

Supporting Information

Reinforced silica monoliths functionalised with metal hexacyanoferrates for Cesium decontamination: A combination of one-pot procedure and skeleton calcination

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Experimental part

The synthesis procedure to obtain monoliths with hierarchical structure which can provide large surface areas for reaction or large dispersion of active sites at different length scales of pores and shorten diffusion paths giving rise to a novel family of materials for Cs adsorption and encapsulation for nuclear decontamination in a very single process and with a high efficiency and performance is described below. Different experiments were carried out for obtaining the best materials a method of synthesis with high grade of reproducibility.

Synthesis of M(II) silica monoliths

1.075 mL of TEOS (Sigma Aldrich) were added drop by drop to 1.68 mL of an acidic solution of P123 (20wt%) pH=2 containing 192 mg of M(II) nitrate (Sigma Aldrich, purity 99.99%) where M(II) = Cu, Zn or Co. The mixture was let under stirring around 30 min at room temperature and 600 RPM. Once this time has passed, 15 μ L of NaF [8g/L] was put and immediately after an emulsion was carried out at 3400 RPM speed and at room temperature. Cyclohexane (5.1 mL) slowly incorporated to the previous mixture was used as internal phase. The final product was poured in two different plastic molds completely sealed. Both molds were let at room temperature into a desiccator saturated with cyclohexane vapors during one week aging. The monoliths were dried at 80 °C following a ramp heat treatment (36 h until 80 °C were reached and holding this temperature during 15 h). The monoliths were withdrawn from the plastic molds and thermally treated to free all porosities (meso and macro). This treatment consists of heating from room temperature to 250 °C in 6 h, an isothermal plateau during 30 min followed by a second heating to 500 °C in 2 h and an isothermal plateau during 6 h. The obtained samples were labeled as follows: Cu-monolith, Zn-monolith and Co-monolith.

Synthesis of MHCF silica monoliths

The precipitation of M(II)Fe(II) Prussian blue analogue inside the monolith pores is achieved by impregnation with ferrocyanide acidic solution and potassium nitrate solution. The samples were let at 80 °C into an oven to keep them dry. A solution of $K_4[Fe(CN)_6] \cdot 3H_2O$ 0.1 M was prepared and 5 mL were taken for each monolith and let it into different flasks. The flasks were put on a shaker. 342 μ L of HNO_3 (69.9%) were added to each one. After 2 min shaking the dried monoliths were added to each flask and 5 mL of a 0.1 M solution of KNO_3 were also incorporated. The samples were shook during 4.5 h at 200 RPM speed and at room temperature. The color in samples Cu-monolith and Co-monolith changed from green to brown and from blue to violet, respectively showing the PBA precipitation. The sample Zn-monolith remained white. Several washes with milli-Q water (18.2 M Ω .cm) were carried out to eliminate residual ions and samples were dried up at room temperature. The functionalised

materials were labeled as follows: CuFePBA-monolith, ZnFePBA-monolith and CoFePBA-monolith.

Synthesis of bulk MHCF

Bulk compounds were prepared by mixing equimolar solutions of $K_4[Fe(CN)_6]$ and $M(NO_3)_2$ in the presence of HNO_3 . This procedure was established to be representative of the impregnation procedure described in previous part.

Figure S1 shows that XRD data for bulk CoHCF is identical to monolith-CoHCF. The structure $K_2Co[Fe^{II}(CN)_6]$ is favoured. This is in agreement with FT-IR showed in Figure S3. Bulk CuHCF exhibits a mix of two crystalline structures, a cubic $KCu[Fe^{III}(CN)_6]$ and a tetragonal $K_2Cu[Fe^{II}(CN)_6]$. As well as for CoHCF this in agreement with particles microstructure found in monolith-CuHCF where a mix of $-Fe^{III}-CN-$ and of $-Fe^{II}-CN-$ is shown in Figure S3.

