Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

SUPPORTING INFORMATION

Procedure for CuHCF NPs preparation:

The preparation of the colloidal suspensions consisted in a very quick addition of a solution of $Cu(NO_3)_2$ (Sigma Aldrich) to a solution of $K_4Fe(CN)_6$ (Sigma Aldrich). Then, suspensions were centrifuged at 4000 rpm and the solid was washed with deionized water. These two last operations were repeated until stable suspensions were obtained even under centrifugation. The slight amount of non-stable particles was finally removed from the solution. This experimental procedure provides dark red coloured suspensions stable for months. Moreover, the concentrations of each salt were fixed with a slight excess of $K_4Fe(CN)_6$, at 0.0503M and 0.0390M to obtain 9.0 g/l suspensions of $K_{1.77}Cu_{1.16}Fe(CN)_6$ and respectively at 0.151 mol/L and 0.117 mol/L to reach 32.2 g/l of $K_{2.05}Cu_{1.08}Fe(CN)_6$. The stoichiometry of these compounds was assessed by measuring the concentration of each element in the colloidal suspension with an inductively coupled plasma atomic emission spectrometry (ICP-AES). It is noteworthy that increasing salts concentrations allows better insertion of potassium in the crystalline structure of copper HCF.

Procedure for functionalized silica monolith preparation :

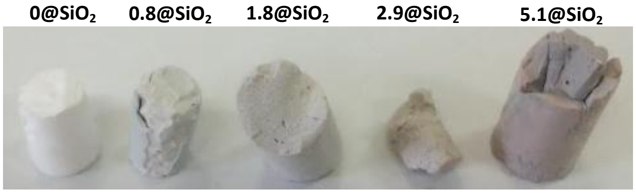
First, silica precursor, basically tetraethoxysilane (TEOS, Sigma Aldrich) was added dropwise to a 20%wt P123 acidic aqueous solution (pH=2, with HCl). This solution was let under stirring during 30 minutes to perform hydrolysis of the silica precursor. Then, this clear solution was carefully mixed with a given volume of copper HCF suspension. The presence of surfactant in the aqueous solution is absolutely necessary to stabilise the emulsion. Afterwards, 10µL of 8g/L NaF (Sigma Aldrich) solution was added to intiate polycondensation of silica precursor just before the emulsification step. And, finally the emulsification of dodecane is achieved thanks to an Ultra Turrax T25 device. The volume ratio of each reactant, $V_{CuHCF\_Coll.Susp.} + V_{P123\_20\%wt\_pH2} / V_{TEOS} / V_{NaF\_8g/l} / V_{dodecane}$ was respectively fixed as follows, 1.94 / 1 / 9,3.10^{-3} / 4,75.
Then, the obtained emulsion was let for aging at 40°C during a week. After this waiting time, the monoliths are washed with THF using a soxhlet device. This treatment is performed in order to remove dodecane. The oil droplets are therefore emptied and the macroporosity is released. And, finally, the monoliths are let for drying at room temperature for a week.

TEM measurements :

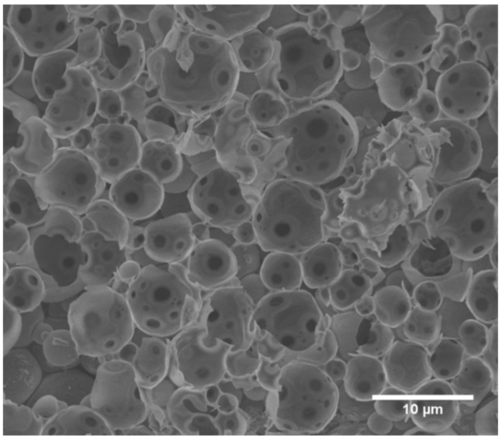
Ultramicrotomy technique was used to prepare samples as 20nm thin slices so that TEM observations of single spheres were possible. For example, Fig. 2 shows silica sphere section of 5.10@SiO_2 monolith.

