Supplementary Information for:

Magnetic Framework Composites for Polycyclic Aromatic Hydrocarbon Sequestration

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Experimental Details

All chemicals were of analytical grade quality and were used without further purification.

Preparation of Nanofibers. The nanofibers were produced by electrospinning a polymer solution containing the metallic precursors. Polyvinylpyrrolidone (PVP) (2.6 g) was first dissolved in 20 mL of ethanol for 90 minutes. The metallic precursors (Alfa Aesar) were subsequently added to the solution. For the $NiFe_2O_4$ nanofibers, 6.060 g of iron (III) anhydrous nitrate and 2.181 g of nickel (II) nitrate hexahydrate were added, in addition to 10 mL of distilled water. The solution was then stirred for 18 h at 50°C. An identical procedure was used to prepare the $CoFe_2O_4$ nanofibers, using identical proportions of the metallic precursor compounds.

To prepare the fibers, the solution was introduced into a 20 mL syringe and pumped (KDScientific model 200) via a tube made of PVC with an inside diameter of 3.175 mm. The tube ended with a hollow stainless steel needle (internal diameter 0.685 mm) to which a high positive voltage was applied relative to the ground collector electrode. As the solution exits the hollow needle, electrostatic forces overcome the surface tension of the liquid and a 'Taylor cone' is created at the needle tip which then generates a thin jet that is attracted to the ground electrode. Due to higher than usual conductivity of the solutions containing metallic ions, instabilities in the formation of the 'Taylor cone' and a tendency of the fibers to not form a dense mat, a higher than usual current of nearly 1000 nA was drawn from the high voltage power supply. The nanofibers were "actively" collected on a spinning grounded cylinder which spun at 1000 rpm, as measured by a digital tachometer. The distance from the needle tip and the cylinder surface was 12 cm, the voltage applied to the hollow needle was 9.6 kV. These experiments were done at temperatures and relative humidities ranging from 30.1°C to 33.4°C and 41.1% to 47.0% respectively.

The accumulated fibers were carefully removed from the cylinder, dried in ambient air for 1 h, then calcinated on a silicon wafer in atmosphere in a programmable

Carbolite 17/5 furnace. Two 0.5°C/min up-ramps were used for the calcination, with plateaus at 300°C (1 h), 900°C (1 h) followed by a down-ramp to room temperature of the same rate.

Preparation of Composite Frameworks. Pluronic F127, 1,2 benzanthracene, 1,4-benzenedicarboxylic acid (BDC), diethylformamide (DEF), $Zn(NO_3)_2$ were purchased from Aldrich and used without further purification. A mother batch of MOF-5 precursor was first synthesized by dissolving $Zn(NO_3)_2.6H_2O$ (1.98 g, 6.655 mmol) and BDC (0.225 g, 13.544 mmol) in DEF (52.5 mL). The resulting solution was then divided into 3.5 mL aliquots, one for each of the fiber types ($CoFe_2O_4$ FCs and $NiFe_2O_4$ FCs), plus a control sample. The magnetic fibers (0.6 mg) and Pluronic F127 (2g) were added to each of the aliquots, and the mixture was suspended in an ultrasonic bath for 30 min. With this procedure, 4 vials were prepared for the synthesis of $CoFe_2O_4$ FCs and 4 vials were prepared for the synthesis $NiFe_2O_4$ FCs. No fibers were added to the control solution. All the vials were Teflon-sealed and heated at 95°C for 24 h; during this time the crystal formation occurred. The four vials of each nanofiber type FC were washed using fresh DEF, dichloromethane, and toluene (4 times 5 mL) over 48 hours. All vials containing the same type of FCs (e.g. $CoFe_2O_4$) were collected in one 4 mL glass bottle. The two batches of different ferrite nanofiber FCs (one containing $CoFe_2O_4$ FCs and another one containing $NiFe_2O_4$ FCs) were filled with 1.5 mL of THF.

Scanning Electron Microscopy. SEM was performed using a Philips XL30 Field Emission Scanning Electron Microscope (FESEM) equipped with an Energy Dispersive X-ray detector (EDS, Oxford Instruments). The samples were coated with iridium prior to measurement.

X-Ray Diffraction. XRD measurements were performed at the Australian Synchrotron Powder Diffraction Beamline using 15 keV source and a rotating capillary sample mount. Data was collected for 15 minutes.