Finally bulk ZnHCF compound exhibits rhombohedral structure with $K_2Zn_3[Fe^{II}(CN)_6]_2$ stoichiometry. A mix with the bulk compound free of potassium ($Zn_3[Fe^{III}(CN)_6]_2$, pdf 00-025-1022, monoclinic) can explain the inversion of peak intensity between lattice reflection at 16.4° and 21.8° . While $K_2Zn_3[Fe^{II}(CN)_6]_2$ is present in both monolith and bulk compounds, it is noticeable that the oxidised form $Zn_3[Fe^{III}(CN)_6]_2$ free of potassium shifts from a monoclinic form in the case of bulk ZnHCF to cubic structure in the case of monolith-ZnHCF.

Cesium sorption experiments

From water solutions

10 mg of a selected solid (Cu-monolith, CuHCF-monolith, Zn-monolith, ZnHCF-monolith, Co-monolith, CoHCF-monolith, were added to 20 mL of $CsNO_3$ aqueous solution made with milli-Q water (18.2 M Ω .cm) at a defined concentration, contained in centrifuge tubes. The range concentration used was from 0.1 mM to 8mM. The mixture was vigorously shaken during 48 h. After that, the solution was filtrated trough a 0.2 μ m cellulose acetate membrane. An aliquot was taken to perform ionic chromatography and analyze the remaining Cesium concentration. For concentrations higher than 0.1 mM a dilution was needed before the analysis. The solid was washed with milli-Q water (18.2 M Ω .cm) and dried at room temperature.

From water solutions in presence of sodium

10 mg of a selected solid were incorporated into a Na and Cs nitrate aqueous solution at a defined concentration (being 10 times higher the Na concentration than Cs concentration), contained in centrifuge tubes. The range used was from 0.1 mM to 2 mM for Cs and from 1 mM to 20 mM for Na. All together were vigorously shaken during 48 h. After that, the solution of each tube was filtrated trough a 0.2 μ m cellulose acetate membrane. A dilution of the solution was made, if necessary, before carry out the analisis by ion chromatography. An aliquot was taken to determine the remaining Na and Cs concentrations. The solids were washed with milli-Q water (18.2 M Ω .cm) and dried at room temperature.

Materials characterization

Small-Angle X-Ray Scattering (SAXS)

SAXS experiments were conducted using a Guinier-Mering setup with a 2D image plate detector. The X-ray source was a molybdenum anode, which delivered a high-energy monochromatic beam ($\lambda = 0.71 \text{ \AA}$, $E = 17.4 \text{ keV}$), providing structural information over scattering vectors q ranging from 0.01 to 1.5 \AA^{-1} . Helium flowed between the sample and the image plate to prevent air adsorption. The sample acquisition time was 900s. Data corrections and radial averaging were performed by standard procedures. The image azimuthal average was determined by FIT2D software from ESRF (France).

X-Ray Diffraction (XRD)

Monoliths X-ray diffraction diagrams were obtained using a Bruker D8 Advance diffractometer in Bragg–Brentano geometry with Ni-filtered and Cu-K α radiation, between $2\theta = 5^\circ$ and 120° , step size 0.01° and one second per step.

Fourier-Transform Infra-Red Spectroscopy (FTIR)

Infra-red spectra were performed with the FT-IR Spectrum 100 from PerkinElmer. Spectra are recorded in the range 400–4000 cm^{-1} with a scanning resolution of 4 cm^{-1} , in ATR mode. The IR spectra were corrected for the background line using the Spectrum PerkinElmer software.

Nitrogen Adsorption-Desorption

Nitrogen adsorption/desorption analysis (77 K) was carried out with a Micromeritics ASAP-2020 instrument. Before each measurement, samples were outgassed at 80°C for 48h, reaching a pressure below 1 mmHg. The gas used for analysis was 99.9% pure nitrogen. The specific surface and pore volume were calculated by using the classic BET (Brunauer, Emmett, Teller) method based on a multilayer adsorption model¹.

