Supplementary Information

Novel DFO SAM on mesoporous silica for iron sensing. Part 2. Experimental detection of free iron concentration (pFe) in urine samples.

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Physico-chemical characterization of DFO-MS

FT-IR analysis

In Figure S1 the FT-IR spectra of DFO-MS, obtained is shown with the black line. The spectrum of GPTMS-MS is also reported with the grey line for comparison.

The FT-IR spectrum of DFO-MS presents an amide I band of the C=O stretching vibrations, at 1630 cm^{-1}, at wavenumber a little lower than expected (1695-1650 cm^{-1}), possibly due to intra-molecular hydrogen bond that reduces the frequency of the carbonyl stretching, according to what observed in deferoxamine sample or DFO grafted on MS-coated wafer.[s1,s2] At higher wavenumber region, between 3200 and 3370 cm^{-1}, the stretching vibrations of N-H and O-H are overlapped in a unique band. This band is also observed on DFO samples.[s2] The amide I band is absent in the GPTMS-MS spectrum, while the O-H stretching vibrations, present in the high wavenumber region, even if at small intensity, could be caused by a partial hydrolization of the epoxy group.
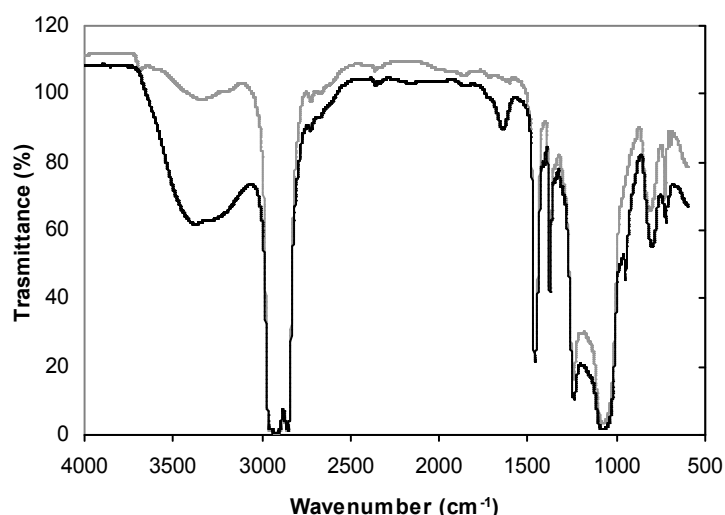

Figure S1: FT-IR spectrum of DFO-MS (black line) and GPTMS-MS (grey line).

SEM/TEM images and EDS analysis

TEM analysis was performed on the material loaded with Fe(III) (Figure S2). The results of the microelementary analysis are also shown in the same figure. With these techniques only the surface is available to the analysis and the atoms "hidden" inside the pore structure are not detected. The iron was found to be between 1 and 2 wt%.

Similar results were found on the same samples by SEM-EDS analysis: the Si/O ratio, equal to 3.1(2)/6.8(2), was as expected, and the iron percentage was estimated around 1.1 to 1.4 wt %.

The iron percentage corresponds to a amount of 0.2 mmol g^{-1}, not so far from the value found as

maximum sorption capacity from sorption isotherms, suggesting that the DFO-GPTMS fragment is likely larger than the pore size of the silica and DFO should be present mainly on the surface.
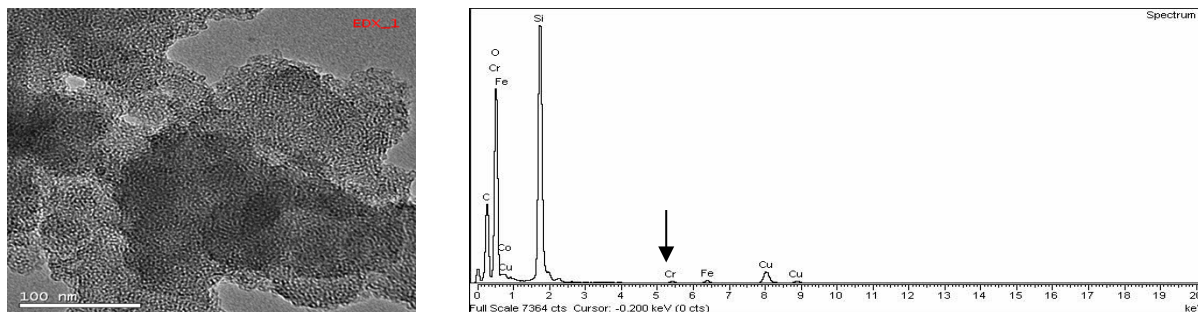

Figure S2: TEM analysis of DFO-MS loaded with iron(III). On the right the results of the microelementary analysis.