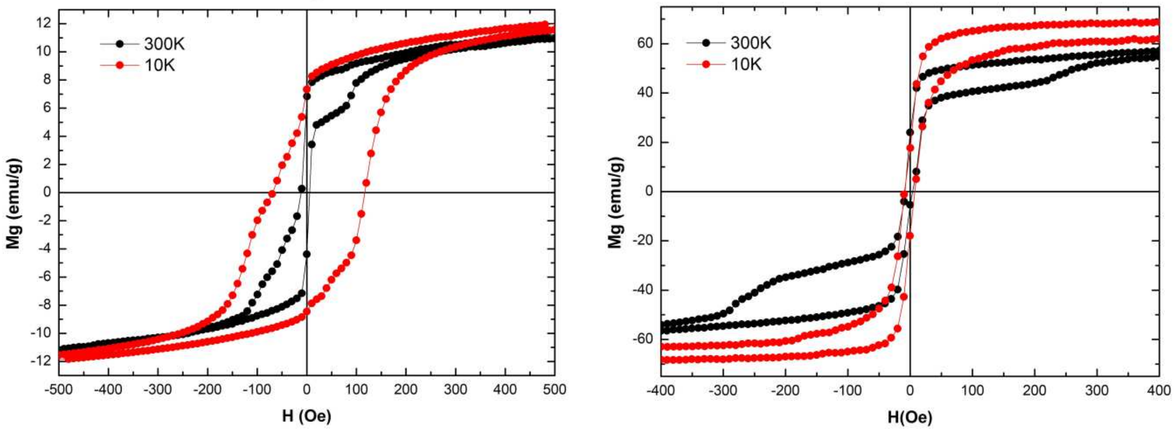
Gas Sorption. Argon sorption isotherms were conducted at 87.3 K for MOF-5 on a 2420 Micromeritics micropore analyser. The samples were degassed at 150 °C for 16 hours prior to measurement.

Spectrofluorometry. The pollutant agent 1,2 benzanthracene, (12 mg, 0.05263 mmol) was dissolved in 3 mL of THF and from this solution, 16 μL was added to each bottle containing 95 mg nanofiber FCs in 1.5 ml THF (final concentration of benzanthracene was 0.185 mmol L^{-1}). The real time adsorption test presented in the manuscript is related to the $CoFe_2O_4$ FCs. The solutions were transferred into a quartz cuvette and placed into the dark sampling chamber of the Varian Spectrofluorometer. The excitation wavelength of the spectrofluorometer was set to 347 nm. A real time acquisition procedure was used to collect the emission spectra in the 380-420 nm range.

Supporting Results

Magnetic Measurement of Nanofibers

The magnetic measurements have been performed using a Physical Properties Measurement System (PPMS) Model 6000, Quantum Design (qdusa.com). The instrument is equipped with a 9 T superconducting magnet. For the measurements of the hysteresis an ACMS probe (magnetometer) was employed. The "DC Extraction method" was used to perform the measurements.



(a) **(b)**

Figure S1. Magnetization curves of (a) $NiFe_2O_4$ and (b) $CoFe_2O_4$ nanofibers.

XRD diffraction pattern from the magnetic FCs

As presented in other work related to framework composites,[1] the analysis on the X-ray diffraction (XRD) pattern and its comparison with the calculated diffraction signal[1] reveal the quality of the MOF-5 crystals.

Hafizovic and al.[2] found and confirmed important qualitative correlations between the XRD pattern generated by MOF-5 samples and their crystalline quality; their study aimed to explain the wide range of MOF-5 specific surface values reported in the literature, which vary from a low of 722 m^2/g[3] to highs of 3400 m^2/g.[4] It was found that the relative intensities of the 6.9° and 9.7° diffraction signals are strongly affected by the presence of lattice defects, adsorbed species (solvent molecules included), and unreacted Zn centers. As those peaks are the direct evidence of the large MOF-5 pore arrangements, the authors outlined a qualitative relationship between the diffraction plots and the structural quality of MOF-5. Chen and co-workers[4] have recently extended this analysis correlating the intensity of the diffraction peak at 13.8°, corresponding to the <400> plane, to the extent of crystal interpenetration.

On this basis, our measured diffraction plots show the features typical of high quality and non interpenetrated MOF-5 crystals, as the relative intensities of the low angle peaks are consistent with the simulated plots and with the analysis presented previously.[2,4]

This evaluation criterion to qualitatively measure the crystal quality is very important, especially if the amount of functional nanomaterial is not easily synthesized in the amount required to permit reliable BET measurements; this is the case of the proposed magnetic nano-fibers as magnetic functional materials.