Scanning Electron Microscopy

Scanning Electron Microscopy measurements were performed with a Philips Quanta 200 operating at 15 kV equipped with a Bruker detector. System software for EDX analysis was developed by Bruker.

Transmission Electronic Microscopy

Transmission Electronic Microscopy measurements were led in University of Montpellier (France). The device used was a Hitachi H7100 transmission electron microscope equipped with an AMT digital camera and with a working acceleration tension set at 100kV.

X-Ray fluorescence

The MHCF content in the monoliths was determined with a SPECTRO XEPOS EDXRF spectrometer. For the measurement, 500mg of crashed monolith were introduced into the standard disposable microcell for solid samples. Spectra were recorded in helium atmosphere and analyzed by X-LabPro software.

¹ S. Brunauer, P. H. Emmett and E. Teller, Journal of the American Chemical Society, 1938, 60, 309-319.

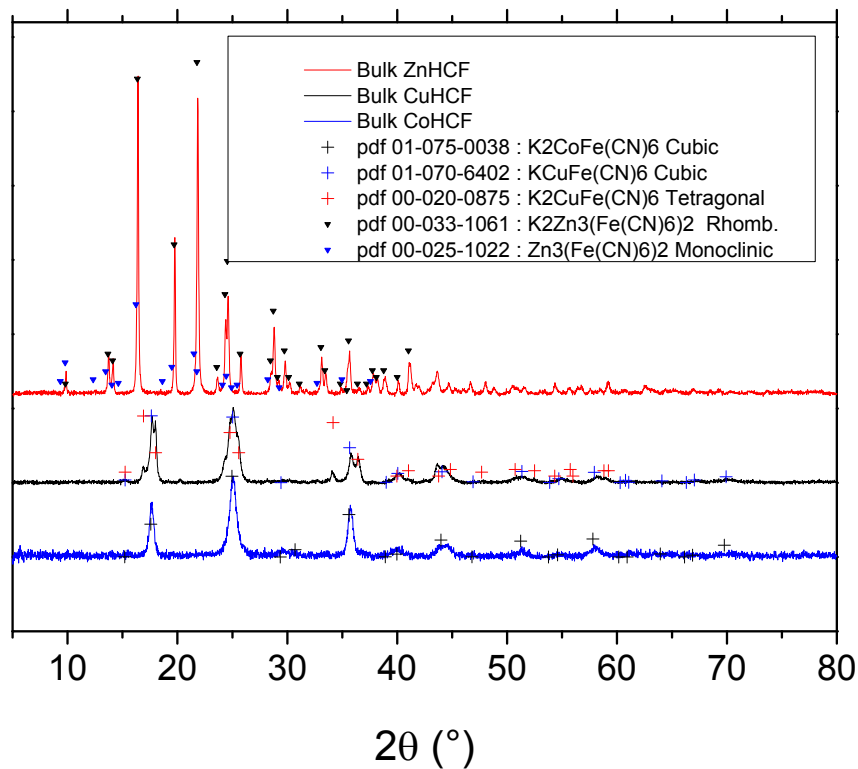


Figure S1: XRD data for all bulks MHCF studied.

