

**Electronic Supplementary Information (ESI) for**

**Hydrofluoric Acid-induced Fluorination and**

**Formation of Silica Nanocapsules for  $^{19}\text{F}$  Magnetic**

**Resonance Imaging**

*Luís M. F. Lopes and Laura M. Ilharco\**

CQFM - Centro de Química-Física Molecular and IN - Institute of Nanoscience and  
Nanotechnology, Instituto Superior Técnico, Universidade de Lisboa,  
Av. Rovisco Pais 1, 1049-001 Lisboa, Portugal.

**Corresponding Author**

\* To whom correspondence should be addressed: Tel: +351-218419220, Fax: +351-  
218464455, E-mail: [lilharco@ist.utl.pt](mailto:lilharco@ist.utl.pt).

## MATERIALS AND REAGENTS

Tetraethoxysilane (TEOS, 98%), 3-aminopropyl-trimethoxysilane (APTS, 97%) and 1-hexanol (98%) were purchased from Sigma-Aldrich. Ethanol (99.5%) and ammonia (25% NH<sub>3</sub>) were obtained from Panreac, whereas the Triton X-100 (~1% H<sub>2</sub>O) and cyclohexane (99%) were provided by Roth. The hydrofluoric acid (HF, 40%) was acquired from Fluka and used to prepare aqueous solutions of 4 and 8 %wt in HF. All chemicals were used without further purification. Water purified by a Milli Q system with an electrical resistance of ~20 MΩ.cm was used throughout the sol-gel synthesis and in the preparation of aqueous solutions.

## SYNTHESIS PROCEDURES

The fluorinated silica nanocapsules (SiO<sub>2</sub>-F) were synthesized by combination of a water-in-oil emulsion method with the sol-gel process, adapting a procedure reported in the literature.<sup>1</sup> The surfactant Triton X-100 was dissolved in cyclohexane, and n-hexanol (the co-surfactant) was added to the solution. An aqueous solution of HF (4% wt) was added under stirring, and the emulsion left to stabilize for 15 min before the addition of TEOS. Two hours later a solution of NH<sub>3</sub> (25% wt) was added and the reaction left to proceed for 2 hours. The molar ratios cyclohexane:H<sub>2</sub>O:hexanol:TritonX-100:NH<sub>3</sub>:HF:TEOS were 800:214:142:37:18:9:1. An ethanol solution of APTS 0.8 M (200 μL) was then added to the mixture. The reaction was stopped after 45 hours by addition of 20 mL of ethanol, and centrifuged at 15000 rpm. The white solid obtained was repeatedly washed with a mixture of ethanol:water and centrifuged (at least three times), in order to remove the tensioactive and residual reactant species. Drying was carried out at room temperature under vacuum. For *post* fluorination of bulk silica nanoparticles, an aqueous solution of HF 8%wt (1 mL) was added

to the final mixture of bulk silica nanoparticles (obtained by the same procedure described above in absence of HF), after 45 hours of reaction.

The preparation of the dilute solutions of HF was carried out in a *hotte*, using goggles and gloves.

## CHARACTERIZATION

The morphology of the silica nanocapsules was observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM images were recorded on a FEG-SEM microscope JEOL JSM-7001F operated at an accelerating voltage of 10 keV. The samples' surface was sputter coated with gold prior to the analysis. The TEM images were obtained in an electron microscope Hitachi H-8100, operated at 200 kV, with a LaB6 filament. The instrument was equipped with an energy dispersive X-ray spectroscopic (EDS) detector for light elements from ThermoNoran and used to perform quantitative elemental analysis. The samples were previously dispersed in ethanol and then dropped onto a Formvar®-coated Cu grid and left to evaporate. The average diameter of the particles based on the TEM images ( $\phi_{\text{TEM}}$ ) was estimated using the image processing program ImageJ version 1.41.

The size distribution of the nanoparticles was determined by dynamic light scattering (DLS). The measurements were performed at 25 °C using a Spectra Physics model 127 He-Ne Laser (632.8 nm 35 mW) and a Brookhaven instrument with a BI-200SM goniometer, a BI-2030AT autocorrelator and APD detector. DLS data were analyzed following the CONTIN method.

