Gate-opening effect in ZIF-8: First experimental proof using inelastic neutron scattering

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SUPPORTING INFORMATION

Experimental Section

Synthesis of hybrids ZIF-8@AC

For the synthesis of the hybrid material, 16 mmol of 2-methylimidazole (1.312 g) were dissolved in 700 mmol of methanol (22.4 g, solution 1). Activated carbon in proportions of 10, 20, 30 and 50 wt.% was added to the solution. Percentages are calculated assuming 100% of yield in the ZIF-8 synthesis. In a separate flask, 2 mmol of Zn(NO₃)₂.6H₂O (0.594 g) was dissolved in 700 mmol of methanol (22.4 g, solution 2). Solution 2 was slowly added to solution 1 under stirring at room temperature for 2 hours. Stirring is maintained for the duration of the reaction. The resulting solid was collected and washed with ethanol for several times. The final materials were labeled ZIF-8@AC10, ZIF-8@AC20, ZIF-8@AC30, ZIF-8@AC50. Notice that in this synthesis the yield of ZIF-8 is less than 30 %, and the actual percentage of AC in the hybrids was recalculated by weighing. The final hybrids contain 24, 41, 57 and 72 % of AC, respectively. Pure MOF was prepared under the same experimental conditions.

Density function theory (DFT) calculations

Density function theory (DFT) calculations were performed using CASTEP [1]. The Generalized Gradient Approximation (GGA), as implemented by Perdew-Burke-Ernzerhof (PBE), was used to describe the exchange-correlation interactions. Ultrasoft pseudopotentials were employed to account for the effects of core electrons. The unit cell configurations of ZIF-8 and ZIF-8 + N₂ -published in ref. [2] and determined by XRD- were used as the initial structure for the simulations. The unit cells are large, which poses a computational cost challenge for the application of DFT methods, even with supercomputers. Some of the N₂ sites have partial occupancy (e.g., 0.25) in the ZIF-8 + N₂ configuration. To account for this properly a supercell calculation would be desirable, but too costly in practice. Instead, a single unit cell was used and the partially occupied sites were modified to be either occupied or unoccupied, according to their local environment (there needs to be either a complete N_2 molecule or no molecule) and symmetry (the overall probability of being occupied needs to be proportional to the actual occupancy). The lattice constant was 16.99322 Å for the blank ZIF-8 (276 atoms), and 17.10727 Å for the ZIF-8 dosed with N₂ (an additional 51 N₂ molecules in the unit cell; ca. 0.6 % lattice expansion). The atomic coordinates were relaxed with no imposed symmetry to allow minimization of the potential energy and the interatomic forces. The energy tolerance for the electronic structure calculations was 5x10⁻¹⁰ eV, and the energy tolerance for ionic relaxation was 5x10⁻⁹ eV. The tolerance for the interatomic forces was 0.001 eV/Å. After convergence was reached, the force constants and the dynamical matrix were obtained using the finite displacement method, from which the phonon frequencies and vibrational modes were calculated. The electronic structure calculations and the phonon calculations were

performed at the gamma-point only. The aClimax software was used to convert the DFT-calculated phonon results to the simulated INS spectra [3].

Computational work was conducted on the Oak Ridge Leadership Computing Facility (OLCF) supported by the DOE. The computing resources were made available through the VirtuES (Virtual Experiments in Spectroscopy) project, funded by Laboratory Directed Research and Development program (LDRD project No. 7739), as well as the Center for Accelerating Materials Modeling (CAMM) supported by BES, DOE.

Samples characterization

Nitrogen adsorption isotherm measurements at 77 K were performed in a home-made fully automated manometric equipment designed and constructed by the Advanced Materials Group (LMA), and now commercialized as N₂GSorb-6 (Gas to Materials Technologies; <u>www.g2mtech.com</u>). Before the adsorption experiments, the samples were outgassed at 473 K for 8h under vacuum (10^{-3} Pa). Nitrogen adsorption data were used to determine: (i) the total pore volume V_t at a relative pressure of 0.95,ii) the BET-specific surface area (S_{BET}), and iii) the micropore volume V_{DR}, after application of the Dubinin-Radushkevich equation.