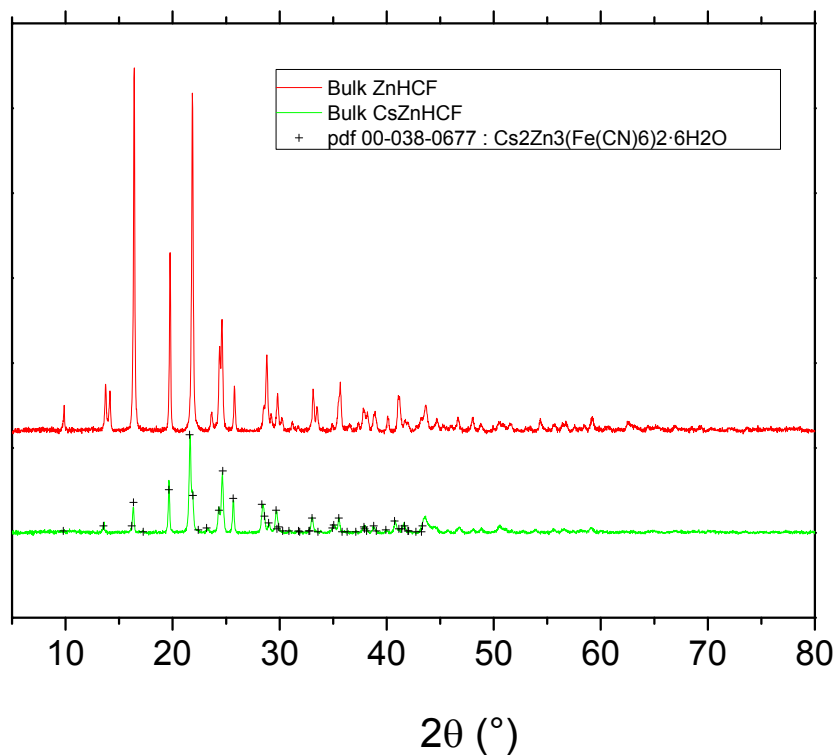


Figure S2: XRD data for bulks ZnHCF before and after Cs sorption.

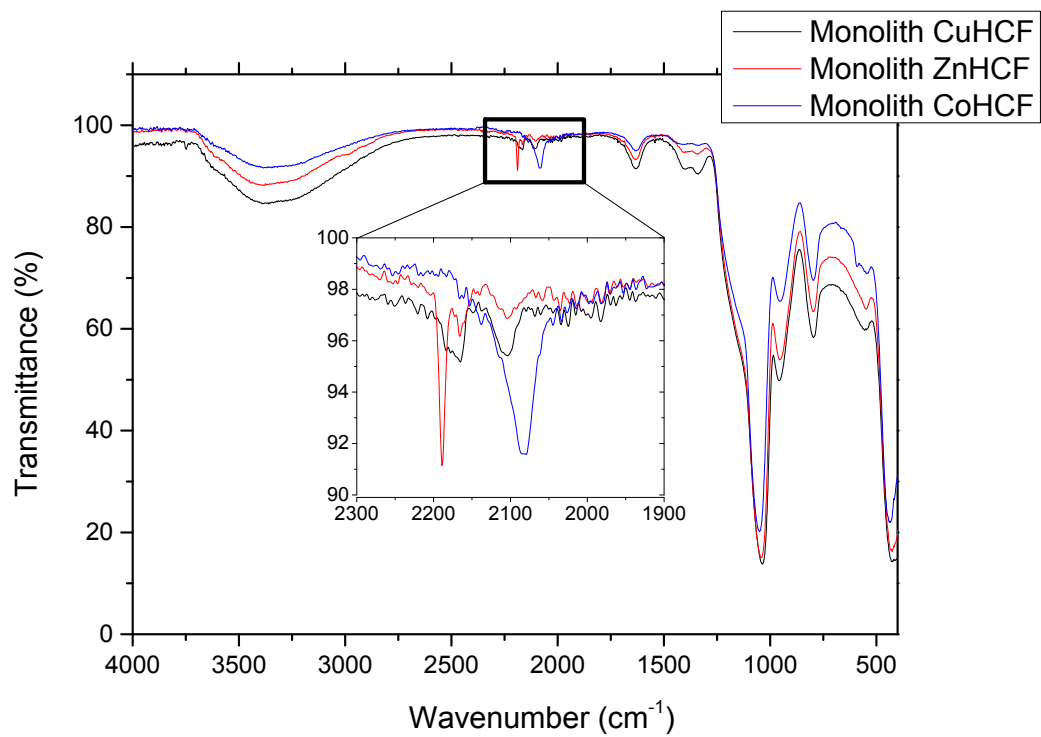


Figure S3: FT-IR data for silica monoliths functionalised with MHCF.