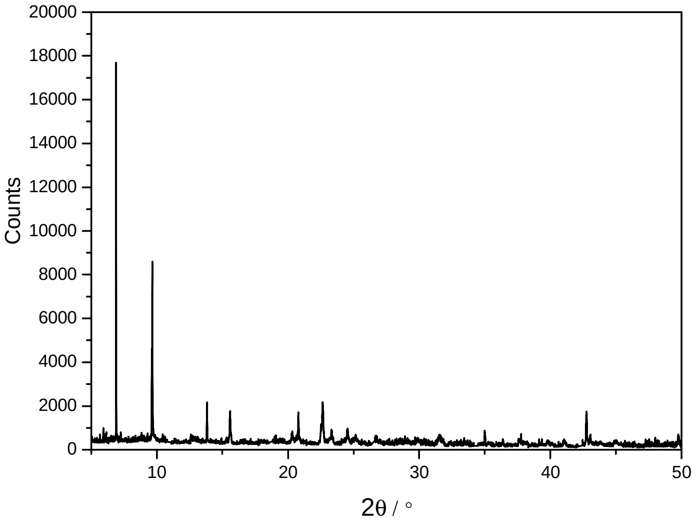
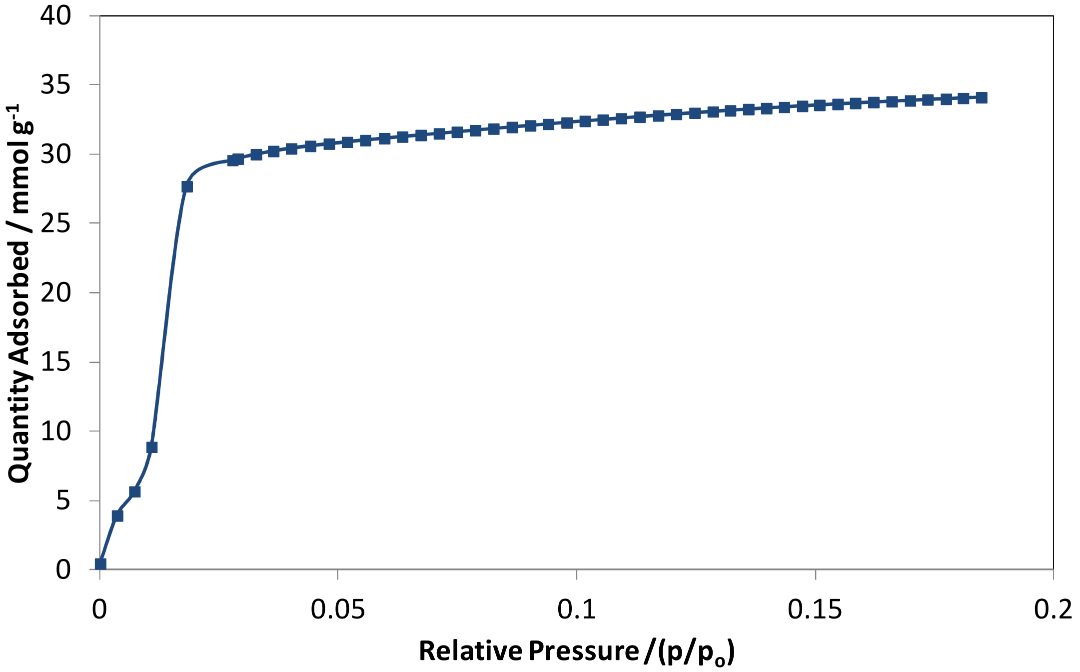
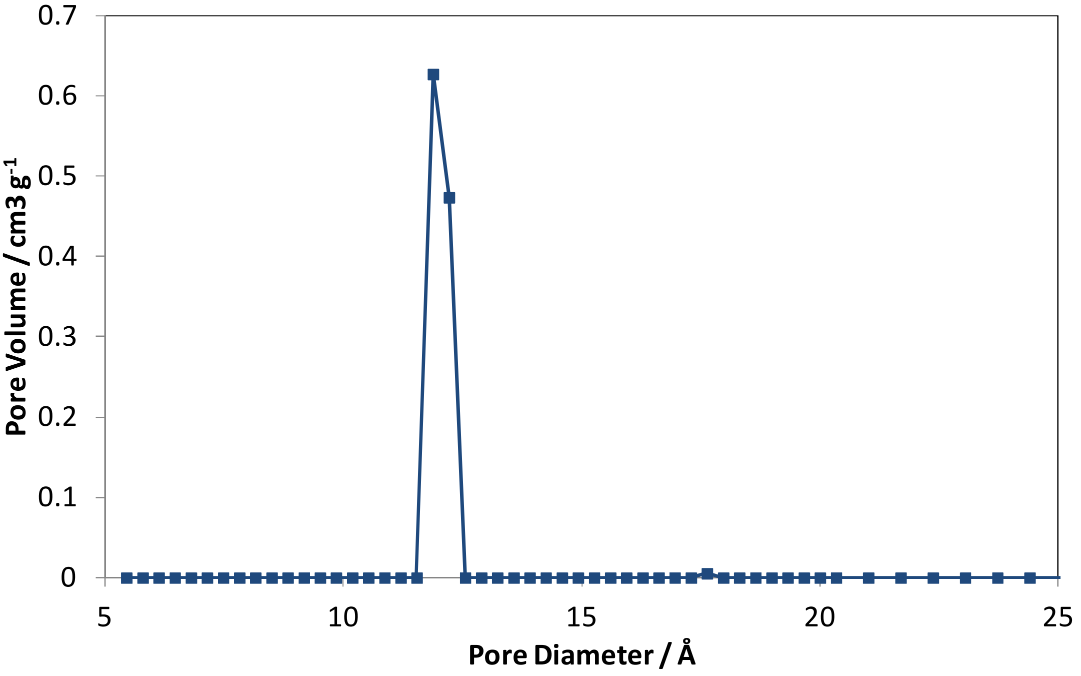