X-ray diffraction (XRD) patterns were recorded with a Bruker D8-Advance diffractometer equipped with a Goebel mirror (non-planar samples) with CuK α radiation (40 KV-40 mA). Measurements were made over a range of 5°<2 θ <65°, in 0.05° step width with a 1°/min scanning rate.

Inelastic neutron scattering experiments

Three samples (ZIF-8, ZIF-8@AC24, and ZIF-8@AC57) were studied using INS at the VISION beamline (BL-16B) of the Spallation Neutron Source (SNS), Oak Ridge National Laboratory (ORNL). About 1g of each sample was loaded in an AI sample holder connected to a gas handling system. The blank samples were first measured at 10 K for 6~8hrs to collect the INS spectra (the background from the instrument and the sample holder is negligible in this case since the hydrogeneous samples scatter neutrons very strongly). They were then warmed up *in situ* to 77 K. After temperature equilibrium was reached, the samples were exposed to 80 kPa of N₂ for 10min. The dosed samples were then cooled back to 10 K to re-measure the INS spectra for about the same time (6~8hrs), and compared with the spectra collected before dosing. This research was made possible by the use of the VISION beamline at ORNL's Spallation Neutron Source, which is supported by the Scientific User Facilities Division, Office of Basic Energy Sciences (BES), U.S. Department of Energy (DOE), under Contract No. DE-AC0500OR22725 with UT Battelle, LLC.

Experimental results



Figure S1. Nitrogen adsorption/desorption isotherm at 77 K for sample ZIF-8.



Figure S2. M1: Methyl Torsion. (Left) a synchronized methyl torsion mode in ZIF-8 giving rise to the sharp M1 peak in Figure 1, and (right) a methyl torsion mode in ZIF-8@ N_2 showing less synchronization.



Figure S3. M2: Methyl bending out-of-plane.



Figure S4. M3: Methyl bending in-plane.



Figure S5. M4: Ring deformation.



Figure S6. M5: Ring deformation.



Figure S7. M6: Out-of-plane C-H bending (symmetric).



Figure S8. M7: Out-of-plane C-H bending (asymmetric).



Figure S9. M8: In-plane C-H bending (symmetric).



Figure S10. M9: In-plane C-H bending (asymmetric).



Figure S11. Snapshot of the gif animation of the gate-opening effect (the gif file is uploaded separately).



Figure S12. Snapshot of the gif animation of the gate-opening effect (the gif file is uploaded separately).



Figure S13. X-ray diffraction pattern of the different hybrid ZIF-8@ACx materials.

The purity and crystallinity of the hybrid MOF@ACx (x= wt.% carbon) materials was evaluated using powder X-ray diffraction (PXRD). As can be observed, all samples exhibit the characteristic pattern of the original ZIF-8, independently of the host-guest ratio, with Bragg peaks at 20: 7.5 (110), 10 (200), 12.6 (211), 14.6 (220), 16.4 (310) and 18 (222). This observation confirms the successful nucleation and growth of ZIF-8 in the confined nanospace of activated carbons.



Figure S14. Nitrogen adsorption/desorption isotherms at 77 K for the different hybrid ZIF-8@AC materials.



Figure S15. SEM images of the hybrid sample ZIF-8@AC57.

Sample	S_{BET} (m ² /g)	V _{DR} (cm ³ /g)	Vt (cm ³ /g)
ZIF-8	1630	0.721	0.724
ZIF-8@AC24	1685	0.722	0.923
ZIF-8@AC41	1671	0.685	1.046
ZIF-8@AC57	1700	0.682	1.194
AC	3425	1.155	2.435

Table 1. Textural properties of the different confined ZIF-8@ACx hybrids.

References

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