Salts composition of the solution containing ^{137}Cs

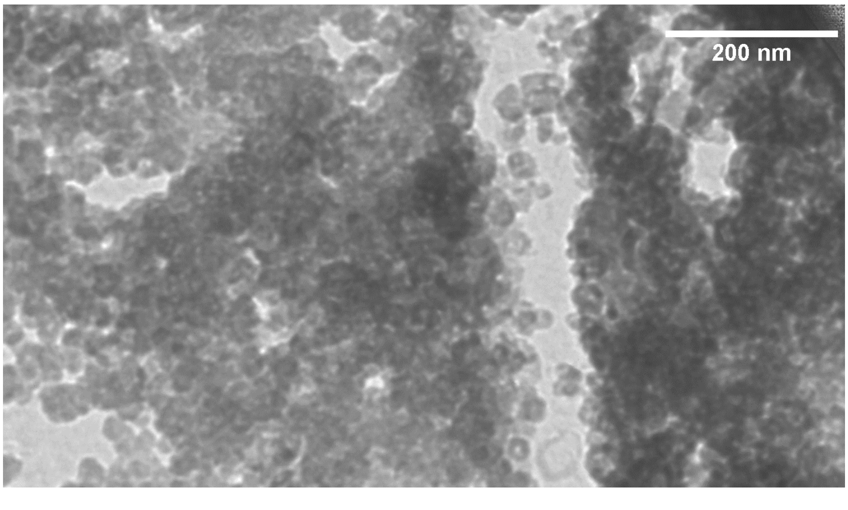
$[Na^+]$ = 0.652 mol/L
$[K^+]$ = 0.0015 mol/L
$[Mg^{2+}]$ = 0.0020 mol/L
$[NO_3^-]$ = 0.542 mol/L
$[SO_4^{2-}]$ = 0.0080 mol/L
$[PO_4^{3-}]$ = 0.105 mol/L)



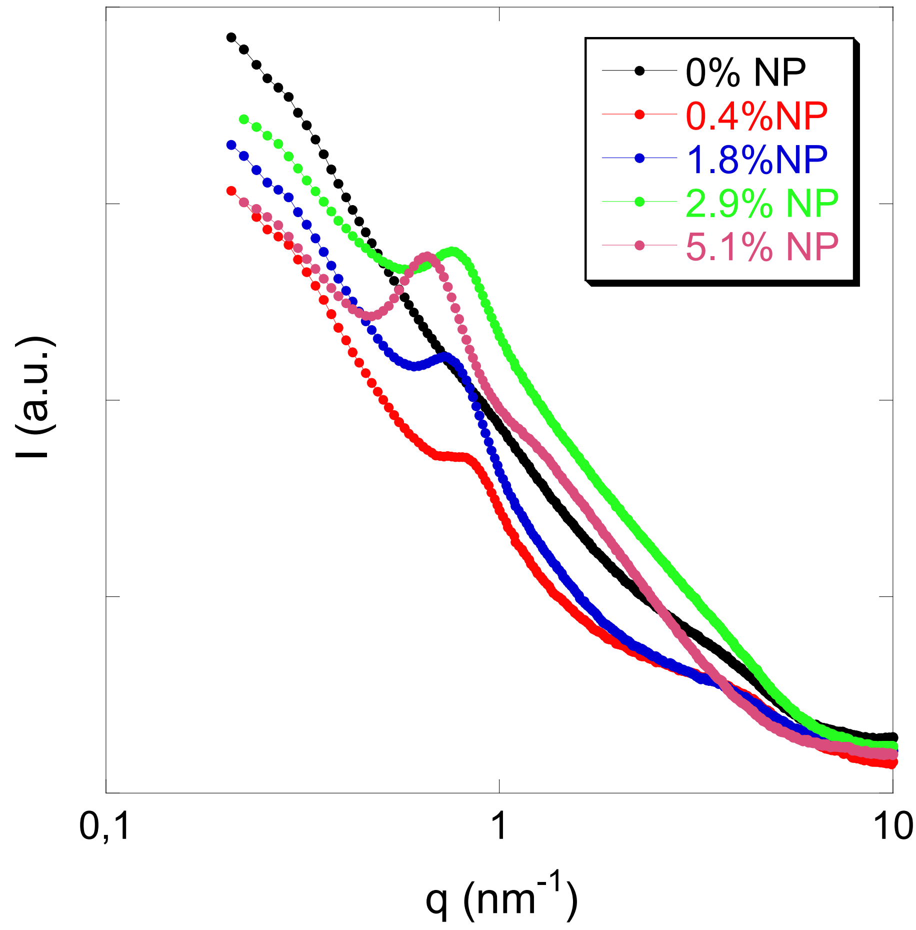
S1: Monoliths with various concentrations of CuHCF NPs