Figure S2. XRD pattern from FC prepared with $CoFe_2O_4$ nanofibers. The pattern shows the quality of the MOF-5 crystals. Due to the low concentration of the $CoFe_2O_4$ nanofibers, these peaks are not detectable in the FC.



(a)



(b)

Figure S3. Argon adsorption isotherm (a) and pore size distribution (b) for MOF-5. The sample featured a surface area of 2380 m^2/g and an average pore diameter of 12 Å using the density functional theory (DFT) with the micromeritics instrument software. Previous studies showed a drop in surface area of 4% for a framework composite[5] which is consistent with the reduction in sequestration that we saw between MOF-5 sample and the FC.

Emission measurements

The excitation wavelength of the Varian spectrofluorometer was set to 347 nm. A real time acquisition procedure was used to collect the emission spectra in the 380-420 nm range. A similar measurement has been performed on a diluted solution of 1,2 benzanthracene. The spectra recorded exhibits the typical triplet band of 1,2 benzanthracene[6,7], and the emission spectrum does not change along with time (Figure S4). The spectra indicates that the 1,2 benzanthracene is stable in solution and under the excitation light conditions used.

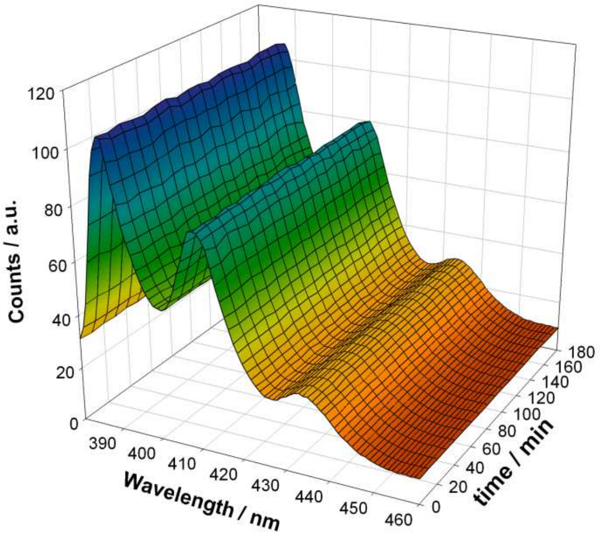


Figure S3. Emission spectra for 1,2 benzanthracene

LOESS regression

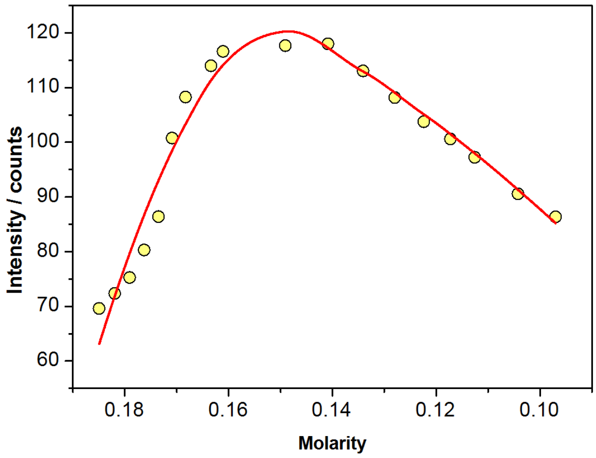


Figure S4. Profile of the 387 peak with time fitted using a LOESS model. The fitting provides a correlation between the detected intensity and the molarity; the correlation has been used to calculate the 1,2 benzanthracene percentage change with time in the system where MOFs are sequestrating the four aromatic ring molecule.

References

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