N₂ adsorption/desorption

The nitrogen adsorption/desorption experiments were conducted on the non-derivatized silica MCM-41 and on the DFO-MS obtained by the *one-pot* synthesis. The results are reported in Figure S3 and clearly demonstrate that the pore volume of the native material compared to that of the hybrid one is not significantly different, demonstrating that the DFO-GPTMS units do not enter the silica pores.
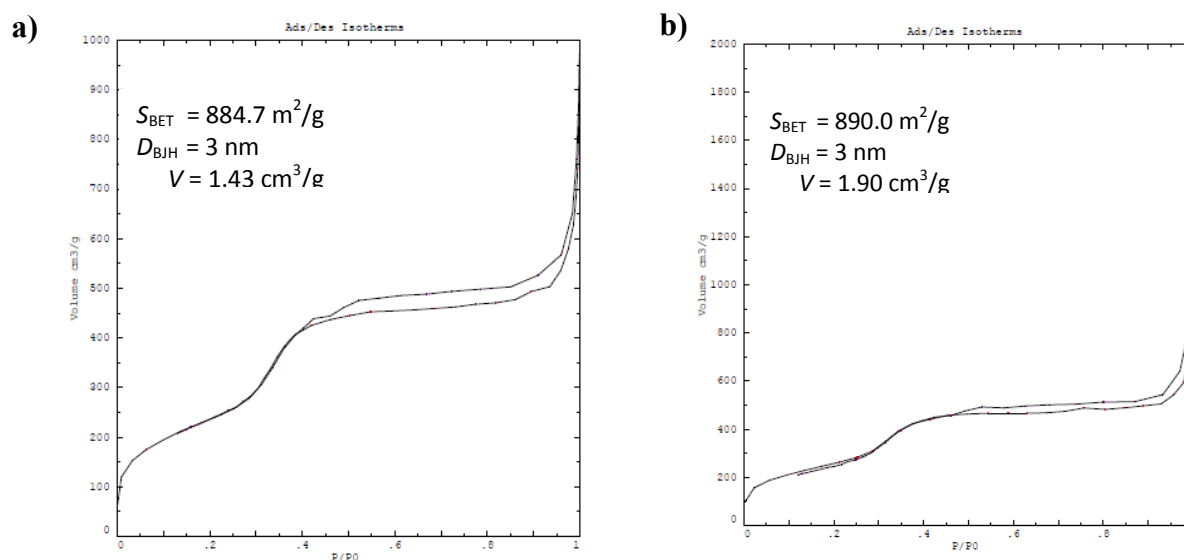

Figure S3: N₂ adsorption/desorption isotherms of **a)** MCM-41; **b)** DFO-MS (one-pot synthesis). S_{BET} = surface areas calculated by the BET model; D_{BJH} average pore diameters calculated by the BJH model; V = total pore volume

Maximum sorption capacity and stability of DFO-MS

The maximum sorption capacity of 0.33 mmol g^{-1} was obtained for the optimised DFO-MS product and it was considered satisfactory and totally unexpected before starting the optimization of the synthesis[s3]. Under these conditions, several batches have been produced, always with a reproducible value of the maximum sorption capacity, with a coefficient of variability around 6%, on data obtained from 6 different batches, by different operators.

The material is stable for at list three cycles of Fe(III) sorption/desorption. From our evidence, the recycling of the material is only limited by mechanical chipping, while it resulted stable for months, dry or wet, in its free or bounded to iron forms, when not stirred all the time long. It was decided to use the DFO

References

s1   E.G. Roy, C.H. Jiang, M.L. Wells, C. Tripp, *Analytical Chemistry*, 2008, **80**, 4689.

s2   C.C.P. Chan, N. R. Choudhurya, P. Majewskib *Colloids and Surfaces A: Physicochem. Eng. Aspects* , 2011, **377**, 20.

s3   R. Biesuz, G. Emma, C. Milanese, et al. Novel DFO SAM on mesoporous silica for iron sensing. Part I. Synthesis optimization and characterization of the material. *Submitted to Analyst.*