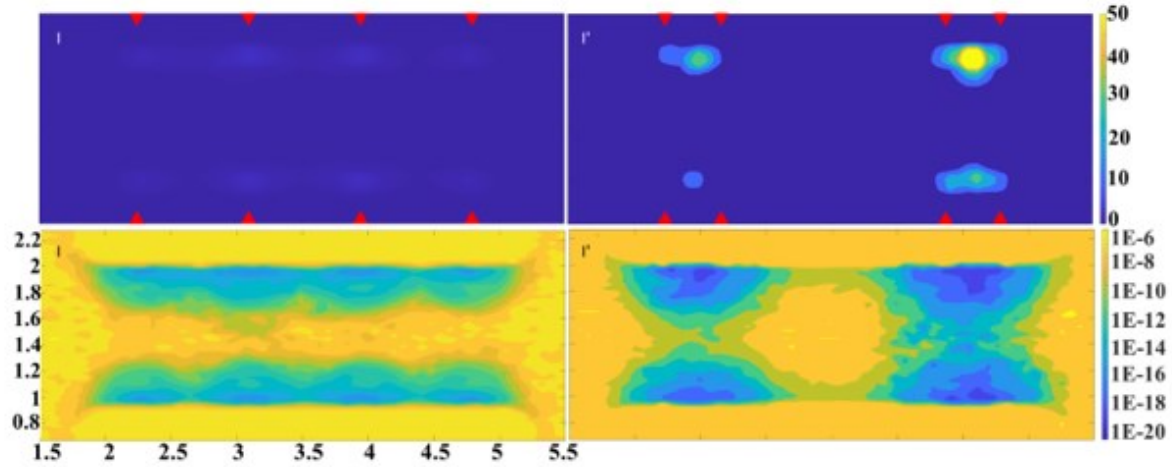

Figure S6. 2D density (top) and compressibility (bottom) distributions for selected points marked in the water isotherm at 298 K in Figure 8c for amine group. Red triangles are indicative of the positions of FGs in x-direction.