Infrared analysis of all the samples was performed by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, using a Mattson RS1 FTIR spectrometer with a Specac Selector, in the 400-4000  $\text{cm}^{-1}$  range (wide band MCT detector), at 4  $\text{cm}^{-1}$  resolution.

The spectra were the result of 500 co-added scans for each sample, ratioed against the same number of scans for the background (ground KBr, FTIR grade, from Aldrich). The samples were previously ground and mixed with KBr in appropriate proportions to obtain spectral absorbance in the range of applicability of the Kubelka-Munk transformation.<sup>2</sup>

Table S1. Assignments of the DRIFT spectra of all the synthesized silica nanoparticles.

Wavenumber /cm <sup>-1</sup>			Assignments
Bulk SiO <sub>2</sub>	SiO <sub>2</sub> -F	SiO <sub>2</sub> - <i>post</i> F	
3614 <sub>vw</sub>	3615 <sub>w</sub>		vO-H (free)
~3300-2800 <sub>vw</sub>	~3300-2800 <sub>vw</sub>	~3500-2800 <sub>w</sub>	vO-H (H bonded)
		3313 <sub>w</sub>	vN-H (weakly H bonded)
	3236 <sub>w</sub>		vN-H/vO-H
	3199 <sub>w</sub>		vN-H/vO-H
	3161 <sub>w</sub>		vN-H/vO-H
	3035 <sub>w</sub>		vN-H/vO-H
2943 <sub>vw</sub>	2954 <sub>w</sub>	2943 <sub>w</sub>	v <sub>as</sub> CH <sub>2</sub>
2898 <sub>vw</sub>	2897 <sub>sh</sub>	2902 <sub>w</sub>	v <sub>s</sub> CH <sub>2</sub>
1649 <sub>w</sub> /1637 <sub>sh</sub>		1624 <sub>w</sub>	δH-O-H
	1606 <sub>w</sub>		δ <sub>sc</sub> NH <sub>2</sub>
1543 <sub>vw</sub>	1512 <sub>vw</sub>	1525 <sub>vw</sub>	δ <sub>sc</sub> NH <sub>2</sub>
	1471 <sub>sh</sub>	1471 <sub>sh</sub>	δCH <sub>2</sub>
	1450 <sub>sh</sub>	1431 <sub>m</sub>	δCH <sub>2</sub>
1076 <sub>VS</sub>	1066 <sub>m</sub>	1076 <sub>VS</sub>	v <sub>as</sub> Si-O-Si
	991 <sub>w</sub>		vSi-F <sub>2</sub> (O <sub>2/2</sub> SiF <sub>2</sub> ) and vSi-F <sub>3</sub> (O <sub>1/2</sub> SiF <sub>3</sub> ) tetrahedral species
957 <sub>m</sub>	937 <sub>w</sub>	955 <sub>m</sub>	vSi-OH/vSi-O-
795 <sub>m</sub>			v <sub>s</sub> Si-O-Si
	746 <sub>VS</sub>	741 <sub>VS</sub>	vSi-F (O <sub>4/2</sub> SiF)
			vSi-O coupled with δSi-O-Si and δO-Si-O (in 4-member siloxane rings)
566 <sub>w</sub>	555 <sub>w</sub>	555 <sub>sh</sub> /546 <sub>m</sub>	
	482 <sub>VS</sub>	482 <sub>VS</sub>	ρO, ⊥ Si-O-Si plane

VS - very strong; S - strong; m - medium; w - weak; vw - very weak; br - broad; sh -shoulder.

## REFERENCES

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- <sup>1</sup> Lin, Y.-S.; Wu, S.-H.; Tseng, C.-T.; Hung, Y.; Chang, C.; Mou, C.-Y. Synthesis of hollow silica nanospheres with microemulsion as template. *Chem. Commun.* **2009**, 3542-3544.
  - <sup>2</sup> Kubelka, P.; Munk, F. *Z. Tech. Phys.* **1931**, *12*, 593-601.