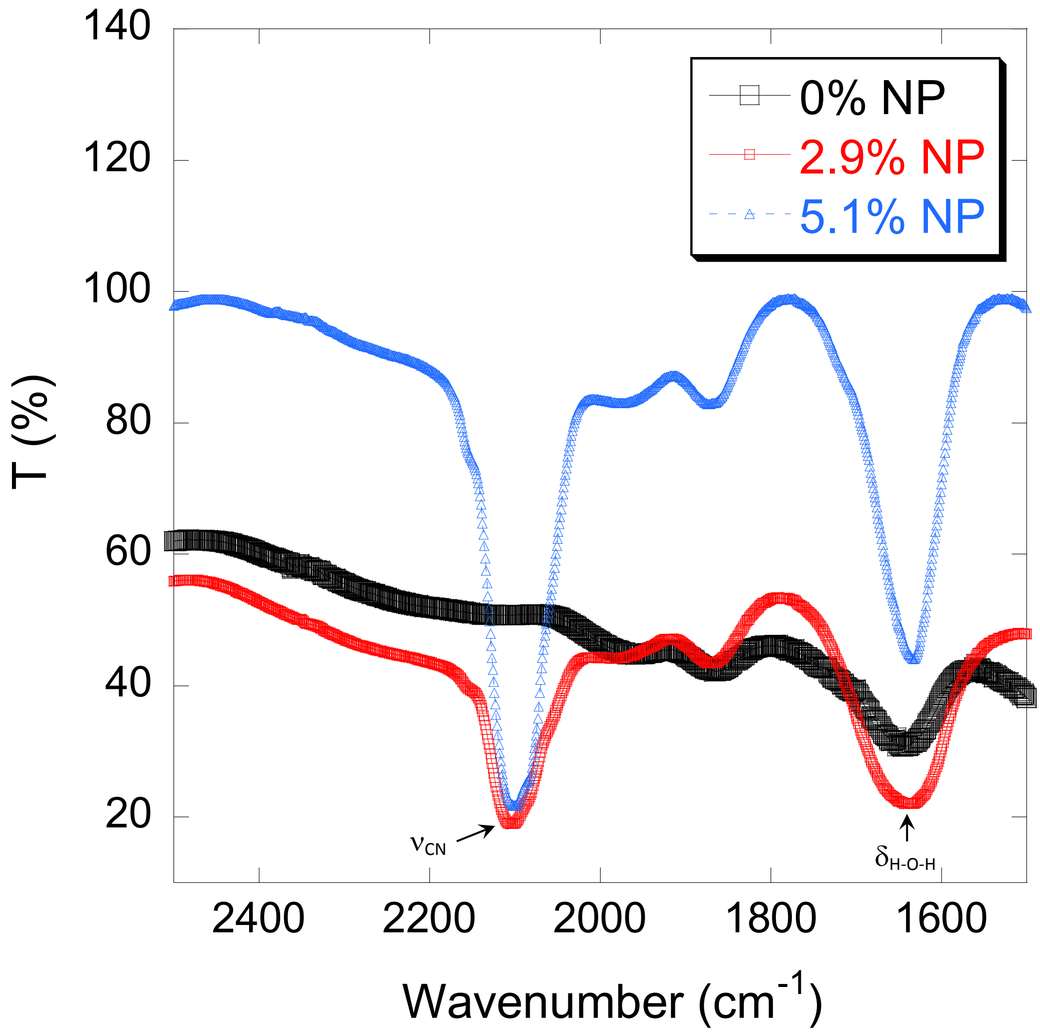
S2: ESEM images of monoliths



S3: TEM image of CuHCF NPs from 32g/L colloidal suspension



S4: SAXS measurements for monoliths with various mass concentrations of CuHCF NPs



S5: FT-IR spectra of functionalised and unfunctionalised monoliths. $\delta_{H\text{-}O\text{-}H}$=1610cm^{-1} – ν_{CN}=2090cm^{-1}